Tetrahedron Vol 37, No 14, pp 2473 to 2476, 1981
Printed in Great Britain

0040-4020/81/142473-04$02.00/0
Pergamon Press Ltd

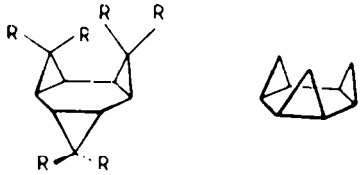
APPROACH TO THE SYNTHESIS OF "HEXACHLORO TRIS-σ-HOMOBENZENE"

MD. ABUL HASHEM and PETER WEYERSTAHL*
Institut für Organische Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, Germany

(*Received in Germany* 12 *November* 1980)

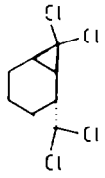
Abstract—Oxidation of the cyclohexa-1,3-diene-CCl_2 bis-adduct **4** with chromium(VI) oxide in acetic acid gives the diketone **10**. Subsequent reduction with sodium borohydride, giving **11**, formation of thionocarbonate **12**, and elimination with trimethyl phosphite provides a facile synthesis of the tetrachloro bis-σ-homobenzene **9**, which is totally resistant to further attack of CCl_2 and epoxidation. Evidently the formation of hexachloro-tris-σ-homobenzene **3** is extremely hindered. Reaction of tetraphenyl allene **6** with CCl_2 gives the heptafulvene **13** in low yield. The previously-described[1] hexachloro tris-σ-homobenzene derivative **7**, however, could not be isolated.

Tetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane ("tris-σ-homobenzene") and tris-hetero-σ-homobenzenes have been investigated several times from both the synthetic and theoretical points of view.[2,3] Whereas the *anti* isomer **1** is stable,[2a] the *syn* isomer **1'** has not yet been isolated due to the cycloreversion leading to tris-π-homobenzene.[2c,4] Substituents R larger than hydrogen evidently decrease the stability of tris-σ-homobenzenes as indicated by the isomerization of **2** above 120°.[4]

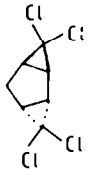


	R
1	H
2	Me
3	Cl

1'



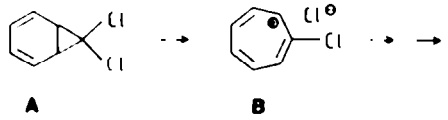
4



5

In connection with our investigation of the reaction of dichlorocarbene with aromatic hydrocarbons,[5] and of the stereochemical assignment of CCl_2 bis adducts to cyclic diolefins,[6] we were interested in the synthesis of 3,3,6,6,9,9, - hexachloro - tetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane ("hexachloro tris-σ-homobenzene"), **3**. However, for **3** a large strain can be predicted because even in the *anti* structure two vicinal cyclopropane rings are *cis*-standing, caused by high sterical hindrance by the two *endo* chlorine atoms.

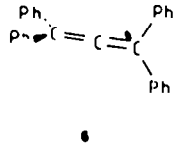
Evidently, the 1,3-cyclohexadiene-CCl_2 bis-adduct **4**, readily accessible in high yield, is formed only as an *anti* isomer.[6] On the other hand, the facile formation of **4**, and even **5**[6,7] (from cyclopentadiene, only a small amount of chlorobenzene as by-product) shows the power of the phase transfer method for a repeated addition of CCl_2 to diolefins. These observations prompted us to look for a synthesis of **3** despite expected stereochemical difficulties also shown by molecular models. Unfortunately, the simplest synthesis of **3**, threefold addition of CCl_2 to benzene must be unsuccessful for at least two reasons. First, benzene itself is completely unreactive towards CCl_2, even generated under most drastic conditions of phase transfer method.[5] Furthermore, the hypothetical CCl_2 mono adduct to benzene, the noncaradiene derivative **A** should be notoriously unstable leading to the tropylium derivative **B** and its subsequent products.



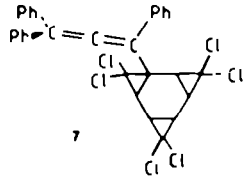
A **B**

This can unequivocally be predicted in consideration of the CCl_2 reaction with toluene,[5a] naphthalene,[5b] and many other simple aromatic hydrocarbons.[5a-c] Only at aromatic systems extremely high substituted with electron donors (1,4,5,8-tetramethoxy naphthalene,[8a] octamethyl naphthalene[8b]), a further addition of CCl_2 to the norcaradiene intermediate proceeds faster than the rearrangement to the tropylium system.

All these results regarding the behaviour of aromatic compounds during the reaction with CCl_2 seem to be contrary to an observation of Greibrokk[1] who claimed a non-crystalline compound with M = 590 to be the hexachloro tris-σ-homobenzene derivative **7** as the only reaction product (10% yield) from tetraphenyl allene **6** and CCl_2. This publication[1] has been for us an additional stimulation to investigate systematically the problem mentioned above.



6

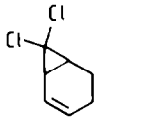


7

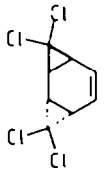
Synthesis and properties of tetrachloro bis-σ-homobenzene **9**

The precursor for a synthesis of **3** should be the tetrachloro bis-σ-homobenzene **9**, the so called benzene-CCl_2 bis adduct. A further CCl_2 addition, if possible, should lead to **3**. On the way to the hitherto unknown **9** we had to avoid the stage of the norcaradiene **A**. There-

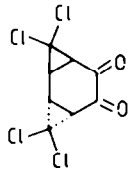
fore, the synthesis strategy had to be focussed to two key steps. Either an additional functional group will be introduced into **8** which allows after a further CCl_2 addition to generate compound, or bis-adduct **4** is capable to be functionalized in order to obtain **9**. We started the first way from **8**, most readily accessible by treatment of 1,3-cyclo-hexadiene with equivalent amounts of CCl_2 [chloroform/NaOH/benzyltriethylammonium chloride (BTEAC)] in methylene chloride. However, reaction of **8** with NBS failed under various conditions.[9] Obviously, the reactivity of the double bond is decreased by the dichloro cyclopropane ring. Treatment of **8** with t-butyl chromate gave a complex mixture of many compounds not easily to separate.



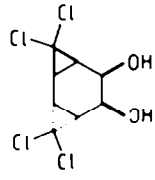
8



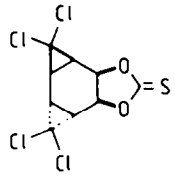
9



10



11



12

We turned now to the oxidation of **4**. Again bromination by several methods failed,[9] even reaction with ozone on silica gel furnished only starting material although bis-σ-homobenzene (without chloro substituents) could be readily converted to the respective ketone by this method.[2b] This behaviour shows again the decreased reactivity of functional groups by dichloro cyclopropane rings.

Finally, we succeeded by reaction of **4** with chromic acid in glacial acetic acid at 80° to obtain the diketone **10**. The yield remained low despite attempts to optimize the reaction. After 1.5h reaction time 10% of **10** could be obtained, whereas longer reaction time favoured side reactions. **10** has a highly symmetrical structure indicated by both ^1H (AA'BB'-system) and ^{13}C NMR spectra (4 signals). **10** was smoothly converted to the diol **11** by treatment with sodium borohydride in aqueous ethanol at room temperature. The hydroxy groups of **11** are spectroscopically shown to be *cis*, because equivalent C- and H-atoms (e.g. C-3, -8 and H-5, -6) gave different signals. According to the method of Corey and Winter[10] **11** has been transformed *via* thiono-carbonate **12** into the desired compound **9**. All the spectroscopic data provide unequivocal evidence for the structure. In the ^1H NMR spectrum the olefinic and allylic protons show an AA'XX'-system with $J_{XX'} = 9$ Hz for the olefinic protons. The non-allylic cyclopropane protons are more downfield shifted than the allylic protons by the anisotropic effect of the chloro atoms in a very close position.

However, **9** is completely unreactive towards further CCl_2 addition. Neither the classical route from chloroform and potassium t-butoxide[11] nor the phase transfer method[6,12] with various catalysts gave any result. Even after 100h refluxing with chloroform/NaOH/BTEAC no traces of **3** could be detected, the starting material **9** was recovered. Obviously, even a dichloro-cyclopropane and an oxirane ring on the same side of the six-membered ring are extremely hindered, because treatment of **9** with m-chloroperoxybenzoic acid (MCPBA) at various temperatures up to 90°[13] was also absolutely unsuccessful.

Reaction of tetraphenyl allene **6** *with* CCl_2

Since in view of our experiments with **9** the results of Greibrokk[1] seem surprising, we repeated carefully the reaction of **6** with CCl_2. Under normal conditions[1] we obtained only starting material. Under changed conditions with much more catalyst[14] we isolated after removing starting material a crystalline compound by tlc in 8% yield. According to MS the formula is $C_{28}H_{20}Cl_2$, formed by addition of CCl_2 to **6**. Neither ^1H nor ^{13}C NMR spectra show other signals than those for conjugated double bonds. A possible reaction pathway could lead to **13** via addition of CCl_2 to one of the three different aromatic double bonds and subsequent rearrangement. There are some reasons for this assumption: addition of *one* CCl_2 to an aromatic system with high electron density occurs easily[5a,8] followed by cleavage of the cyclo-propane ring generating a tropylium system.[5,8] Normally, the tropylium cation is deprotonated at a methyl substituent under formation of a heptafulvene. In our case no proton can be eliminated but the allene system will be able to close this gap, providing the conjugated compound **13**. Addition of CCl_2 to the allenic

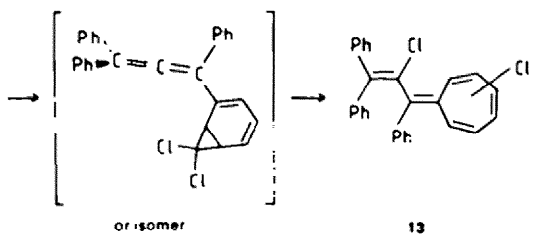
Table 1. ^{13}C chemical shifts[a] of 3,3,8,8-Tetrachloro tricyclo[5.1.0.0^{2,4}]octanes

Compd.	C-1	C-2	C-3	C-8	C-4	C-7	C-5	C-6
4[4]	26.9		65.4		22.4		16.1	
9	(28.4)		64.2		(28.6)		122.4	
10	33.4		60.4		43.1		182.1	
11	26.4	25.2	61.6	60.8	34.2	32.7	64.3	63.7
12[b]	27.0	24.4	59.5	57.9	30.2	28.2	75.6	72.3

a In ppm from Me_4Si; solvent $CDCl_3$; data in brackets are exchangeable.

b C=S: 189.6

double bond with subsequent rearrangement can be excluded by the spectroscopic data of **13**.



or isomer **13**

CONCLUSION

Tetrachloro bis-σ-homobenzene **9** is a completely unreactive compound and resists further attack of CCl_2, even under most drastic conditions. Therefore, it might be impossible or at least very difficult to synthesize **3** or any related hexachloro tris-σ-homobenzenes because the spatial interaction of the two *endo* chloro atoms is prohibitive. With respect to our results we believe structure **7** assigned by Greibrokk[1] must be wrong. A possible structure for the compound[1] with M = 590 obtained by Greibrokk could be given by further twofold addition of CCl_2 to the more reactive double bond of **13**, although we have never detected such a compound.

EXPERIMENTAL

All b.ps and m.ps are uncorrected. IR spectra were determined using Perkin–Elmer 225 (KBr) and 257 (CCl_4) spectrometers, UV spectra using a Beckman DK 2A spectrometer. ^{1}H NMR spectra ($CDCl_3$) using a Bruker WH 270 spectrometer; ^{13}C NMR spectra ($CDCl_3$) using a Varian CFT-20 spectrometer (TMS as internal standard). MS spectra were determined on a Varian MAT 711 spectrometer (70 eV). Purity was checked by tlc and GC (Perkin–Elmer F-7, glass column 82 S 557, N_2). All organic solns after work-up were dried over $MgSO_4$. (PE = Petroleum ether).

7,7-Dichlorobicyclo[4.1.0]hept-2-ene **8**

To a stirred soln of 1,3-cyclohexadiene (12.0 g; 0.15 mole), $CHCl_3$ (19.2 g; 0.16 mole), and benzyltriethylammonium chloride (BTEAC; 0.3 g) in CH_2Cl_2 (50 ml) at r.t, 15 ml of 50% NaOHaq was added slowly dropwise. After 6h refluxing the cooled mixture was diluted with 200 ml water and separated. The aqueous layer was extracted thrice with CH_2Cl_2. The combined organic layers were washed with water, evaporated, and distilled to give 16.3 g (67%) **8**, b.p. 76–78°/12 torr (lit[15], b.p. 52.5–53°/1.25 torr). IR (CCl_4): 3040 *s*, 1650 *w* cm^{-1}. ^{1}H NMR: δ 1.75–2.15 (*m*, 6H), 5.88, 5.93 (*br. AB*-system, J_{AB} = 11 Hz, 2-, 3-H). ^{13}C NMR: δ 16.0, 20.9 (2 × *d*), 27.1, 28.8 (2 × *t*), 67.3 (*s*), 120.3, 130.0 (2 × *d*).

5,5,8,8-Tetrachlorotricyclo[5.1.0.0^{4,6}]octane-2,3-dione **10**

To a stirred soln of 13.0 g CrO_3 in 350 ml glacial acetic acid (HOAc) at 80° a soln of 5.5 g (22.4 mmole) of **4**[5] in 100 ml HOAc was added within 20 min. After 1.5h at 80° the mixture was cooled and most of HOAc was removed at 40° *in vacuo*. To the residue 300 ml $CHCl_3$ was added, and this soln was washed four times with water. After removing the $CHCl_3$, 50 ml PE was added; orange-red crystals were filtered off, and recrystallized from $CHCl_3$, m.p. 215–218°. The PE soln gave after evaporation 2.0 g **4**. Total yield of **10**: 0.41 g (10.5%). IR (KBr): 1722 *s*, 1708 *vs* cm^{-1}. UV (MeOH): λ (nm) 233 (ε = 2140), 420 (25). ^{1}H-NMR: δ 3.00, 3.07 (*AA'BB'*-system, $J_{AB} = J_{A'B'}$ = 8, $J_{AA'}$ = 6.5, $J_{AB'} = J_{BB'}$ = 0 Hz). MS: *m/e* 272, 274, 276, 278 (M$^+$, Cl-isotope pattern, 4%), 216, 218, 220, 222 (M–2 CO, 45), 181, 183, 185 (M–2 CO, –Cl, 90), 146, 148, 150 (M–2 CO, –2Cl, 56), 111, 113 (M–2 CO, –3Cl, 36), 75 (M–2 CO, –3Cl, –HCl, 55), 73 (65), 69 (30), 63 (30), 50 (32), 43 (100). Found: C, 35.29; H, 1.58; Cl, 51.92. $C_8H_4Cl_4O_2$ requires: C, 35.08; H, 1.47; Cl, 51.77%.

5,5,8,8-Tetrachlorotricyclo[5.1.0.0^{4,6}]octane-2,3-diol **11**

0.33 g (1.2 mmole) of **10** was dissolved in 150 ml EtOH, 15 ml water, and 0.06 g $NaBH_4$ were added, and stirred for 24h. Most of the solvent was removed *in vacuo*, 50 ml water was added, and acidified by addition of 10% aq HCl. After extraction thrice with ether and evaporation, 0.32 crude oil remained. Chromatography on silica gel with $CHCl_3$ afforded 0.17 g (51%) colourless crystals, m.p. 124–126° (ether/PE). IR (KBr): 3600–3150 *br* cm^{-1}. ^{1}H NMR: δ 2.0–2.2 (*m*, 1-, 4-, 6-, 7-*H*), 2.65, (*d*, *J* = 8.5 Hz, OH), 2.75 (d, *J* = 7 Hz, OH), 4.03 (*ddd*, *J* = 8.5, 6, 2.5 Hz, 2-H), 4.44 (*ddd*, *J* = 7, 6.5, 6 Hz, 3-H). MS: *m/e* no M$^+$, 216, 218, 220, 222 (M–2 CHOH, Cl-isotope pattern, 16%), 181, 183, 185 (M–2 CHOH, –Cl, 25), 141 (23), 113 (25), 77 (27), 60 (64), 58 (34), 43 (100). Found: C, 34.44; H, 2.81; Cl, 51.26. $C_8H_8Cl_4O_2$ requires: C, 34.57; H, 2.90; Cl, 51.02%.

8,8,11,11-Tetrachloro-3,5-dioxatetracyclo[8.1.0.0^{2,4}0^{7,9}]undecane-4-thione (*11-thionocarbonate*) **12**

To a soln of 0.15 g (0.84 mmol) of N,N-thiocarbonyl diimidazole[16] in 50 ml dry toluene at 120° a soln of 0.23 g (0.83 mmole) **11** in 100 ml dry toluene was added (N_2 atmosphere). After 2h refluxing the soln was cooled, and poured into 200 ml water. The layers were separated, the organic layer washed thrice with water and concentrated *in vacuo*. Chromatography of the crude oil on silica gel with ether/PE (1:1) afforded 0.18 g (68%) **12**, m.p. 209–211° (ether/PE). ^{1}H-NMR: δ 2.27 (*dd*, *J* = 10.5, 8.5 Hz, 1-H), 2.41, 2.45 (*AB*-system, J_{AB} = 10 Hz, H_A as *d*, *J* = 1.5 Hz, H_B as *d*, *J* = 1 Hz, 9-, 7-H), 2.52 (*dd*, *J* = 10.5, 1.5 Hz, 10-H), 5.17 (*dd*, *J* = 9.5, 1 Hz, 6-H), 5.46 (*dd*, *J* = 9.5, 8.5 Hz; 2-H). MS: *m/e* = 318, 320, 322, 324 (M$^+$, Cl-isotope pattern, 4%), 241, 243, 245 (8), 206, 208, 210 (7), 193, 195, 197 (11), 176, 178, 180 (20), 159, 161, 163 (85), 125 (100). Found: C, 33.62; H, 1.75; Cl, 44.17. $C_9H_4Cl_4O_2S$ requires: C, 33.78; H, 1.89; Cl, 44.31%.

5,5,8,8-Tetrachlorotricyclo[5.1.0.0^{4,6}]oct-2-ene **9**

A soln of 0.20 g (0.63 mmol) of **12** in 10 ml trimethylphosphite was refluxed for 80h (N_2 atmosphere.[10] After addition of 20 ml 20% aq NaOH the mixture was extracted with ether. The ether phase was washed with eater, and evaporated. Chromatography of the residue on silica gel with PE afforded 80 mg (53%) **9**, m.p. 76–78°. IR: (KBr): 3060 *m*, 3030 *s*, 1650 *w* cm^{-1}. ^{1}H-NMR: δ 2.00, 5.89 (*AA'XX'*-system, $J_{AA'}$ = 0, J_{AX} = 3, $J_{AX'}$ = $J_{A'X}$ = 1.5, $J_{XX'}$ = 9 Hz, H_A and $H_{A'}$ as *d*, *J* = 10.5 Hz, 1-, 2-, 3-, 4-H), 2.25 (*d*, *J* = 10.5 Hz, 6-, 7-H). MS: *m/e* 242, 244, 246, 248 (M$^+$, Cl-isotope pattern, 5%), 207, 209, 211 (M–Cl, 18), 171, 173, 175 (M–Cl, –HCl, 100), 159, 161, 163, (24), 143, 145, 147 (25), 136, 138 (M–2 Cl, –HCl, 95), 125 (24), 111 (25), 99 (28), 75 (50). Found: C, 39.16; H, 2.31; Cl, 58.05. $C_8H_6Cl_4$ requires: C, 39.39; H, 2.48; Cl, 58.13%.

Experiments on the reaction of **9** *with* CCl_2

(a) A stirred mixture of 30 mg (0.12 mmole) of **9**, 0.4 g KOtBu, 7 ml $CHCl_3$, and 12 ml pentane was allowed to react at 0° for 12h. After usual work-up only starting material was isolated. (b) A stirred mixture of 35 mg (0.14 mmole) of **9**, 15 ml $CHCl_3$, 8 ml 50% aq NaOH, and 40 mg BTEAC was refluxed for 8h. After usual work-up only starting material was isolated. (c) As (b) but 40h refluxing. (d) As (b) but 100h refluxing. (e) As (b) but with 25 mg dibenzo-18-crown-6 as catalyst, 8h refluxing. (f) As (e) but 40h refluxing. (c)-(f) gave the same result; only starting material in various amounts was isolated. No other compounds were detected (tlc).

Experiments on the reaction of **9** *with MCPBA*

(A) A soln of 25 mg (0.1 mmole) of **9** in 12 ml dry CH_2Cl_2 was allowed to react with 30 mg (0.17 mmole) MCPBA for 5 days at 0°. After usual work-up only starting material could be isolated. (b) As (a) but 5 days at r.t. Only starting material was obtained. (c) As (a) but in 1,2-dichloro ethane for 6h at 90° (reflux). Only starting material was obtained.

Tetraphenylallene **6** obtained according to Ref. [17], *via* 1,3,3-tri-phenylprop-2-ene-1-one,[18] m.p. 163–165° (lit[6] 165–166°). ^{13}C NMR: δ 112.7 (Ph_2C=), 127.5, 128.5, 136.5 (phenyl), 208.5 (=C=). MS: *m/e* 344 (*M*$^+$, 100%), 267 (M-phenyl, 35), 252 (10) 154 (12), 105 (11).

Reaction of **6** *with* CCl_2

A mixture of 0.34 g (1.0 mmole of **6**, 25 ml $CHCl_3$, 25 ml 50% NaOHaq, and 0.2 g BTEAC was stirred for 3 days at 0°. After usual work-up 0.44 g residue was obtained. Preparative layer chromatography on silica gel with PE/ether (98:2) allowed separation of 0.28 g **6** (first fraction), and 37 mg (9%) x-Chloro-7-[1-(1-chloro-2,2-diphenylethyl) - 1 - phenyl] - methyliden - 1,3,5 - cycloheptatriene **13** (second fraction), m.p. 63–66° (PE/$CHCl_3$). IR (KBr): 1700 *s* (br.), 1675 *s* (br.), 1595 *m* cm^{-1}. ^1H NMR: δ 7.1–7.8 (*m*). ^{13}C NMR: δ 125.2, 125.8, 127.0, 127.2, 127.4, 127.6, 128.0, 128.2, 128.6, 128.9, 129.3, 129.5, 129.8, 130.1, 130.4, 130.7, 138.7, 142.0, 142.2. MS: *m/e* 426, 428 (M^+, Cl-isotope pattern, 4%), 425, 427 (17), 391, 389 (M–Cl, 20), 390, 288 (M–HCl, 16), 372 (28), 371 (30), 356 (M–2Cl, 18), 355 (M–Cl, –HCl, 24), 354 (M–2HCl, 17). MS (high resoln): $C_{28}H_{20}{}^{35}Cl_2$ calc. 426.0929, obs. 426.0916, $C_{28}H_{19}{}^{35}Cl_2$ calc. 425.0868, obs. 425.0872.

Acknowledgement—Md. A. H. thanks the Deutsche Akademische Austauschdienst (DAAD) for a grant.

REFERENCES

[1]T. Greibrokk, *Acta Chem. Scand.* **27**, 3207 (1973).

[2]*Tris-σ-homobenzenes*: [a]M. Engelhard and W. Lüttke, *Angew. Chem.* **84**, 346 (1972); *Ibid. Int. Ed. Engl.* **11**, 310 (1972); [b]W. Spielmann, D. Kaufmann and A. de Meijere, *Angew. Chem.* **90**, 470 (1978); *Ibid. Int. Ed. Engl.* **17**, 440 (1978); [c]J. Spanget-Larsen and R. Gleiter, *Angew. Chem.* **90**, 471 (1978); *Ibid. Int. Ed. Engl.* **17**, 441 (1978); [d]W. Spielmann, H.-H. Fick, L. U. Meyer and A. de Meijere, *Tetrahedron Lett.* 4057 (1976).

[3]*Tris-hetero-σ-homobenzenes*: [a]E. Vogel, H.-J. Altenbach and C. D. Sommerfeld, *Angew. Chem.* **84**, 986 (1972); *Ibid. Int. Ed. Engl.* **11**, 939 (1972); [b]R. Schwesinger and H. Prinzbach, *Angew. Chem.* **84**, 990 (1972); *Ibid. Int. Ed. Engl.* **11**, 942 (1972); [c]C. H. Foster and G. A. Berchtold, *J. Am. Chem. Soc.* **94**, 7939 (1972); [d]R. Schwesinger, H. Fritz and H. Prinzbach, *Chem. Ber.* **112**, 3318 (1979); [e]R. Keller, R. Schwesinger, W. Fritsche, H.-W. Schneider, D. Hunkler and H. Prinzbach, *Chem. Ber.* **112**, 3347 (1979); [f]M. Breuninger, B. Gallenkamp, H.-H. Müller, H. Fritz, H. Prinzbach, J. J. Daly and P. Schönholzer, *Angew. Chem.* **91**, 1030 (1979); *Ibid. Int. Ed. Engl.* **18**, 964 (1979); [g]R. Schwesinger, M. Breuninger, B. Gallenkamp, K.-H. Müller, D. Hunkler and H. Prinzbach, *Chem. Ber.* **113**, 3127 (1980).

[4]P. Binger, G. Schroth and J. McMeeking, *Angew. Chem.* **86**, 518 (1974); *Ibid. Int. Ed. Engl.* **13**, 465 (1974).

[5a]P. Weyerstahl and G. Blume, *Tetrahedron* **28**, 5281 (1972); [b]G. Blume, T. Neumann and P. Weyerstahl, *Liebigs Ann. Chem.* 201 (1975); [c]B. Müller and P. Weyerstahl, *Tetrahedron* **32**, 865 (1976).

[6]W. Kuhn, H. Marschall and P. Weyerstahl, *Chem. Ber.* **110**, 1564 (1977).

[7]E. V. Dehmlow, *Tetrahedron* **28**, 175 (1972).

[8a]J. Trunetsugu, M. Sato and S. Ebine, *J. Chem. Soc. Chem. Commun.* 363 (1973); [b]A. Oku, T. Hino and K. Matsumoto, *J. Org. Chem.* **40**, 695 (1975).

[9]W. Kuhn, *Dissertation, Techn. Univ. Berlin* 1972.

[10]E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.* **85**, 2677 (1963).

[11]W. v. E. Doering and A. K. Hoffmann, *Ibid.* **76**, 6162 (1954).

[12]M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.* 4659 (1969).

[13]Y. Kishi, M. Aratani, H. Tanino, T. Fukuyama, T. Goto, S. Inone, S. Sugiura and H. Kakoi, *J. Chem. Soc. Chem. Commun.* 64 (1972).

[14]T. Greibrokk, Private communication of 20 April 1979.

[15]M. G. Banwell, R. Blattner, A. R. Browne, J. T. Craig and B. Halton, *J. Chem. Soc. Perkin I* 2165 (1977).

[16]H. A. Staab and G. Walther, *Liebigs Ann. Chem.* **657**, 98 (1962).

[17]A. R. Ubbelohde and J. A. Burgess, *J. Chem. Soc. (B)*, 1106 (1970).

[18]J. P. Freeman, *J. Am. Chem. Soc.* **80**, 1926 (1958).