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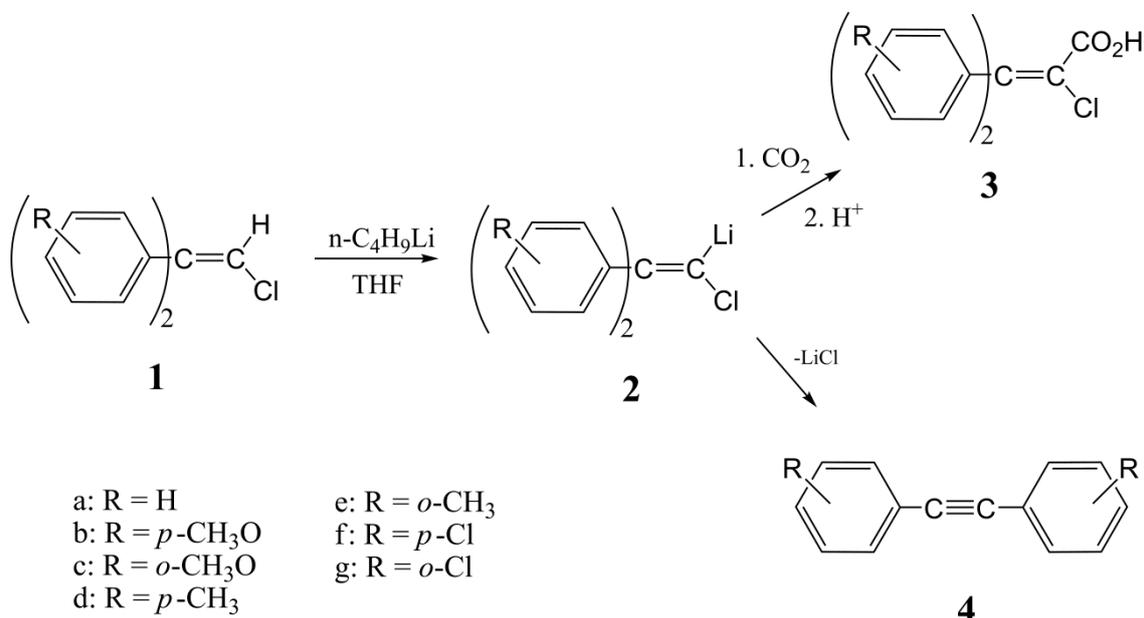
The formation and thermal stability of 1-chloro-2,2-diaryl-vinyl lithium compounds¹
by

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■
Metalation rates of the ring-substituted Diarylhalogenethylene **1** and stability of the resulting organolithium **2** follow the series CH₃ O < H < Cl and ortho < para. The mechanistic consequences for the Fritsch-Butt-Wiechell rearrangement are discussed. In the *o*-methoxy derivative **2c** rearrangement competes with cyclization to a benzofuran derivative which is regarded as the electrophilic reaction of the metalated carbon.
■

The above analysis revealed that 1-chloro-2,2-diphenyl-vinyl-lithium (**2a**) by metallation of Halogenolefins **1a** with butyllithium in tetrahydrofuran (THF) can easily present at low temperature, eg by conversion into the acrylic acid **3a** can be characterized, and when heated with lithium chloride elimination quantitatively in diphenylacetylene (**4a**) rearranges (Fritsch-Butt-Wiechell rearrangement)². We have carried out some reactions of the respective ortho- and para- substituted 2,2-diaryl-chloroethylenes of structure **1**³ which we did with the intention to meet the substituent effect on rate of formation and thermal stability of the organolithium **2**⁴.



1. XIV. Mitteil über Kohlenstoffe mit Halogen- und Alkalimetallsubstituenten (Communication about carbons with halogen and Alkalimetal substituents). XIII. Mitteil. : G. Köbrich und H. Trapp².

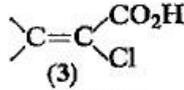
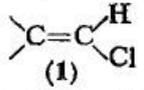
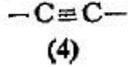
2. G. Köbrich and H. Trapp, Chem. Ber. 99, 670 (1966), as in the above reference.

3. In order to measure these compounds use footnote 9 of the above work

4. Preliminary communications: G. Köbrich and H. Trapp, Z. Naturforsch. 18b, 1125 (1963); G. Köbrich, H. Trapp and I. Hornke, Tetrahedron Letters [London] 1964, 1131.

An equimolar solution of n-butyllithium in petroleum ether was treated with the haloolefins of structure **1** under the following standard conditions; used as solvent in all experiments was a mixture of THF, diethyl ether and petroleum ether (50-70 °C) in a ratio of 4:1:1, which below 100 °C has a relatively low viscosity. This yielded the carboxylation product after a defined time. The carboxylic acids **3a-3g** and were purified from the unreacted substrate where appropriate by column chromatography. The diarylacetylenes produced (**4**) can be found in Table 1.

Metalation of chloroolefins **1** at different temperatures
(solvent: THF (16 mL), diethyl ether (4 mL) and olefin-free petroleum ether (50-70 °C) (4 mL) for every 10 mMol of **1**, temperature constancy ± 3 °C)

Experiment number	R in 1	Temp.	Metallation time (Min.)	Reaktionsprodukte (%)		
						
1	H	-108°	45	85	14	—
2		-72°	60	83	4	10
3		-43°	20	0.8	—	97
4	(<i>p</i>)CH ₃ O	-108°	45	67	28	—
5		-72°	45	3	11	85
6	(<i>o</i>)CH ₃ O	-108°	45	8	88	—
7		-72°	45	Spur *)	59	14
8	(<i>p</i>)CH ₃	-108°	50	78	16	—
9		-72°	45	51	—	47
10	(<i>o</i>)CH ₃	-108°	50	45	50	—
11		-72°	45	1.2	17	77
12	(<i>p</i>)Cl	-108°	45	85	14	—
13		-41°	20	86	4	4.6
14		-12°	5	32	—	61
15	(<i>o</i>)Cl	-108°	45	76	24	—
16		-40°	20	63	4	30
17		-12°	5	2.5	—	93

*) In addition 14% of the acid 16 (see text)

The metalation are completed at -108 °C after 45-50 min in any case, as indicated by the recovery of each substrate. On the other hand, the organolithium compounds formed are stable under these conditions because no decomposition product (**4**) is detectable. The yield of the acids **3a-3g** is therefore a measure of the relative velocity of the metalation substrates **1a-1g**. It falls in the range:



wherein the *p*-substituted compounds more rapidly convert than the *o*-isomers.

This substitution pattern corresponds what is expected from inductive and mesomeric effects which are likely to increase lithiation rate in sequence of the electronegativity of the α -carbon to be metallated due to the related discouragment of deprotonation. It is initially surprising that the same lithiation rate was observed for both the *p*- and *o*-substituted derivatives. A consideration of what the space-filling model teaches us is confirmed by the UV absorptions of the chloro-olefins **1** (Figure 1), namely the aryl groups of the *o*-compounds due to steric interaction become rotated out of the plane of the olefin that no appreciable resonance relationship between the aromatic group and the double bond can develop. However it can happen in the case of the parent compound **1a**

with a rotation of 26° and hence it is also entirely possible with the *p*-compounds. If on the other hand, only the inductive (field) effect of *ortho*-substituents on the α -carbon is significant, the order $\text{Cl} > \text{CH}_3\text{O} > \text{CH}_3$ would be expected instead of that observed. Apparently, the acidity of the vinyl proton is mainly defined by its angle of rotation and is independent of the inductive effect of the aromatic group, which in turn depends on the substituents in accordance with their M- and I- effect. From comparison of the *p*- and *o*- substitution it is evident that strong deceleration of the metalation is probably due to the steric shielding of said vinyl hydrogen by the *ortho*-substituents.

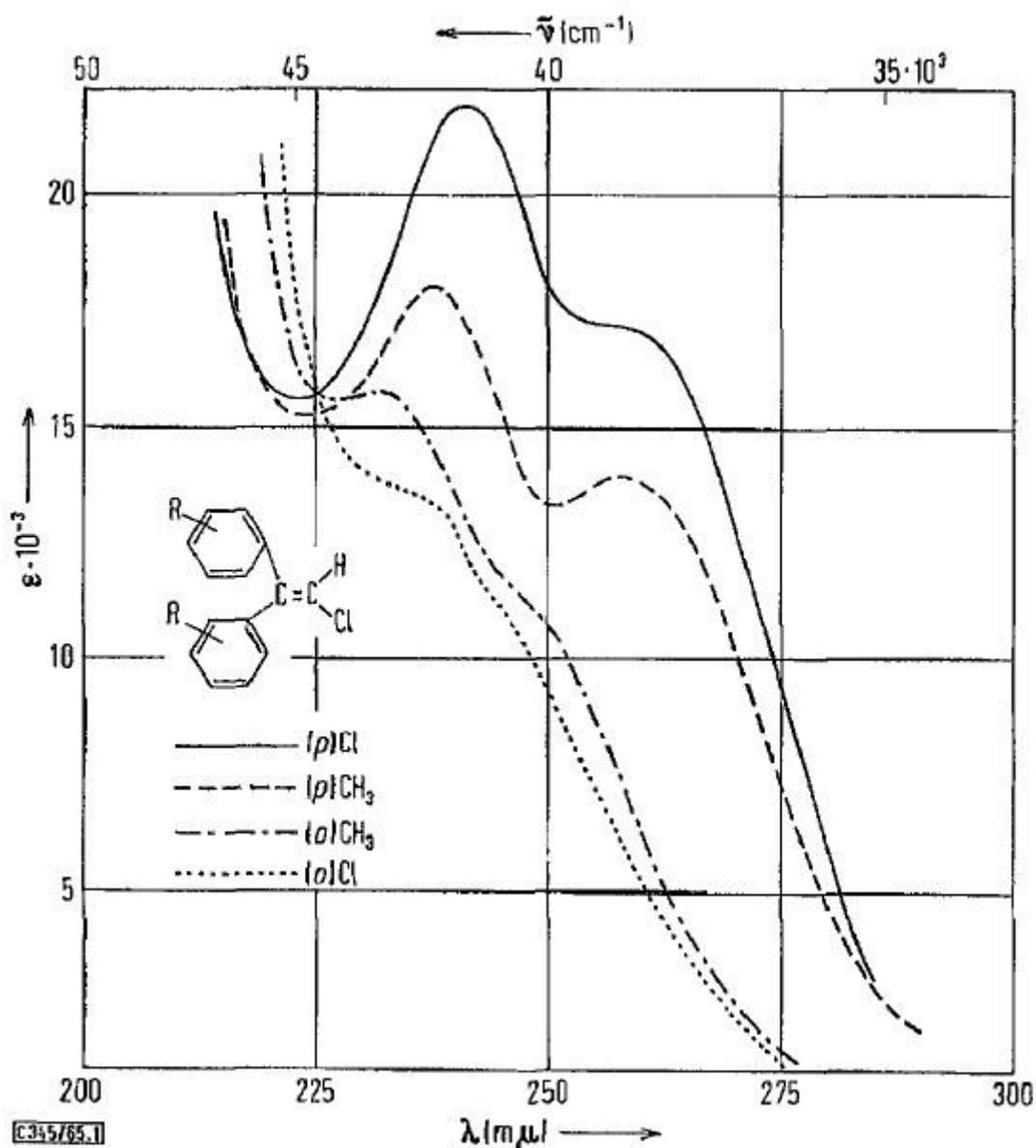


Figure 1. UV spectra of various chloro-olefins 1 in methanol

The metalation carried out at and above -72°C produces the lithium compounds **2a-2g** and in addition there is always some of the decomposition products **4a-4g**. The readiness of isomerization proves to be (as shown in the table) strongly substituent dependent. Thus the methoxy compounds **2b** and **2c** are grasped only at lower

5. M. Simonetta and S. Carrá, Tetrahedron [London] **19**, Suppl. 2, 467 (1963).

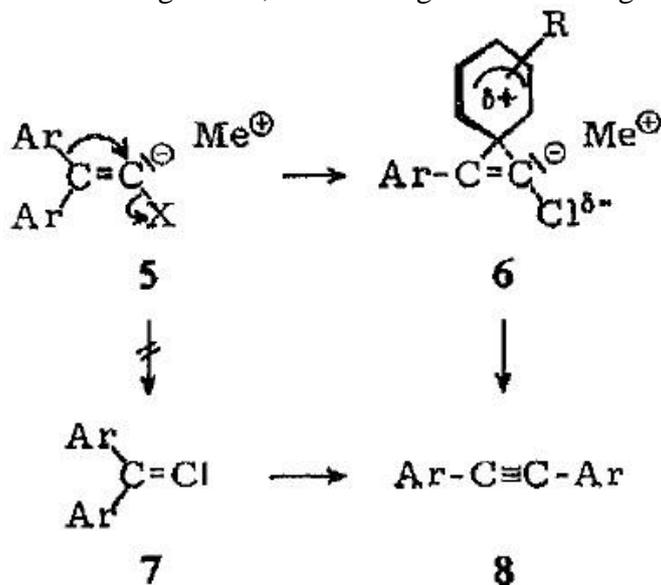
temperature, whereas **2a** can also be prepared at $-72\text{ }^{\circ}\text{C}$ (Experiments 2 and 5). **2a** is on the one hand at $-41\text{ }^{\circ}\text{C}$ almost completely decomposed within 20 min, while on the other hand, the *p*-chloro derivative **2f** proves to be largely stable (experiments 3 and 13) and are still working with vigour even at $-12\text{ }^{\circ}\text{C}$ where the decarboxylation product can be detected (experiment 14).

The decomposition the α -chloro-vinyl lithium compounds **2** increases accordingly - the inverse of the rate of formation - in the series:

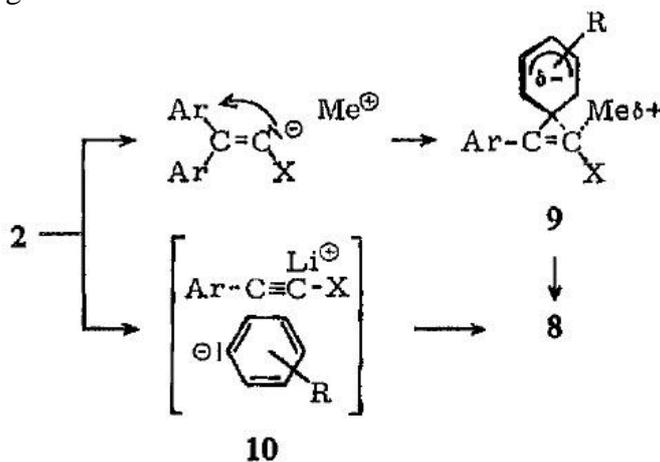


where in each case the *o*-isomer decomposes more rapidly.

These conclusions for this for the chemistry become obvious on consideration of the Fritsch-Butt-Wiechell rearrangement $2 \rightarrow 4$ ⁶? Bothner-By⁷ and Curtin and Mitarbb⁸ have yielded a suitably substituted, isotopically labeled diarylhalogenethylene to prove that changes over both in *tert*-butyl alcohol as well as in ethereal media preferred the halogen to be trans to the substituent of the neighboring carbon and therefore to have no stereospecific reaction – for olefinic symmetry - carbene intermediate **7** may be responsible. According to Bothner-By⁷ this is by an electrophilic substitution at the migrating aromatics. According to this, the rearrangement is analogous to the



Beckmann rearrangement with the nonbonding electron pair bound to a negatively charged carbon (structure **5**) and therefore takes on a partial positive charge in the transition state **6**. Its stabilization by electron-donating substituents should cause an accelerated rearrangement.



The isomerization by carbanion rearrangement¹⁰ was reported to occur by an attack of the electron pair on the aromatics, either as $\text{S}_{\text{N}}1$ reaction with a cleavage-recombination

6. Literature by Köbrich, *Agew. Chem.* **77**, 75 (1965); *Angew. Chem. internat. Edit.* **4**, 49 (1965).

7. A. A. Bothner-By, *J. Amer. Chem. Soc.* **77**, 3293 (1955).

8. D. Y. Curtin, E. W. Flynn und R. F. Nystrom, *J. Amer. Chem. Soc.* **80**, 4599 (1958).

9. Übersicht: P. A. S. Smith in P. De Mayo, *Molecular Rearrangements*, Vol. **I**, S. 83, Interscience Publishers, New York-London 1963.

10. Overviews (Übersichten): G. Köbrich, *Agew. Chem.* **74**, 453 (1962); *Angew. Chem. internat. Edit.* **1**, 382 (1962); H. E. Zimmerman in P. De Mayo, *Molecular Rearrangements*, Vol. **I**, S. 83, Interscience Publishers, New York-London 1963.

mechanism via an internal ion pair **10**, or the negative charge may wander through the neighboring carbons of the aromatic intermediate. In this case, would be the reverse substituent effect - a first order deceleration by substituents - would be expected.

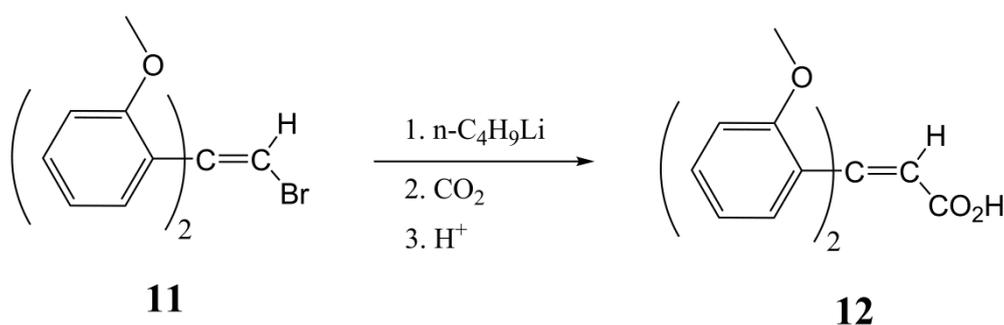
The experimental findings stand only for the Bothner-Byschen mechanism, but not with the carbanion mechanism in accordance with¹¹.

The question of to what extent the aryl moiety on the β -carbon effects the rate of the migration responsible for the observed rearrangement can not be answered with the compounds described herein (**2**) which have two identical aryl groups.

By means of formal shift of the *p*-substituents in the *o*-position a rearrangement acceleration is produced that is in parallel to the findings in the Chapman rearrangement of substituted acetophenone-oxime-trinitrophenylether¹² and can be interpreted similarly: in the absence of *o*-substituents the better coplanarity makes possible a resonance relationship between the aromatics and the double bond. The transition state **6**, in which these planes are perpendicular to each other, must therefore be paid for with a loss of resonance energy. This energy expenditure does not apply to the *o*-derivatives **2**, where the aromatics are already rotated out of the olefin plane.

The specific case of 1-chloro-2,2-bis-[*o*-methoxy-phenyl]-vinyl lithium (**2c**)

The organolithiums **2** are decomposed by heating to give diarylacetylenes in quantitative yield. Thus the corresponding **4b**, **4d** and **4g** are obtained respectively from **2b**, **2d** and **2g** at -108°C in 99% yield. In contrast, the *o*-methoxy derivative **2c** has another way of being stabilized. Metallization of the haloethylene **1c** occurs at -72°C , subsequent carboxylation of **2c** provides trace amounts of the expected acid **3c** which the sole non-halogenated carboxylic acid is obtained at -108°C (experiment 6) in 14% yield, mp $207\text{-}208.5^\circ\text{C}$. It is not identical with the acid **12** which was prepared for comparative purposes from compound **11**, which melts at $137\text{-}138^\circ\text{C}$.



Analysis of the mass spectrum molecular peak ($m/e = 268$) calculated formula $\text{C}_{16}\text{H}_{12}\text{O}_4$ is compared to **12** which is poorer by CH_4 . As the molecule contains only one of the

11. The same result from the kinetic study of Halogenethylene of type 1 in the systems ethanolate / ethanol and glycolate / glycol. The findings here, while small, did observe substituent effects: *W. M. Jones* und *R. Damico*, *J. Amer. Chem. Soc.* **85**, 2273 (1963); *P. Beltram* und *S. Carrá*, *Gazz. Chim. ital.* **91**, 889 (1962). Theoretical consideration of the Fritsch-Buttenberg-Wiechell-Umlagerung: *M. Simonetta* und *S. Carrá*⁵.

12. *R. Huisgen*, *J. Witte*, *H. Walz* und *W. Jira*, *Liebigs Ann. Chem.* **604**, 191 (1957).

two methoxy groups originally present in the NMR spectrum and no vinyl proton is detectable, the demethylated phenol oxygen must be connected to an olefinic carbon. The resultant acid has the structure of **16** which is similar to that of the benzofuran carboxylic acid shown in (Figure 2), but structure **16** is supported by additional aromatic bathochromic shifts in the UV spectrum (Figure 2). Signals appear in the mass spectra at $m/e = 253$, 237 and 223 which correspond to the respective loss of CH_3 , CH_3O and CO_2H cations. A peak at $m/e = 175$ can be assigned to the resultant fragment of **16** giving the ion $[(o)\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{CO}_2]^+$.

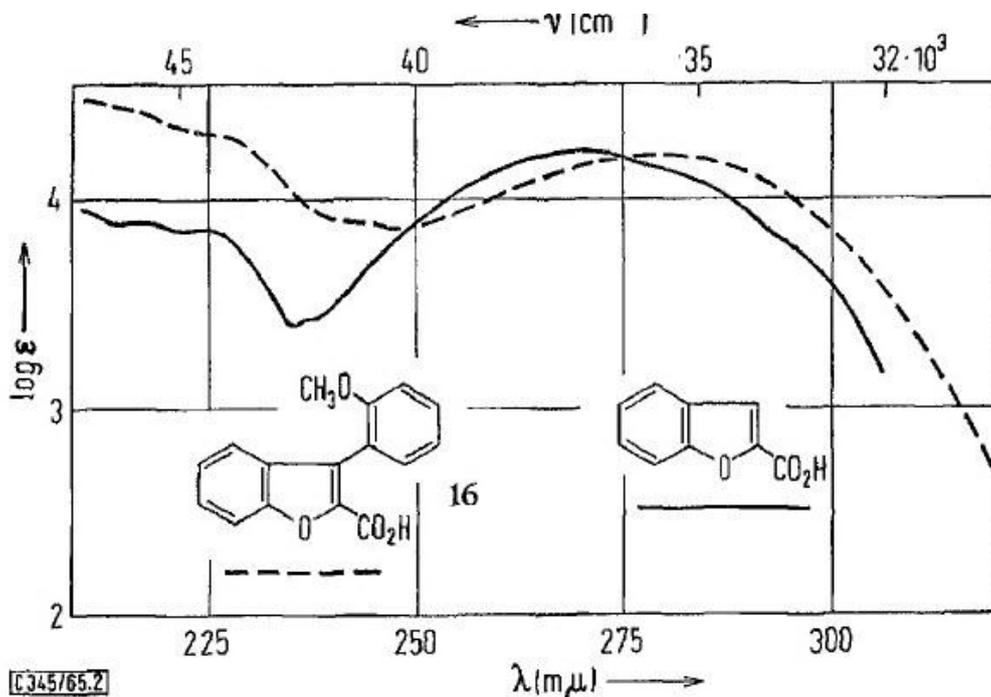
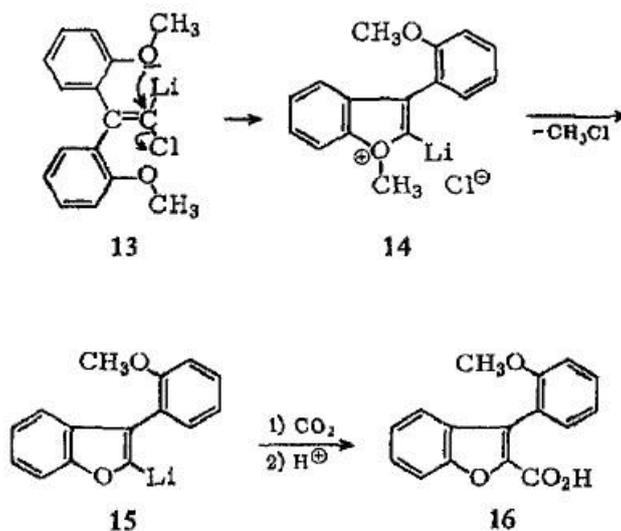


Figure 2. UV-spectra of **16** (in methanol) and benzofuran-carboxylic acid¹³ (in ethanol)



The formation of the acid can be interpreted as outlined above¹⁴.

13. Absorption Spectra in the Ultraviolet and Visible Region, Vol. I, Publishing House of the Hungarian Academy of Science, Budapest 1964.

14. A carbene intermediate (like **7**) is not yet safely ruled out, however it appears analogous to the Fritsch-Butt-Wiechell rearrangement and others, meanwhile the demonstrated electrophilic reactions of α -halo-organolithiums can be dismissed.

The extent to which the cyclization **2c** → **16** is able to compete with the Fritsch-Butt-Wiechell rearrangement depends on the reaction temperature. At $-72\text{ }^{\circ}\text{C}$, both paths are equal (yield ratio **4c** : **16** = 1 : 1), at $-2\text{ }^{\circ}\text{C}$, the aryl rearrangement is favored by a factor of 80. The transition state for the Fritsch-Butt-Wiechell rearrangement has thus a higher activation energy than that for the cyclization, which presumably has a discrete close-meeting orientation of the five membered heterocycle which needs a strong negative entropy¹⁵.

These preliminary experiments allow for and expect further clarification.

It is fair to assume that the Fritsch Butt-Wiechell rearrangement in alcoholic media always gives substitution of the halogen by an alkoxy group to form vinyl ethers¹⁶ and that attachment of the carbanion intermediate **5** is a competing reaction. This agrees with the findings of¹⁶; that the substitution occurs in the opposite manner to the previous isomerization when the substrate **1** contains electron-donating substituents and therefore assiduously rearranges to comprise aromatic residues.

We are obliged to thank the *German research foundation* (Deutschen Forschungsgemeinschaft), the *economic ministry of Baden-Württemberg* and the *foundation for chemical industries* (Fonds der Chemischen Industrie) for financial support of this work. We thank *Fräulein S. Rincke* for measuring the UV spectra and *Herr Ch. Wünsche* for the mass spectra.

Description of Experiments

Mp's are corrected. Methods for carrying out the organometallic reactions are described below. Pretreatment of solvents, etc., have already been stated². Woelm neutral alumina was used for column chromatography. UV spectra were recorded in methanol with an instrument from Perkin-Elmer & Co., Model 350.

Confirmation of the chloroethylenes **1** : **1a**, **1b**, **1d** and **1f** were obtained in a known manner by Friedel-Crafts reacting dichloroacetaldehyde-diethylacetal with the corresponding aromatic compounds followed by dehydrochlorination¹⁶. Confirmation of the remaining compounds is described below¹⁷.

1. General procedure for the metalation of **1** at $-108\text{ }^{\circ}\text{C}$

Example: 1-Chloro-2,2-bis-[4-methyl-phenyl]-vinyl lithium (**2d**): A twin manifold line was attached to 250 mL three-necked flask, heated under vacuum and then filled with ultrapure nitrogen. The flask contained a solution of 4.86 g (20 mmol) of **1d** in a mixture of 32 mL THF, 8 mL of diethyl ether and 8 mL of hexane or petroleum ether ($50\text{-}60\text{ }^{\circ}\text{C}$). The flask was equipped with a stirrer, a low-temperature thermometer and a pressure equalizing addition funnel. It was stirred to achieve an inner temperature of $-108\text{ }^{\circ}\text{C}$ and the funnel then used to add dropwise with stirring over 35 min a

15. An appropriate statement for isomerization and use of nitrogen ylides: the Stevens rearrangement prefers higher temperatures with suitable substrates, at lower temperature the Sommelet rearrangement occurs by a five-membered cyclic transition state : *G. Wittig, H. Tenhaeff, W. Schoch and G. Koenig*, Liebigs Ann. Chem. **572**, 1 (1951); *S. W. Kantor und C. R. Hauser*, J. Amer. Chem. Soc. **73**, 4122 (1951); *G. Wittig and H. Streib*, Liebigs Ann. Chem. **584**, 1 (1953). Discussion: *H. E. Zimmerman*, I. C.¹⁰, S. 387.
16. *W. P. Bottenberg*, Liebigs Ann. Chem. **279**, 324 (1894); *H. Wiechell*, ebenda **279**, 337 (1894).
17. *G. Köbrich, H. Trapp, K. Flory and W. Drischel*, Chem. Ber. **99**, 689 (1966), nachstehend.

20 mmol solution of *n*-butyllithium in petroleum ether with the dropping rate chosen so that the reaction vessel temp had no more than a 2 °C increase. The yellow reaction mixture was stirred for a further 15 min. The dropping funnel was then removed and neck of flask connected to an erlenmeyer flask via a short, wide rubber tube with a ground stopper (size 29) fitted to each end. This erlenmeyer flask contained dry ice which was very free of moisture, had been finely ground and was pre-cooled by liquid nitrogen to about -120 °C. The dry ice was poured as soon as possible into the reaction vessel by tilting the Erlenmeyer flask (which caused the contents to become de-coloured), the temperature was not allowed to rise above -105 °C. After stirring at low temperature (15-40 min), the cooling bath was removed, the reaction mixture allowed to reach room temperature. The flask was opened to the ambient atmosphere and treated with 30 mL water. After removal the organic solvent by rotary evaporator, the aqueous phase was exhaustively extracted with diethyl ether, freed of CO₂ by treatment with dilute sulfuric acid, then extracted again several times with diethyl ether. Both lots of ethereal extract were washed with water, dried with calcium chloride, filtered and freed from solvent.

Neutral fraction: Gave 1.20 g after crystallization from ethanol to obtain 0.78 g (16%) of pure **1d** of mp 62-63 °C (mixed melting point)

Acid fraction: Gave 4.45 g (78%) of 2-chloro-3,3-bis-[4-methyl-phenyl]-acrylic acid (**3d**) as colorless crystals (crude mp 188-189 °C). After two recrystallizations from toluene the melting point increased to 191 -192 °C.

C₁₇H₁₅ClO₂ (286.8) Calc'd: C 71.20, H 5.30, Cl 12.37. Found: C 71.47, H 5.57, Cl 12.27.

2. General procedure for metalation of the chloroethylene **1** at and above -72 °C
Example: 1-Chloro-2,2-bis-[4-chloro-phenyl]-vinyl lithium (**2f**): 3.23 g (15 mmol) of **1f** was dissolved with stirring at -41 °C in 24 mL of THF, 6 mL of ether and 6 mL of hexane or petroleum ether (50-60 °C) using the apparatus described in example 1 (the addition of ether and petroleum ether is dispensable for synthetic approaches, see text), a 15 mmol solution of *n*-butyllithium in petroleum ether was added dropwise over 8 min. The orange mixture was stirred for another 12 min and then a slurry of excess dry ice in anhydrous diethyl ether quickly poured into a mantle around the flask. Workup was analogous to example 1.

Neutral fraction: Gave 0.45 g of opaque yellow crystals. One takes in a little petroleum ether (50-70 °C) which was chromatographed with the same solvent (Al₂O₃, Akt.-St. II) and receives in several fractions a total of 0.17 g (4.6%) of 4,4'-dichloro-tolan (**4f**) melting at 172-174 °C (Lit18: 175-176 °C) as well as 0.17 g (4%) of the parent compound **1f** with mp 65-66 °C (mixed melting point).

Acid fraction: The lithium salt of the acid **3f** is - in contrast to all other acids with structure **3** - poorly soluble in water but dissolves in THF. Therefore after separation from the neutral fraction by digestion with diethyl ether in THF it is treated with excess dilute sulfuric acid and after removal of the solvent by evaporation the residues dissolved in diethyl ether. Further work-up (following that of example 1) yields 4.3 g (86%) of 2-chloro-3,3-bis-[4-chloro-phenyl]-acrylic acid (**3f**) with a crude mp of

18. J. Kenner and E. Witham, J. Chem. Soc. [London] **97**, 1960 (1910).

170-171 °C. The mp increased to 170.5-171.5 °C after being twice recrystallized from toluene/cyclohexane.

$C_{15}H_{19}Cl_3O_2$ (327.6) Calc'd: C 54.99, H 2.77, Cl 32.47. Found: C 54.97, H 3.08, Cl 32.54.

3. Characterization of the other carboxylic acids **3** listed in Table S. 681.

2-Chloro-3,3-bis-[4-methoxy-phenyl]-acrylic acid (**3b**): Mp 141-142 °C (from benzene).

$C_{17}H_{15}ClO_4$ (318.8) Calc'd: C 64.05, H 4.74, Cl 11.12. Found: C 63.96, H 5.13, Cl 11.28.

2-Chloro-3,3-bis-[2-methoxy-phenyl]-acrylic acid (**3c**): Mp 169-171.5 °C (from toluene/cyclohexane).

$C_{17}H_{15}ClO_4$ (318.8) Calc'd: C 64.05, H 4.74, Cl 11.12. Found: C 64.19, H 4.83, Cl 10.99.

2-Chloro-3,3-bis-[2-methyl-phenyl]-acrylic acid (**3e**): Mp 195-196 °C (from benzene).

$C_{17}H_{15}ClO_2$ (286.7) Calc'd: C 71.20, H 5.30, Cl 12.37. Found: C 71.09, H 5.34, Cl 12.54.

2-Chloro-3,3-bis-[2-chloro-phenyl]-acrylic acid (**3g**): Mp 199.5-200 °C (from toluene).

$C_{17}H_{15}ClO_4$ (327.6) Calc'd: C 54.99, H 2.77, Cl 32.47. Found: C 55.18, H 2.95, Cl 32.35.

4. Thermal decomposition of 1-chloro-2,2-bis-[4-methoxy-phenyl]-vinyl lithium (**2b**): 20 mmol of the lithium compound prepared in example 1 (**2b**) were placed in a cold bath and slowly warmed to room temp over several hours. The initially yellow mixture turned a yellow-orange at -90 °C, and colourless precipitate formed at -65 °C. This was filtered, allowed to hydrolyze and washed with diethyl ether: 2.07 g of 4,4'-dimethoxy-diphenylacetylene (**4b**) with mp 146-147 °C (Lit¹⁹: 145 °). A further 2.41 g was obtained upon concentration of the mother liquor and the wash solution. The remaining mother liquor was then taken to dryness and the residue passed through a column of alumina using petroleum ether.

This gave 0.20 g and the same treatment of **2d** and **2g** provided the acetylenes **4d** and **4g** as 99% yield in each case.

5. Metallation of 1-chloro-2,2-bis-[2-methoxy-phenyl]-ethylene (**1c**)

a) At -72 °C: 4.13 g (15 mmol) **1c** was metalated with *n*-butyllithium and carboxylated over 45 min following the procedure from example 2. The standard work-up gave a neutral fraction which yielded 3.14 g of a yellow oil which crystallized after several days (mp 71-82 °C). This oil proved to be a mixture of substrate **1c** (59%) of mp 98-99 °C and 2,2'-dimethoxy-diphenylacetylene (**4c**) (14%) of mp 120-125 °C (Lit²⁰: 126 °C) after separation of fractions by column chromatography using aliquots of petroleum ether (50-70 °C).

$C_{16}H_{14}O_2$ (238.3) Calc'd: C 80.65, H 5.92. Found: C 80.61, H 6.12.

19. W. Schlenk and E. Bergmann, Liebigs Ann. Chem. **463**, 82 (1928).

20. C. Weygand and T. Siebenmark, Ber. Dtsch. Chem. Ges. **73**, 765 (1940).

From the crude melting point acid fraction of 0.8 g, 0.5 g were obtained by reprecipitation from toluene/cyclohexane and a further 0.1 g from residue taken from the concentrated mother liquor to give a total of 0.6 (14%) of 3-[2-methoxy-phenyl]-benzofuran-carboxylic acid-(2) (**16**) with mp 207-208.5 °C (negative Beilstein test). The halogen-containing residue (0.2 g) is a mixture of **3c** and **16** present (showed by the UV-spectrum).

16: UV-spectrum (Figure 2): λ_{\max} 279 m μ ($\log \epsilon = 4.21$). Molecular peak in the mass spectrum of $m/e = 268$. In the NMR spectrum no vinyl protons are visible; aromatic (7.3 ppm) and aliphatic (3.74 ppm) protons are in ratio of 8:2.8 (calculated 8:3).

$C_{16}H_{12}O_4$ (268.3) Calc'd: C 71.62, H 4.52, CH_3O 11.58. Found: C 71.42, H 4.67, CH_3O 11.44.

b) In an analogous way to example a) but at -2 °C (± 2 °C) the performed metalation of **1c** gave a total of 2.1 g (88%) **4c**, and 0.03 g (1%) of crude **16** with mp 205-207.5 °C.

6. 3,3-Bis-[2-methoxy-phenyl]-acrylic acid (**12**): 1.28 g (4.0 mmol) 1-bromo-2,2-bis-[2-methoxy-phenyl]-ethylene (**11**)¹⁷ were dissolved in 27 mL of THF and 10 mL of diethyl ether at -70 °C and were, in the same way as example 2, treated with a 4.0 mmol solution of *n*-butyllithium. Following carboxylation, the usual workup of the neutral fraction gave 370 mg of solids which were recrystallized from ethanol to give 250 mg (26%) with a mp of 125-126 °C **4c**. The acid fraction gave 0.79 g (70%) of **12** with a crude mp of 130-133 °C, however this increased to 137-138 °C after repeated crystallization from cyclohexane/benzene (9:1).

$C_{17}H_{16}O_4$ (284.3) Calc'd: C 71.82, H 5.67. Found: C 71.67, H 5.71.

End of translation.