doi:10.2533/chimia.2014.522 Chimia 68 (2014) 522–530

# The von Auwers Reaction – History and Synthetic Applications

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*Abstract:* Dienones obtained from the facile dearomatization of phenols, can be further transformed to semi-benzenes prone to rearomatize in clean, but sometimes unexpected, fashion. Over a hundred years ago, K. von Auwers found that adding Grignards on dienones would lead spontaneously to subsequent dehydration and a novel aromatizing rearrangement. This reaction was ignored for 50 years before Melvin Newman re-investigated these findings, studied the mechanism, and developed variations on the same theme. Since then, despite the tremendous potential of the reactions, those studies were only rarely mentioned, before finally falling into oblivion. This review aims to provide the reader with a detailed history and comprehensive bibliography of the von Auwers rearrangement, some of its synthetic applications, and new unpublished material in the hope to open new perspectives on this forgotten reaction.

**Keywords:** Radical · Rearomatization · Rearrangement · Semi-benzene · von Auwers reaction

## 1. Introduction

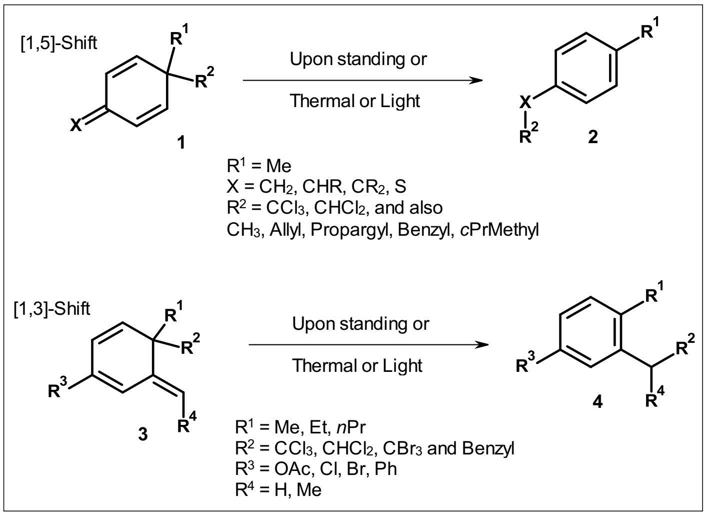
Von Auwers rearrangements are encompassed by the two generic reactions depicted in Scheme 1. Two variants of this reaction – also known as 'semi-benzene rearrangement' – exist, namely the [1,5]- and the [1,3]-migration. Semi-benzenes **1** (X = carbon) and **3** are not often observed or isolated, but rather prepared *in situ* from suitable precursors, as the [1,n]-shift occurs rapidly at room temperature or upon standing – especially when $R^2$ is a stable radical.

This review describes the history of these reactions, in an attempt to provide the reader with a comprehensive bibliography, from their discovery in 1903 to the latest example published in 1996. Unprecedented extensions of the reactions, like a new [1,7]-shift as well as a few synthetic applications will be disclosed.

## 2. History of the von Auwers Rearrangement

### 2.1 *The Early Years (1903–1922); Karl von Auwers and Theodor Zincke*

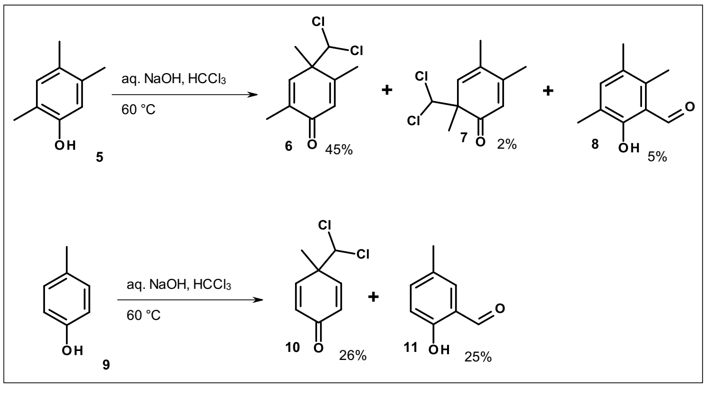
In 1876, a salicylaldehyde synthesis from phenol, chloroform and alkali was published by Reimer and Tiemann.[1]



Scheme 1. Known von Auwers rearrangements; both variants.

Von Auwers soon extended the scope of this reaction and reported in a series of publications the formation of chlorinated cyclohexadienones from *ortho*- and *para*-substituted phenols (Scheme 2).[2] The simplest example, *p*-cresol, gives a 1:1 mixture of the expected arylaldehyde **11**, together with the chlorinated cyclohexadienone **10**. Nowadays dienones arising from these reactions are called *abnormal Reimer-Tiemann products*.

Von Auwers started shortly afterwards to investigate the functionalization of these abnormal products and in 1903, reported the effect of the addition of methyl Grignard on dienones **10** and **12**.[3]



Scheme 2. Discovery of the abnormal Reimer-Tiemann reaction by Karl von Auwers.

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As the carbonyl group of **12** is hindered by the α-quaternary center, the Grignard reagent added in a 1,4-manner. But in the case of dienone **10**, where the degenerate 1,4-positions are neopentylic, the Grignard only added onto the carbonyl group, and even though alcohol **15** could be observed and isolated, it spontaneously rearranged by loss of water to the aromatic compound **14** (Scheme 3). This seminal example of the von Auwers rearrangement is a formal 1,5-sigmatropic shift of the dichloromethyl group occurring in semi-benzene **16**.

In 1906, another way to dearomatize phenols was reported by Zincke and Suhl who treated *p*-cresol with aluminum trichloride in carbon tetrachloride (Scheme 4).[4] Two years later, they reported the use of the von Auwers rearrangement on **17**.[5]

It is worthy of note that both von Auwers and Zincke had also found that their dienones could easily rearomatize under acidic conditions by a 1,2-shift of the alkyl group (Scheme 5, products **19** and **21b**).[6] Such kinds of rearomatization had already been reported by Andreocci in 1893,[7] and are nowadays known as *Djerassi dienone–phenol rearrangements*. This topic will not be discussed further in this review, although von Auwers formed aryl–aryl C–C bonds from aryl-Grignard reagents using this [1,2]-shift (**21b**) or reductively towards **21a**, two reactions confirmed and reproduced by Newman in 1959.[8]

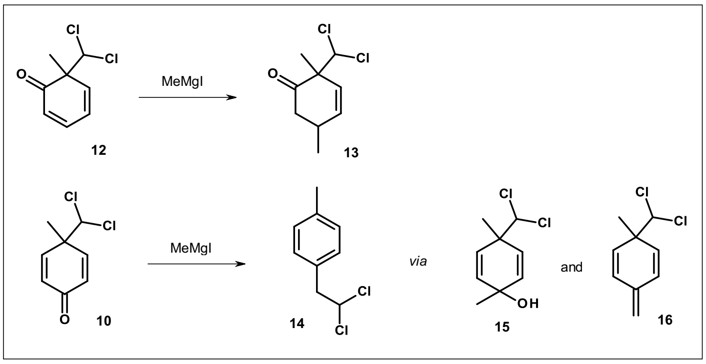
During these early 20th century studies,[3-6,9] other kinds of organometallic nucleophiles were reacted with **10** and **17** and a few examples are given in Scheme 6. All examples reported belong to the [1,5]-class of migrations of either dichloro- or trichloro-methyl groups. It would take another 50 years before a [1,3]-version of this reaction was discovered by Melvin Newman.

## 2.2 *1956–1970; M. Newman's Contribution*

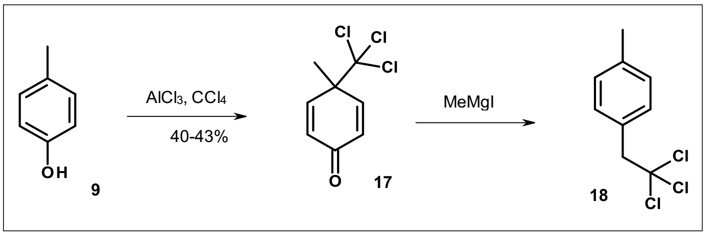
### 2.2.1 *1,5-Migration*

After a 30-year absence from the literature, this chemistry resurfaced in a single paper from Fuson and Miller (Scheme 7), who extended it to the naphthalene series.[10]

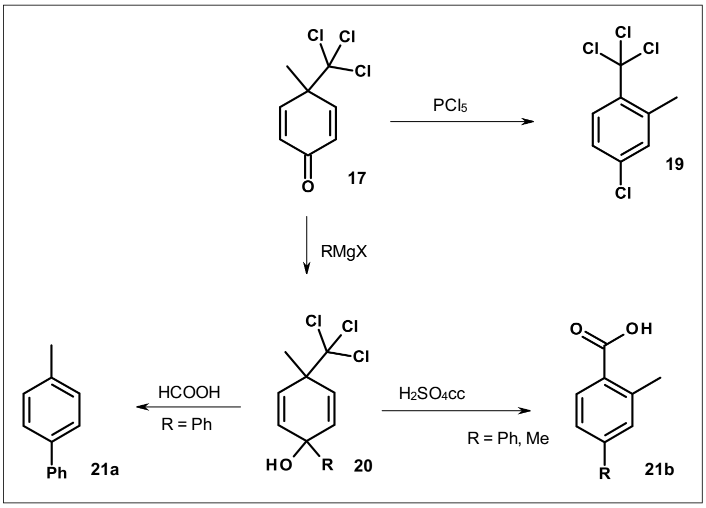
Then, in 1956 Newman initiated the work which led to a series of seven publications, the first of which[11] displayed a non-conventional method to form semi-benzenes. Where von Auwers and Zincke both used C-nucleophiles, which allow the loss of water from the alcohol produced, Newman considered instead using a Meyer-Schuster rearrangement[12] (Scheme 8). All intermediate steps happened during work-up or upon standing, and only the desired product **28** was isolated in good



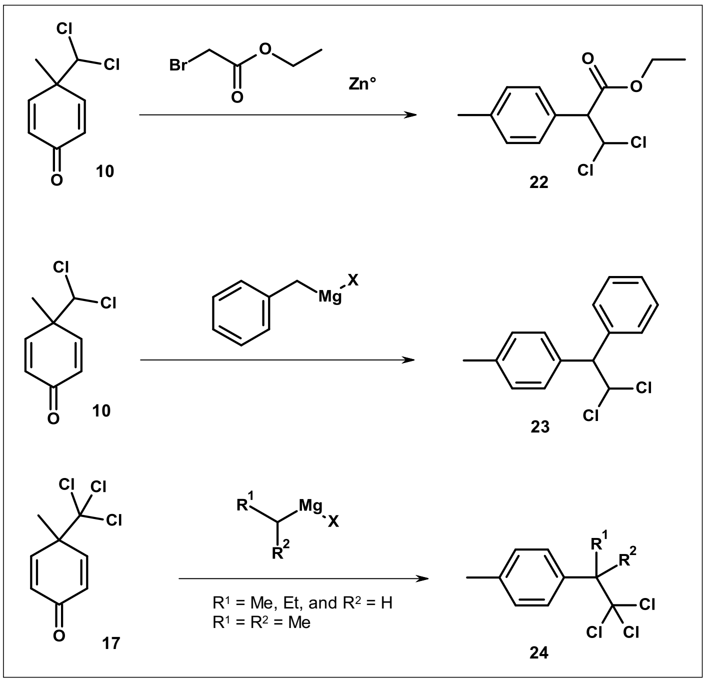
Scheme 3. Seminal example of the von Auwers rearrangement.



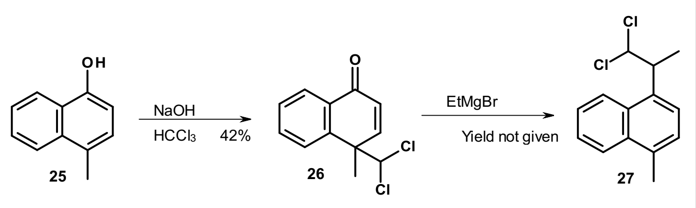
Scheme 4. Trichloromethyl-[1,5]-migration in von Auwers rearrangement.



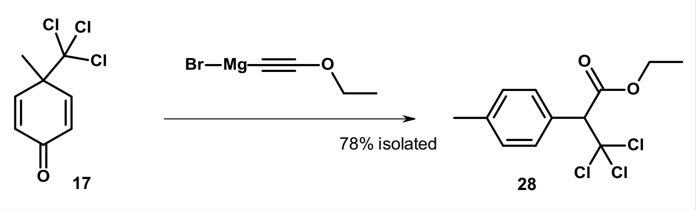
Scheme 5. Other ways of forming C–C bonds from **17**.



Scheme 6. Further examples from Karl von Auwers early studies.



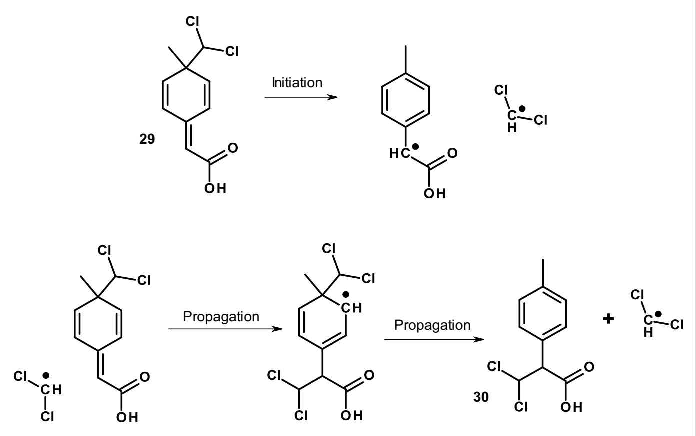
Scheme 7. Extension of the rearrangement to the naphthalene series.



Scheme 8. Tandem Meyer-Schuster/ von Auwers rearrangements.

yield. This paper also contained a first tentative explanation for the mechanism of the trichloromethyl migration, involving a zwitterionic species and bridging chlorine.

Newman's mechanistic hypothesis was immediately questioned by Bird and Cookson, who published in 1959 convincing evidence that the rearrangement takes place *via* a free-radical chain reaction (Scheme 9).[13] Alongside a kinetic study of the rearrangement of **29**, the authors mention that the temperature-dependent induction period of the rearrangement can be shortened by addition of benzoyl peroxide or by UV irradiation, whereas the reaction can be inhibited by addition of duroquinone. The activation energy of the initiation step had been estimated experimentally to be around 40 kcal/mol.

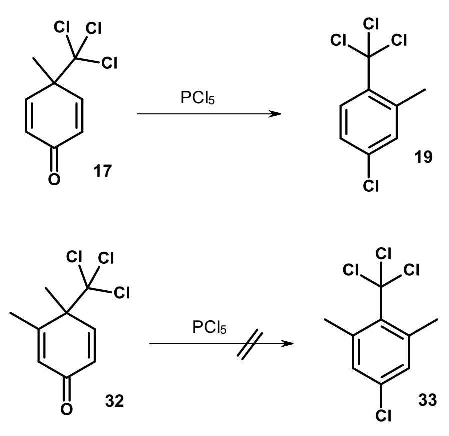


Scheme 9. Proposed mechanism of the [1,5]-migration of dichloromethyl.

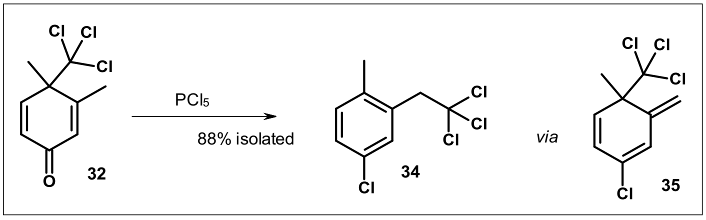
In the meantime, what interested Newman was to make use of the [1,2]-methyl shifts promoted by PCl$_5$ (Scheme 5) in analogous fashion to prepare 3,5-dimethyl-4-trichloromethyl chlorobenzene (**33**) starting from ketone **32** (Scheme 10). However, failure to form **33** led Newman instead to the discovery of the [1,3]-version of the von Auwers rearrangement.

## 2.2.2 *1,3-Migration from Dienone Dehydration*

In fact, the action of PCl$_5$ on **32** led apparently to semi-benzene **35** (not observed: Scheme 11) as a new rearrangement took place: the [1,3]-sigmatropic shift of the trichloromethyl group, which resulted in the formation of **34** in high yield.[14]

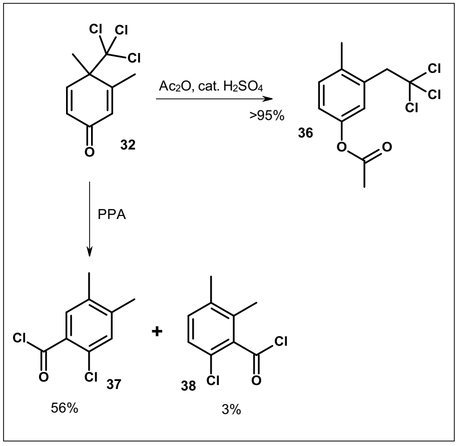


Scheme 10. Thwarted attempt of a Djerassi dienone-phenol rearrangement on **32**.



Scheme 11. Fortuitous discovery of the [1,3]-version of the von Auwers rearrangement.

Activating ketone **32** with acetic anhydride[15] also triggers rearrangement to **36** (Scheme 12), but surprisingly, for a hitherto unknown reason, using polyphosphoric acid (PPA) to initiate semi-benzene formation leads to the formation of 2-chloro-4,5-dimethylbenzoic acid (after hydrolysis of acid chloride **37**).[16]



Scheme 12. Unprecedented (and yet unexplained) rearrangement to **37**.

Similar observations were made again in 1962 on **46**[17] (from the more elaborate 2,4,5-trimethyl-phenol) as well as independently by Miller who used sulphuric acid instead of PPA.[18]

The seminal [1,3]-rearrangement depicted in Scheme 11 was reproduced successfully by Newman, from the dichloromethyl analogue **39**, although the migration of dichloromethane is slower and required harsher conditions.[19] It is surprising that von Auwers did not invent, or at least did not report, the [1,3]-version of the rearrangement, as he had had access to compounds **6** and **39**. von Auwers did report though the methyl Grignard addition on both substrates (Scheme 13), but although two semi-benzenes **a** and **b** might have been formed from each of the intermediate alcohols (and the [1,3]-shift discovered from **a**), only the cross-conjugated **42b** and **43b** seemed to have been generated, as the single products **44** and **45** were isolated from each reaction.[20] Newman observed exactly the same selective semi-benzene formation when adding MeMgBr to **32** (30–50% yield in 1,2-dimethyl-4-(2,2,2-trichloroethyl) benzene).[21]

As could be seen from Scheme 13, when alcohols **40** or **41** have the choice to eliminate water by giving [1,5]- or [1,3]-migration precursors **a** and **b**, cross-conjugated semi-benzenes are formed exclusively. Newman was then interested in creating two competing reactions, a dehydration or a rearrangement, for the formation of semi-benzenes **a** and **b** (Scheme 14). If, instead of a Grignard reagent, an alkynyl anion would be added to **32**, the alcohol would have the choice to eliminate water (leading to a 1,3-migration) or to proceed through a Meyer-Schuster rearrangement (leading to a 1,5-migration). Results teach us that, with ethoxyethynyl magnesium bromide, be it on **32** or **46**, the only products observed and isolated came from [1,5]-migration (**51** and **52**, Scheme 14), regardless of the extra steric hindrance from the 2-methyl of **46** (Scheme 14).[21]

### 2.2.3 *1,3-Migration with C–C Bond Formation*

When dienone **32** was treated with phenyl magnesium bromide, [1,3]-rearranged product **53** was obtained directly from the reaction in 87% yield (Scheme 15). No intermediate alcohol or semi-benzene could be observed or isolated.[21]

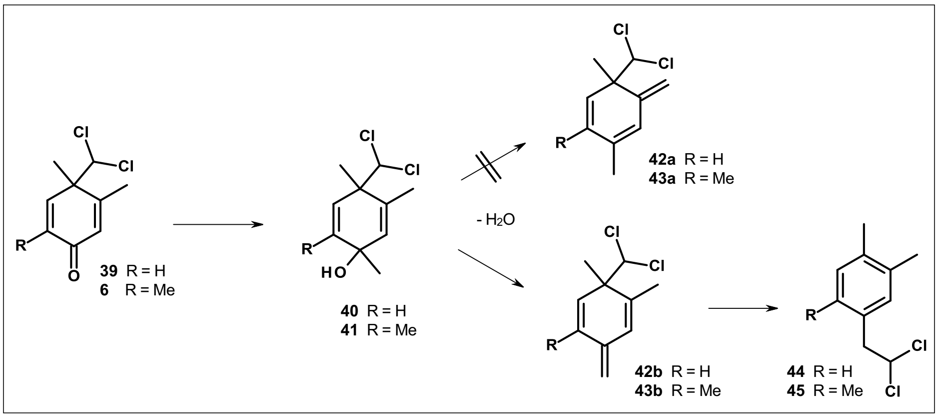
In a later study, Newman extended this [1,3]-shift to the dichloromethyl group with PhMgBr addition on **39**, as well as in the naphthalene series.[19] In the former case, as the induction period for migration is longer with dichloromethyl group, Newman was able to trap the intermediate semi-benzene with tetracyanoethylene (TCNE) in an excellent yield (Scheme 16).

### 2.2.4 *Mechanistic Studies from Newman – 1,5-Migration*

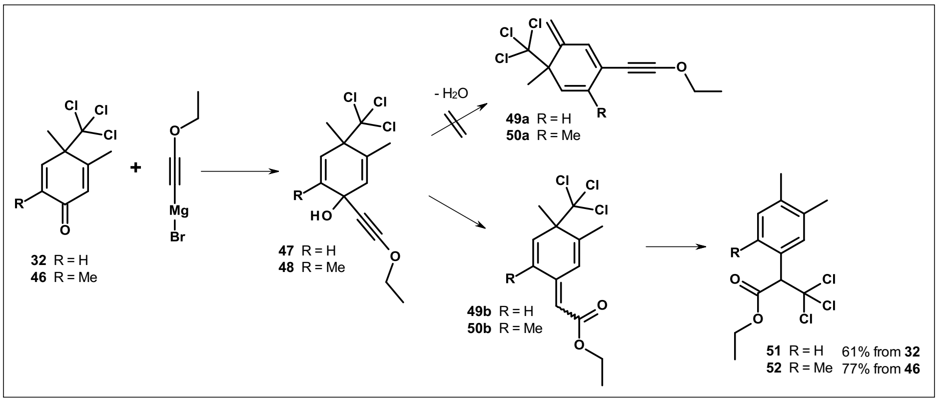
Apparently unaware of the publication by Bird *et al.*,[13] Newman prepared a single enantiomer of **46** and wondered if a [1,5]-migration of the trichloromethyl group would occur with some degree of stereoretention.[22] (+)-**46** was obtained from fractional recrystallization of the two epimers **56** and **57**, followed by heating pure (–)-epimer with levulinic acid (Scheme 17).

Following the steps depicted in Scheme 14, (+)-**46** was readily converted to alcohol (+)-**48**, and rearranged to (–)-**50b** under mild acidic conditions (still confirmed as being a single enantiomer). However, on warming to 85 °C in cyclohexane or exposure to light, **52** rearranged to a racemic mixture.

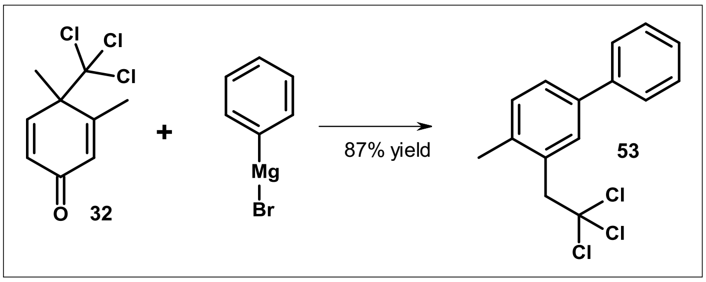
Newman ruled out any post-rearrangement epimerization of the



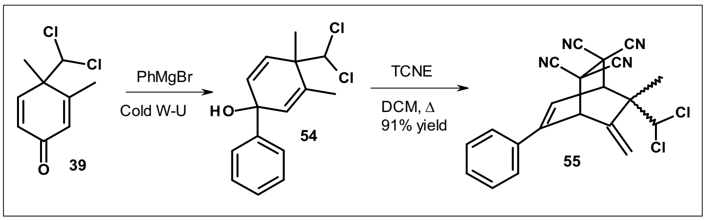
Scheme 13. Selective cross-conjugated semi-benzene formation and [1,5]-shifts.



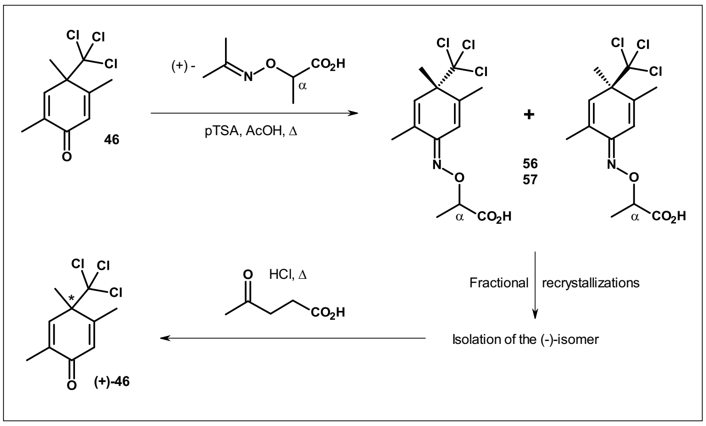
Scheme 14. Selective Meyer-Schuster rearrangements and [1,5]-shifts.



Scheme 15. Direct aryl-aryl C–C bond formation, coupled with [1,3]-shift of $-CCl_3$.

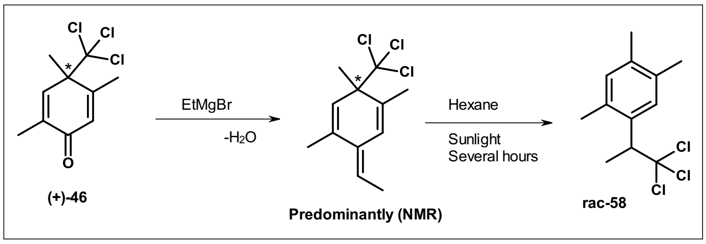


Scheme 16. Trapping of the semi-benzene intermediate.



Scheme 17. Preparation of a single enantiomer of **46**.

ester **52** as an alternative explanation to racemization. He indeed reproduced this study by preparing **58**, which cannot epimerize *after* the [1,5]-shift, but was nevertheless still obtained as a racemate, from the addition of EtMgBr to enantiopure (+)-**46** (Scheme 18).



Scheme 18. Further evidence of the radical nature of the [1,5]-shift.

The kinetic study of the transformation of **50b** to **52**, the observations of the effect of radical trapping agents, as well as results of performing the [1,5]-shift thermally in thiophenol provided Newman with strong evidence of a postulated free-radical mechanism – essentially the same as already published by Bird *et al.*

Even such a mechanism might have led to some transfer of stereochemistry, if the incoming trichloromethyl radical would have felt the influence of the asymmetric quaternary center. Newman postulated that even though it did not happen during the [1,5]-shift, the exocyclic double bond and the quaternary center being contiguous in the [1,3]-case might lead to stereospecific transfers. Also, a concerted electrocyclic mechanism – *a priori* unlikely in the [1,5]-shift – cannot be as easily ruled out in the [1,3]-series on geometric considerations. Unfortunately, Newman never published the results of his mechanistic investigations in the [1,3]-case, and the interesting question of possible stereo-transfer remains unanswered.

## 3. Extensions of the von Auwers Rearrangement

### 3.1 *Migrations on Heteroatoms or 'Contrary to Wisdom'*

The application of Lawesson's reagent onto **17** leads to a migration *on a sulfur atom*, as was shown by Nikaronov *et al.* in 1995 (Scheme 19).[23]

However, the application of nitrogen nucleophiles on **17** or **10** does not lead to von Auwers [1,5]-shifts, as the adducts rearomatize following various different pathways instead, an example of which is depicted in Scheme 20.[24]

Finally, a few spectacular [1,5]-migrations ought to be mentioned, in which the trichloromethyl radical attacks a fully substituted olefin. In 1967, a von Auwers rearrangement was fortuitously observed during photochemical studies of **17** (Scheme 21).[25] After [2+2] cycloaddition of **32** with methyl-2-butene or isobutylene, followed by retro-[2+2], semi-benzene **68** was formed and rearranged thermally into **69**, alas without much detail being given about conditions and yield.

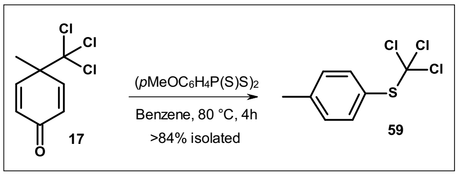
Von Auwers had already added iPrMgBr on ketone **10**, the dichloroanalogue of **17**, to form quaternary centers as early as 1916, with little detail about the results, but in 1984, this exact same chemistry was reproduced and communicated by Rozenberg *et al.*[26] Low yields of semi-benzene were obtained from the *iso*-propyl Grignard addition (25%), but the subsequent rearrangement occurred quite efficiently given the hindrance of the double bond (60% yield) at 70 °C only.

Even more spectacular – for steric *and* stereoelectronic reasons – is the [1,5]-rearrangement on the dimedone Knoevenagel adduct **70** (Scheme 22).[27] Under thermolysis conditions, the rearranged product **71** could be isolated together with lactone **72**, which is reminiscent of the unexplained [1,3]-shift seen in Scheme 12.

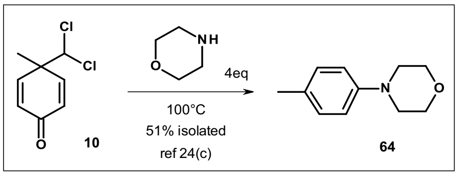
A last few elements worthy of note are depicted in Scheme 23: compound **73**, the only semi-benzene reported to be resistant to thermal rearrangement,[28] and rearrangements on phosphorylated materials.[29]

### 3.2 *[1,7]-Migration*[30]

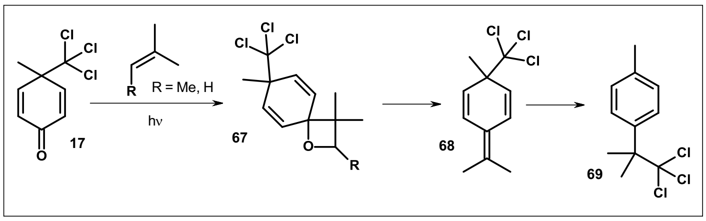
Another extension of the von Auwers rearrangement was invented recently by us, as we wondered if the semi-benzene **76** would rearrange in an unprecedented [1,7]-fashion. We therefore added allyl magnesium bromide to **17** and indeed obtained **77** (Scheme 24). Compounds



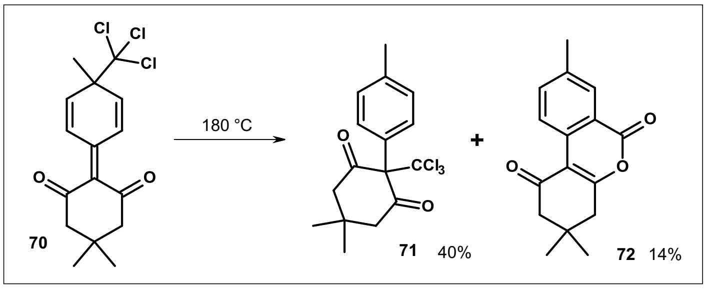
Scheme 19. [1,5]-Migration to a sulfur atom.



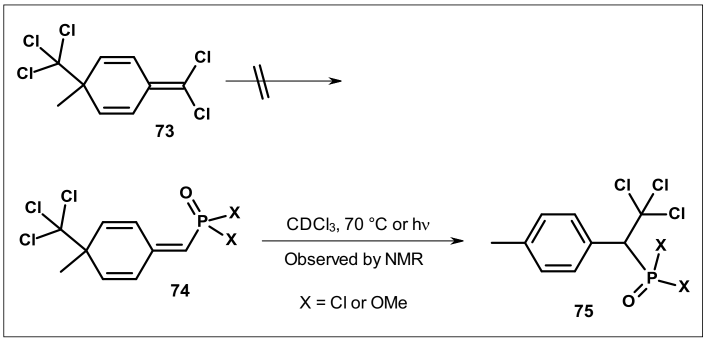
Scheme 20. Unexpected aromatization with the nitrogen analogues of semi-benzenes.



Scheme 21. An example of formation of a quaternary center.

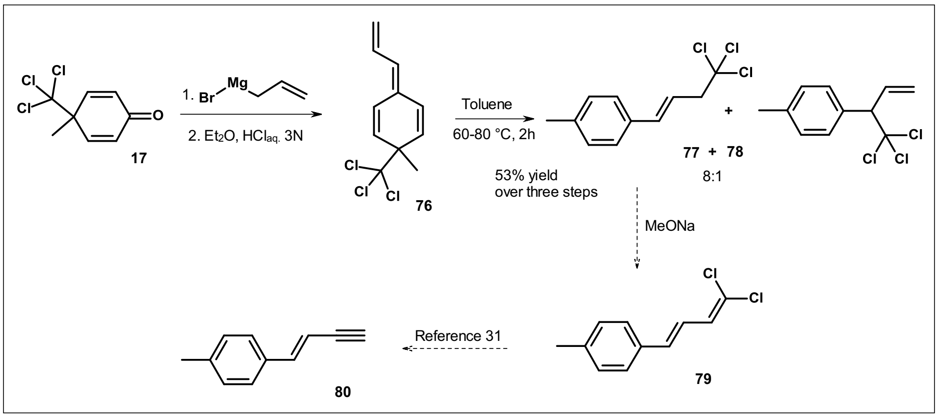


Scheme 22. Remarkable formation of a quaternary center from an electron-poor olefin.



Scheme 23. Last known examples of trichlomethyl-radical migration.

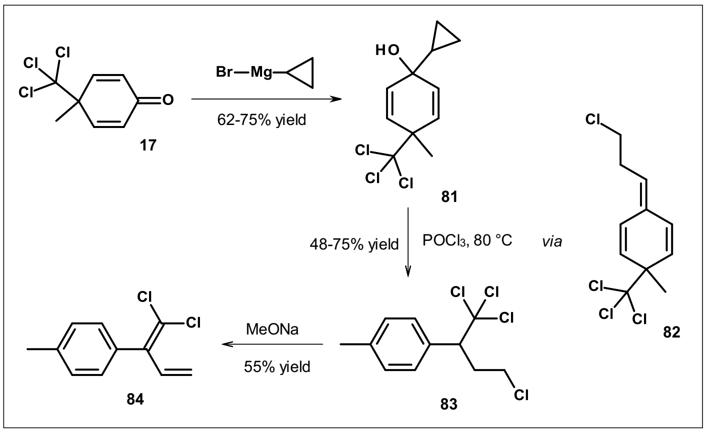
of the type **77** have already been used by others, for example as precursor of enynes **80**, from a Fritsch–Buttenberg–Wiechell rearrangement *via* compound **79**.[31]



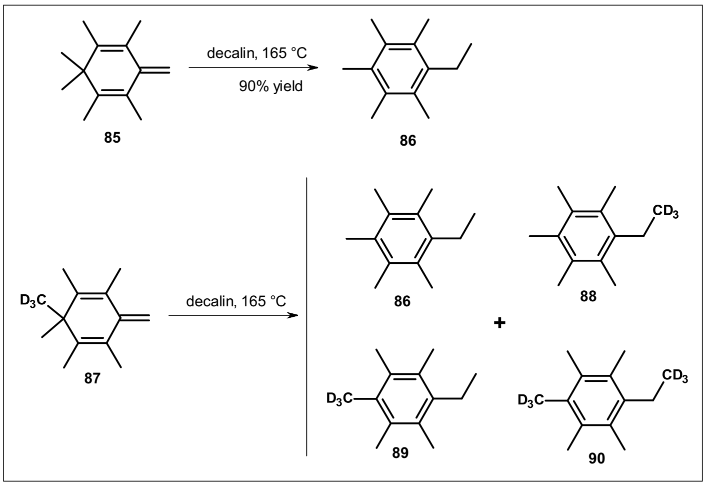
Scheme 24. First example of a [1,7]-von Auwers rearrangement.[30]

## 3.3 *Complementary [1,5]-Products vs [1,7]-Products*

Diene **79** would then come from a new [1,7]-shift, obtained exclusively from addition of allyl magnesium bromide to **17**. From the same starting material it is possible to obtain isomeric diene **84**, from a [1,5]-rearrangement, by using *c*PrMgBr as a surrogate of allyl magnesium bromide. Indeed, addition of *c*PrMgBr to **17** leads to alcohol **81**, which, when dehydrated with POCl$_3$, rearranges by opening the cyclopropyl first, generating semibenzene **82** (postulated, not observed) to finally give *in situ* **83** (Scheme 25). Double elimination of HCl was done efficiently by using methanolate as a base and provided the diene **84**, otherwise inaccessible by the reaction in Scheme 24.



Scheme 25. A way to access the complementary dienes from [1,5]- rather than [1,7]-shift.[30]

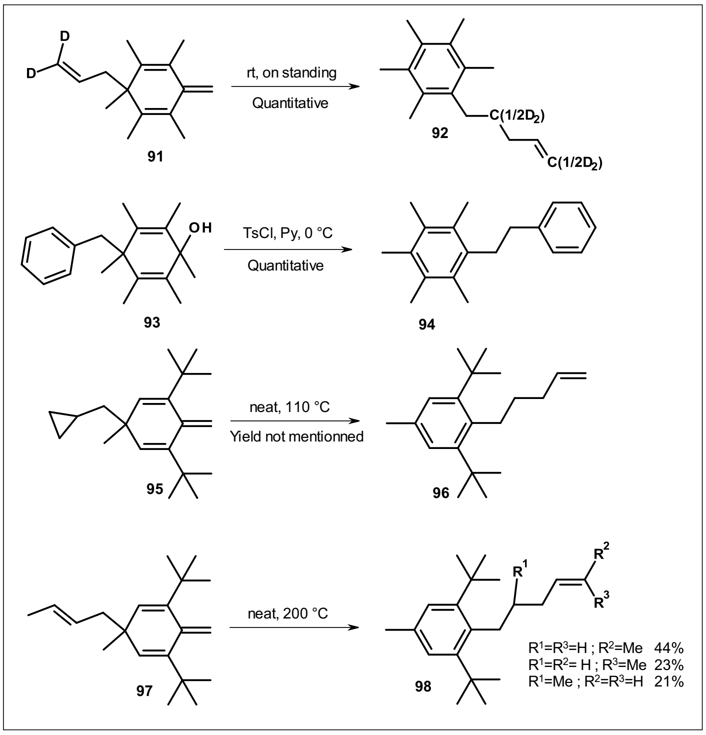


Scheme 26. Radical methyl migration in the von Auwers rearrangements.

## 3.4 *Other Migrating Groups than –CHCl$_2$ or –CCl$_3$*

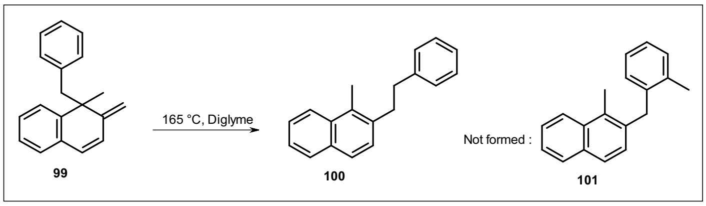
Merchant *et al.* reported that the tribromomethyl-group behaves exactly as its chloro congener.[32] In 1968, Hart *et al.* could show that *even a methyl radical can migrate very efficiently*,[33] although it does require high temperatures for the initiation (Scheme 26). The intermolecular methyl radical chain carrier mechanism was confirmed by starting from deuterated material **87** and observing indeed a pure statistical mixture of all four possible products **86**–**90**.

Shortly after this publication, Miller *et al.* successfully made use of allyl, benzyl and cyclopropylmethyl radicals as chain carriers in 1,5-von Auwers rearrangements (Scheme 27).[34] For allyl- and benzyl radicals, as the [1,5]-product can also theoretically be obtained by concerted mechanisms (double [3,3]-, or single [5,5]-sigmatropic shifts), the free-radical chain transfer mechanism was again unambiguously evidenced by the product distribution of D-labelled starting materials such as **91**, as well as by the detrimental action of radical inhibitors.

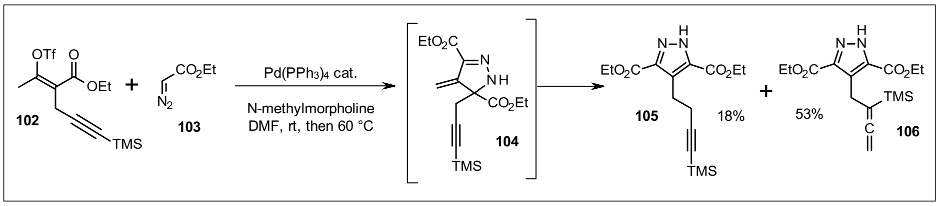


Scheme 27.
Allyl, benzyl and cyclopropylmethyl radicals as chain carriers.

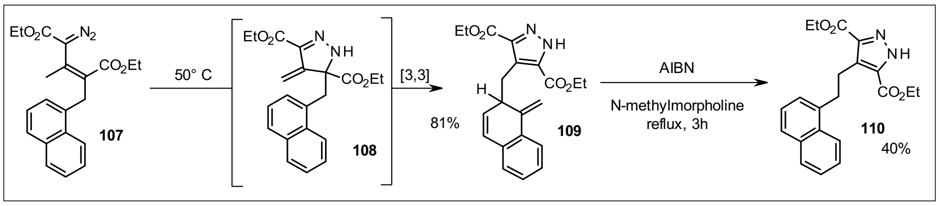
The same research group also perform-



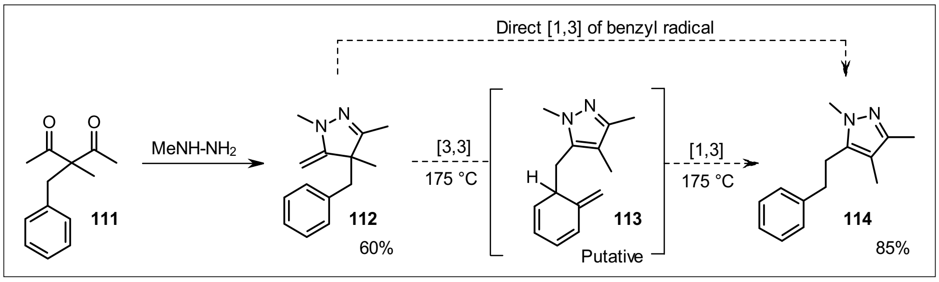
Scheme 28. [1,3]-radical von Auwers shift preferred over [3,3]-sigmatropic shift.



Scheme 29. Competing von Auwers [1,3]-shift and sigmatropic [3,3]-shift.



Scheme 30. Radical AIBN-promoted [1,3]-shift preferred over ionic proton transfer in **109**.



Scheme 31. Direct [1,3]- and/or seminal example of consecutive [3,3]+[1,3]-rearrangement?

ed the [1,3]-transfer of a benzyl radical from **99** (Scheme 28).[35] In this case, any direct [3,3]-sigmatropic shift of the benzyl group would have led to a different product **101**, which was never formed, even at high temperatures. This observation might speak again in favor of a von Auwers typical free-radical chain reaction. On the contrary, it is worthy of note that attempts by Miller to have an allyl- or crotyl group migrating in a [1,3] shift proceeded exclusively through [3,3]-sigmatropic Cope rearrangements instead.

All these observations find an echo in the more recent studies made by the group of Frantz *et al.*, who observed minor [1,3]-von Auwers shifts while studying [3,3]-Cope rearrangements on putative dearomatized pyrazole **104** (Scheme 29).[36] As can be seen from the Scheme, product **105** would come from a [1,3]-von Auwers shift whereas product **106** would be formed *via* a [3,3]-sigmatropic shift of the propargyl moiety.

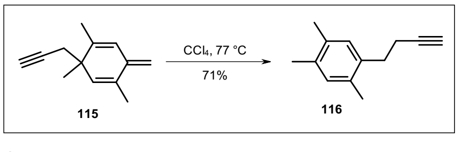
While propargyl groups have a preference for [3,3]- over [1,3]-shifts, benzyl groups may be effectively diverted from this course. Indeed, their relatively easy [3,3]-shift does not lead directly to a final, fully rearomatized product, but actually to a semi-benzene, such as depicted in Scheme 30 with semi-naphthalene **109**.[37] The rearomatization of such semi-benzenes by proton transfer being very slow under neutral conditions,[38] Frantz *et al.* could then isolate and characterize semi-naphtalene **109**, before engaging it into a [1,3]-von Auwers shift by the use of AIBN (Scheme 30). Inversely, in the presence of radical quenchers, semi-naphtalene **109** delivered only the aromatized product of the [3,3]-sigmatropic shift by proton transfer.

Such consecutive rearrangements might actually have been discovered as early as 1968 by Manning *et al.*,[39] but were not recognized as such. Indeed, the formation of **114**, coming formally from a direct [1,3]-shift of the benzyl group from **112**, might also have come from a consecutive [3,3]-sigmatropic shift followed by [1,3]-radical shift of the pyrazole-methyl radical (Scheme 31). If this hypothesis was not mentioned by the authors, the remarkable mechanistic studies of Frantz *et al.* on their related pyrazole system make it quite plausible indeed.

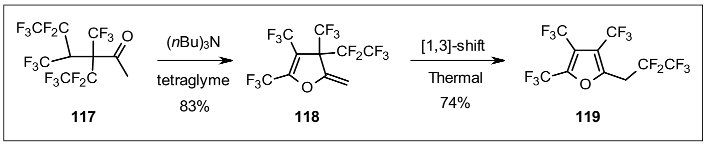
If propargyl groups do prefer sigmatropic shifts over [1,3]-radical migrations, it may be different against [1,5]-von Auwers shifts, as was shown in 1985 by the group of Heimgartner. They indeed successfully, from **115**, took a propargyl radical through a [1,5]-von Auwers rearrangement to afford **116** (Scheme 32).[40] Once again, due to the detrimental action of radical inhibitors and the positive effect of radical initiators on rate and yield, a typical free-radical chain transfer mechanism was put forward by the authors, when two consecutive [3,3]-sigmatropic shifts might have been a valid alternative explanation.

From the [1,3]-rearrangement observed with **104**, and maybe with **112**, it seems that the von Auwers rearrangements can be extended to dearomatized heteroaryls (semi-heteroarenes such as **104**) instead of being limited to the generic semi-benzenes **1** and **3**. Drawing all possible semi-heteroarenes that could engage in [1,3]- or [1,5]-von Auwers shifts is a daunting task, especially if one wants to cover multiple ring sizes (5, 6, *etc.*) and polycyclic structures. Notwithstanding the high number of those possibilities, our literature searches in this area were only rewarded by a single additional example of a [1,3]-shift in a semi-heteroarene, as depicted by **118** in Scheme 33.[41] This is the only report – to the best of our knowledge – of a polyfluoroalkyl radical as chain carrier in a von Auwers rearrangement.

The free radicals reported in this section are the only examples that were found, notwithstanding di- and tri-chloromethyl, to have been used as chain carriers in von Auwers rearrangements.



Scheme 32. Propargyl radical as chain carrier in a [1,5]-shift.



Scheme 33. [1,3]-von Auwers shift in the heterocyclic series.

## 4. Synthetic Applications of von Auwers Rearrangements

Alongside the work reviewed here, which were all inventions, mechanistic investigations and scope studies, there are only very few reports describing practical applications of von Auwers rearrangements for the synthesis of targeted compounds of interest. In 1962, the preparation of DDT analogues by addition of aryl-phophoniums or -phosphonates on **17** (Scheme 34) was reported by Keaveney e*t al.*[42]

Apart from this single report, we are unaware of any published uses of the von Auwers rearrangement in attempts to prepare target molecules. The synthetic usefulness of this methodology is certain though. As a contemporary example, in our laboratory, grams of an elaborated phenylacetic acid **125** (en route to insecticidal products) were obtained in three steps only (Scheme 35). Compound **125** proved very difficult to obtain otherwise.

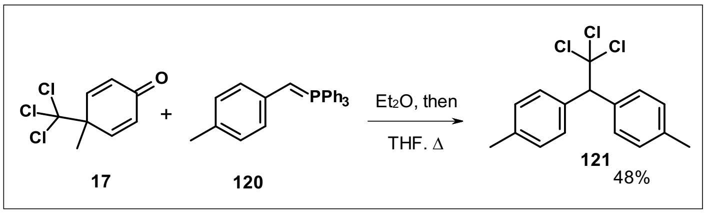
Finally, we are currently using von Auwers rearrangements to access building blocks to prepare various heterocycles. These will be reported in due course.

## 5. Conclusion

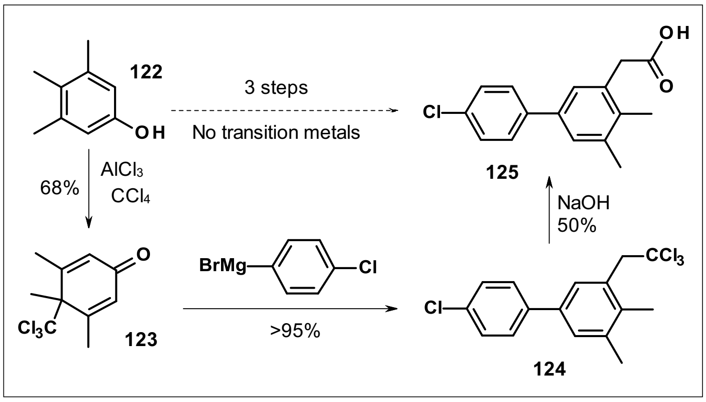
The ground-breaking experiment of Hart *et al.*, in which a methyl radical was shown to migrate, is a striking example of the potential of semi-benzenes to (re) aromatize. Hanging on the brink of a 36 kcal/mol drop in the potential energy surface, these molecules will rearrange at all cost, even if it means overcoming a homolytic cleavage of a C–CH$_3$ bond. In front of such a demonstration, one can only wonder what else would migrate, or what other kinds of Ar–C bonds can be made concomitantly, by simple nucleophilic additions on dienones, *etc.* As the drop in energy is so high, we learned from the examples of this review that, when aromatization happens, it usually does so efficiently and cleanly, to a single product.

Also, in a modern context where more transformations have been invented from trichloromethyl- or dichlorovinyl groups, where numerous ways to dearomatize phenols have been found, the von Auwers reactions lead undeniably to useful intermediates, from readily accessible dienones. With this review, the authors hope to attract the attention of a part of the scientific community to such aromatizations, and more humbly, to pay homage to great chemists and chemistries of the past.

Received: June 10, 2014



Scheme 34. Preparation of DDT analogues using a von Auwers rearrangement.



Scheme 35. Transition-metal-free synthesis of Aryl-substituted phenyl acetic acid.[30]

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[1] a) K. Reimer, *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 423; K. Reimer, F. Tiemann, *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 824; b) K. Reimer, F. Tiemann, *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 1268; c) K. Reimer, F. Tiemann, *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 1285.

[2] a) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2976; b) K. von Auwers, L. Hof, *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 1110; c) K. von Auwers, V. Erggelet, *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 3598; d) K. von Auwers, F. Winternits, *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 465; e) K. von Auwers, G. Keil, *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 4207.

[3] a) K. von Auwers, G. Keil, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 1861; b) K. von Auwers, G. Keil, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3902; c) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 1790.

[4] T. Zincke, R. Suhl, *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 4148. (Improved protocols can be found in: M. S. Newman, A. G. Pinkus, *J. Org. Chem.* **1954**, *19*, 978.)

[5] T. Zincke, F. Schwabe, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 897.

[6] a) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1693; b) K. von Auwers, W. Julicher, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 2167; c) T. Zincke, F. Schwabe, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 897; d) T. Zincke, F. Schwabe, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 1922

[7] A. Andreocci, *Gazz. Chim. Ital.* **1893**, *23*, 468.

[8] M. S. Newman, J. Eberwein, L. L. Wood Jr., *J. Am. Chem. Soc.* **1959**, *81*, 6454.

[9] a) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1905**, *33*, 1697; b) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3748; c) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 588; d) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 788; e) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1595; f) K. von Auwers, *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 2389.

[10] R. C. Fuson, T. G. Miller, *J. Org. Chem.* **1952**, *17*, 316.

[11] R.L.Tse,M.Newman,*J.Org.Chem.***1956**,*21*,638.

[12] For a review, see S. Swaminathan, K. V. Narayanan, *Chem. Rev.* **1971**, *71*, 429.

[13] C. W. Bird, R. C. Cookson, *J. Org. Chem.* **1959**, *24*, 441.

[14] a) M. S. Newman, L. L. Wood Jr, *J. Am. Chem. Soc.* **1958**, 1236. It is unclear whether this [1,3]-sigmatropic shift has the same mechanism as the von Auwers [1,5]-shift (thermal radical dissociation and chain transfer as depicted in Scheme 9) or if it goes *via* a pericyclic concerted mechanism. As is well documented, concerted [1,3]-sigmatropic shifts are 'disfavored' (the required antarafacial geometry cannot be achieved easily) under thermal conditions. However, a C–C bond may migrate [1,3] with inversion of the stereochemistry as antarafacial interaction may happen with the sp3 orbital of the migrating carbon. See: b) J. A. Berson, G. L. Nelson, *J. Am. Chem. Soc.* **1970**, 1096 and references therein.

[15] M. S. Newman, F. Bayerlein, *J. Org. Chem.* **1963**, *28*, 2804. (Reproduced in D. I. Schuster, K. J. Smith, A. C. Brisimitzakis, *J. Org. Chem.* **1981**, *46*, 473.)

[16] M. S. Newman, L. L. Wood Jr, *J. Am. Chem. Soc.* **1959**, *81*, 6450.

[17] M. S. Newman, D. Pawellek, S. Ramachandran, *J. Am. Chem. Soc.* **1962**, *84*, 995.

[18] T. G. Miller, *J. Org. Chem.* **1962**, *27*, 1549.

[19] M. S. Newman, W. X. Bajzer, *J. Org. Chem.* **1970**, *35*, 270.

[20] a) K. von Auwers, *Justus Liebigs Annalen der Chemie* **1906**, 219; b) K. von Auwers, *Justus Liebigs Annalen der Chemie* **1906**, 278; c) K. von Auwers, *Justus Liebigs Annalen der Chemie* **1906**, 288; d) K. von Auwers, *Justus Liebigs Annalen der Chemie* **1906**, 352.

[21] M. S. Newman, J. A. Eberwein, *J. Org. Chem.* **1964**, *29*, 2516.

[22] M. S. Newman, R. L. Layton, *J. Org. Chem.* **1968**, *33*, 2338.

[23] V. A. Nikanorov, A. D. Rogachev, E. I. Mysov, *Russ. Chem. Bull.* **1995**, *44*, 964.

[24] a) A. J. Fry, *J. Am. Chem. Soc.* **1965**, *87*, 1816; b) T. G. Miller, *J. Org. Chem.* **1966**, *31*, 3178; c) K. Nagarajan, A. Venkateswarlu, *Tetrahedron Lett.* **1967**, *4*, 293; d) T. G. Miller, R. C. Hollander, *J. Org. Chem.* **1980**, *45*, 1334; e) K. Abe, M. Takahashi, *Synthesis* **1990**, *10*, 939; f) V. A. Nikanorov, O. L. Tok, S. G. Novikov, S. V. Sergeev, E. V. Vorontsov, I. D. Gridnev, D. V. Zverev, A. T. Lebedev, *Russ. Chem. Bull.* **1997**, *46*, 350.

[25] D. J. Patel, D. I. Schuster, *J. Am. Chem. Soc.* **1967**, *89*, 184.

[26] V. I. Rozenberg, V. A. Nikanorov, G. V. Gavrilova, B. I. Ginzburg, O. A. Reutov, *Zhurnal Organicheskoi Khimii* **1984**, *20*, 208.

[27] V. A. Nikanorov, S. V. Sergeev, P. V. Petrovskii, D. V. Zverev, N. A. Klyuev, A. I. Gamazade, G.

E. Vainer, F. M. Dolgushin, A. I. Yanovskii, Y. T. Struchov, *Russ. Chem. Bull.* **1996**, *45*, 989.

[28] B. Miller, *Tetrahedron Lett.* **1972**, *11*, 1019.

[29] a) V. I. Rozenberg, V. A. Nikanorov, B. I. Ginzburg, O. A. Reutov, *Bull. Acad. Sci. USSR, Chem. Sci.* 1**983**, *32*, 1102; b) V. A. Nikanorov, B. I. Ginzburg, V. I. Bakhmutov, V. I. Rozenberg, O. A. Reutov, *Bull. Acad. Sci. USSR, Chem. Sci.* **1986**, *35*, 2099.

[30] Results from this section are all from R. Dumeunier, S. Jaeckh, A. Scherrer, unpublished material. $^1$H NMR of new compounds: (400 MHz, chloroform-d) *Compound* ***76*** δ ppm 1.54 (s, 3 H) 5.26 (d, *J*=10.27 Hz, 1 H) 5.37 (d, *J*=16.51 Hz, 1 H) 5.97–6.15 (m, 3 H) 6.35 (dd, *J*=9.90, 1.83 Hz, 1 H) 6.78–6.91 (m, 2 H); *Compound* ***77*** δ ppm 2.34 (s, 3 H) 3.53 (dd, *J*=7.34, 1.10 Hz, 2 H) 6.27 (dt, *J*=15.77, 6.97 Hz, 1 H) 6.61 (d, *J*=15.77 Hz, 1 H) 7.15 (d, *J*=8.07 Hz, 2 H) 7.32 (d, *J*=8.07 Hz, 2 H); *Compound* ***81*** δ ppm 0.41–0.49 (m, 4 H) 0.95–1.05 (m, 1 H) 1.48 (s, 3 H) 1.61 (s, 1 H) 5.94 (d, *J*=9.79 Hz, 2 H) 6.07 (d, *J*=9.79 Hz, 2 H); *Compound* ***83*** δ ppm 2.37 (s, 3 H) 2.53 (dddd, *J*=14.21, 11.37, 5.04, 3.85 Hz, 1 H) 2.79 (dddd, *J*=13.89, 10.68, 5.87, 2.93 Hz, 1 H) 3.15 (td, *J*=10.73, 4.95 Hz, 1 H) 3.51–3.58 (m, 1 H) 3.90 (dd, *J*=11.37, 2.93 Hz, 1 H) 7.19 (d, *J*=7.70 Hz, 2 H) 7.33 (d, *J*=7.62 Hz, 2 H); *Compound* ***84*** δ ppm 2.38 (s, 3 H) 4.85 (dd, *J*=17.24, 1.47 Hz, 1 H) 5.31 (dd, *J*=10.64, 1.10 Hz, 1 H) 7.01 (dd, *J*=17.24, 10.64 Hz, 1 H) 7.05 (d, *J*=8.07 Hz, 2 H) 7.21 (d, *J*=7.87 Hz, 2 H); *Compound* ***124*** δ ppm 2.40 (s, 6 H) 4.12 (s, 2 H) 7.38 (bs, 1 H) 7.39 (d, *J*=8.44 Hz, 2 H) 7.51 (d, *J*=8.80 Hz, 2 H) 7.54 (d, *J*=1.83 Hz, 1 H); *Compound* ***125*** δ ppm 2.24 (s, 3 H) 2.35 (s, 3 H) 3.75 (s, 2 H) 7.23 (bs, 1 H) 7.30 (bs, 1 H) 7.37 (d, *J*=8.80 Hz, 2 H) 7.48 (d, *J*=8.80 Hz, 2 H).

[31] J. Villieras, P. Perriot, J. F. Normant, *Synthesis* **1975**, 458.

[32] a) J. R. Merchant, V. B. Desai, *J. Chem. Soc.* **1964**, 2258; b) J. R. Merchant, V. B. Desai, *J. Chem. Soc. C* **1968**, 499.

[33] H. Hart, J. D. DeVrieze, *Tetrahedron Lett.* **1968**, *40*, 4257.

[34] a) B. Miller, K.-H. Lai, *Tetrahedron Lett.* **1971**, *20,* 1617; b) B. Miller, K.-H. Lai, *J. Am. Chem. Soc.* **1972**, *94*, 3472.

[35] a) B. Miller, M. R. Saidi, *Tetrahedron Lett.* **1975**, *21*, 1691; b) B. Miller, M. R. Saidi, *J. Am. Chem. Soc.* **1978**, *98*, 2544.

[36] D. J. Babinski, H. R. Aguilar, R. Still, D. E. Frantz, *J. Org. Chem*. **2011**, *76*, 5915.

[37] D. J. Babinski, X. Bao, M. El Arba, B. Chen, D. A. Hrovat, W. T. Borden, D. E. Frantz, *J. Am. Chem. Soc.* **2012**, *134*, 16139.

[38] M. Bao, H. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc*. **2001**, *123*, 759.

[39] D. T. Manning, H. A. Coleman, R. A. Langdale-Smith, *J. Org. Chem.* **1968**, *33*, 4413.

[40] J. Lukac, H. Heimgartner, *Helv. Chim. Acta* **1985**, *68*, 355.

[41] S. Bartlett, R. D. Chambers, N. M. Kelly, *Tetrahedron Lett.* **1980**, *21*, 1891.

[42] W. P. Keaveney, D. J. Hennessy, *J. Org. Chem.* **1962**, *27*, 1057.