Tetrahedron Vol. 24, pp. 5361 to 5368. Pergamon Press 1968. Printed in Great Britain

HYDRIDE TRANSFER REACTIONS OF THE ADAMANTYL CATION—I

A NEW AND CONVENIENT SYNTHESIS OF ADAMANTANONE

H. W. GELUK and J. L. M. A. SCHLATMANN
N. V. Philips-Duphar Research Laboratories, Weesp, The Netherlands

(*Received in the UK* 2 *March* 1968; *accepted for publication* 15 *March* 1968)

Abstract—Adamantanone can be synthesized from 1-hydroxyadamantane or from adamantane in good yields by treatment with concentrated sulphuric acid. The formation of the ketone is due to disproportionation and oxidation reactions. 2-Hydroxyadamantane—considered to be an intermediate—proved to be formed by a 1,2-hydride shift of the 1-adamantyl cation. Sulphuric acid oxidation of adamantane leading to 1-hydroxyadamantane, followed by a peculiar further sulphuric acid oxidation of 1-hydroxyadamantane, probably via 2-hydroxyadamantane, to adamantanone is reported.

TREATMENT of 1-hydroxyadamantane with concentrated sulphuric acid led to a surprisingly good method (yield 70–80%) for the preparation of adamantanone.[1] Moreover it even proved to be possible to start directly from adamantane, which yields 50–60% of adamantanone.* The simplicity and high yield of this reaction makes it possible to obtain secondary substituted adamantane derivatives,[3] which have previously been difficult to synthesize.[4–9] The identity of the ketone has been established by comparison of its physical constants and those of its derivatives with the data reported.[4, 5]

The startling conversion of adamantane and 1-hydroxyadamantane into adamantanone prompted us to investigate the mechanism of the reactions that occur in sulphuric acid. In particular we studied the behaviour of 1-hydroxyadamantane in sulphuric acid under various reaction conditions. This resulted in the disclosure of a number of interesting phenomena. The reactions which are discussed in this paper are indicated schematically in Fig. 1 They are as follows:

1. The reversible isomerization of 1-hydroxyadamantane into 2-hydroxyadamantane by a 1,2-hydride shift of the tertiary or the secondary adamantyl cation. The key reaction in the formation of adamantanone from 1-hydroxyadamantane is almost certainly the 1,2-hydride shift of the 1-adamantyl cation leading to the intermediate 2-hydroxyadamantane.
2. The disproportionation of 2-hydroxyadamantane into adamantane and adamantanone due to an intermolecular hydride transfer reaction, involving the exchange of the α-hydrogen of the alcohol.
3. The oxidation of 1-hydroxyadamantane to adamantanone by means of sulphuric acid probably via 2-hydroxyadamantane.

---

* In general one can use any adamantane derivative generating adamantyl cations in concentrated sulphuric acid.[2] Complications, however, will be met when the substituent being split off is subjected to further reactions, leading to products which can react in turn with the adamantyl cations.

4. The oxidation of adamantane to 1-hydroxyadamantane by means of sulphuric acid.

Homologues of adamantanone can also be formed by analogous reactions in sulphuric acid. For instance, from 3-methyladamantan-1-ol we obtained 1-methyladamantan-4-one in a yield of 20%. This will be described in a forthcoming paper. In another paper of this series intermolecular hydride transfer reactions of 1-hydroxy- and 2-hydroxyadamantane resulting in the formation of 1,3- and 1,4-disubstituted adamantanes will be discussed.[10]

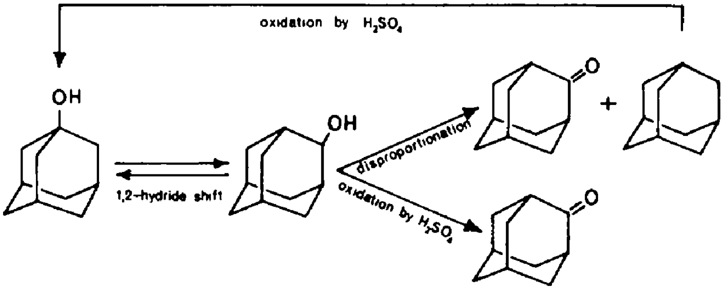

FIG. 1.

1. 1,2-*Hydride transfer reaction of the adamantyl cations*

In accordance with the behaviour of secondary alkyl cations in concentrated sulphuric acid we found that the secondary adamantyl cation was readily transformed into the tertiary cation. However, we also found evidence for the reversibility of this reaction, which is—in our opinion—a hitherto unobserved phenomenon.

A very rapid isomerization of 2-hydroxyadamantane, into 1-hydroxyadamantane occurred in a 0·8 molar solution of the alcohol in 96% sulphuric acid at 28°. It demonstrates the normal 1,2-hydride shift of the 2-adamantyl cation* (Fig. 2).

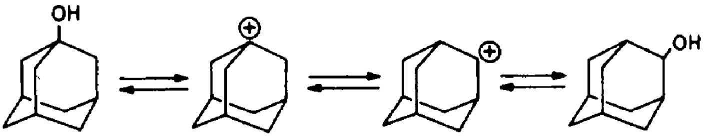

FIG. 2.

The course of the reaction was followed by GLC of samples taken from the reaction mixture. The equilibrium was reached within a few minutes. The reaction was quenched after 10 minutes. The mixture still contained 1·2–1·4% of 2-hydroxyadamantane.

The reverse reaction was demonstrated by means of GLC of samples taken from a 0·8 molar solution of 1-hydroxyadamantane in 96% sulphuric acid at 28°. The formation of 2-hydroxyadamantane was detected almost immediately after dissolution of the 1-hydroxyadamantane. Upon quenching the reaction after 10 minutes 1·2% of 2-hydroxyadamantane—determined by GLC—was found to be present.

---

* The application of a similar reaction has been described by Sun Oil Co.[11]

The identity of the secondary alcohol was confirmed by comparison of its mass spectrum with that of a sample of 2-hydroxyadamantane prepared according to the method described.[4]

As was to be expected, the equilibrium of this intramolecular hydride shift lies far on the side of the 6-adamantyl cation. The rate of the 1,2-hydride shift proved to be strongly influenced by the acidity of the medium. After treatment of 1-hydroxyadamantane with 70% sulphuric acid for 10 minutes at 28° the formation of 2-hydroxyadamantane could not be detected (concentration below 0·01%). Neither did the formation of 1-hydroxyadamantane from 2-hydroxyadamantane occur in 70% sulphuric acid at 28° (again measured after 10 minutes reaction time).

2. *Disproportionation of 2-hydroxyadamantane into adamantane and adamantanone*

The simultaneous formation of adamantane and adamantanone is illustrated by the following typical experiment. From a 0·8 molar solution of 1-hydroxyadamantane in 96% sulphuric acid at 30°, precipitation of adamantane started after a few minutes. The almost simultaneous formation of adamantanone could be demonstrated by means of GLC. After the reaction had continued for 6 hr 16% of adamantane and 14% of adamantanone were present. The recovery of starting material was 67%.

Upon repeating this experiment at one tenth of the original 1-hydroxyadamantane concentration, with otherwise identical reaction conditions, practically no adamantane was detected after the same reaction time. This suggests a reaction of at least second order in 1-hydroxyadamantane.

Factually we assume a mechanism in which a disproportionation reaction is preceded by the formation of 2-hydroxyadamantane (section 1). This secondary alcohol* can disproportionate into adamantane and adamantanone, in accordance with a hydride transfer reaction of known type.[12,13] In this case 2-hydroxyadamantane acts as the hydride donor, splitting off its α-hydrogen. The adamantyl cation, either secondary or tertiary, will be the hydride acceptor (Fig. 3).

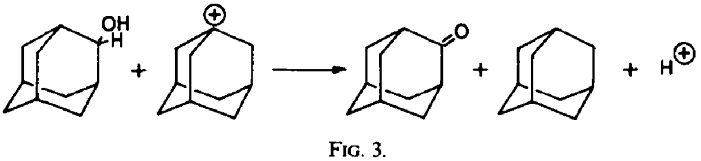

FIG. 3.

Since the concentration of the intermediate 2-hydroxyadamantane is greatly influenced by the acidity of the solution (see section 1), it is clear that the formation of adamantanone must also be dependent on the sulphuric acid concentration. Optimal reaction conditions for this disproportionation were attained in 96% sulphuric acid. At concentrations of 70% or lower the formation of adamantanone from a 0·8 molar solution of 1-hydroxyadamantane could no longer be detected. This limit corresponds with that at which the 1,2-hydride shift failed to produce a detectable quantity of 2-hydroxyadamantane.

---

* Our present data allow of no decision being made concerning the exact nature of the reacting species. Depending on the acidity of the solution, the alcohols may be present in their free, their protonated, or their esterified forms. In our discussion of the reactions we referred to the free alcohols for simplicity.

The appearance of adamantanone in 70% sulphuric acid was, however, observed again when we started from 2-hydroxyadamantane itself. This experimental result provides additional support for the suggested mechanism. Moreover it was possible to affect a hydride transfer reaction of 2-hydroxyadamantane with the triphenylcarbonium ion—generated from triphenylcarbinol—in 75% sulphuric acid. In this case adamantanone and triphenylmethane were found whereas adamantane could not be detected.

Finally it should be remarked that, for a disproportionation of 2-hydroxyadamantane, sulphuric acid can be replaced by other acids such as phosphoric acid and perchloric acid or by a Lewis acid in an appropriate solvent, e.g. BF_3 in acetic acid.

3. *Oxidation of* 1-*hydroxyadamantane to adamantanone*

There was practically no precipitation of adamantane when 1-hydroxyadamantane was dissolved in low concentration (0·08 molar) in 96% sulphuric acid (see section 2). This could be ascribed to the delay of the bimolecular disproportionation reaction at this dilution. Adamantanone formation could therefore hardly be expected as a result of this reaction. Nevertheless a yield of 20% of adamantanone was obtained after a reaction time of 3 hr at 50°. The adamantane content was as low as 1% after that time. Sulphur dioxide evolution observed during the reaction revealed oxidation by sulphuric acid.

Since 1-hydroxyadamantane cannot be oxidized directly to adamantanone, we assume that the oxidation step is preceded by a 1,2-hydride shift. 2-Hydroxyadamantane* formed in this way may be oxidized to adamantanone by sulphuric acid.

Consequently the oxidation of 1-hydroxyadamantane must be limited by the sulphuric acid concentration in two ways. Firstly, the 1,2-hydride shift leading to 2-hydroxyadamantane must be possiole. This is the case at sulphuric acid concentrations of above 70%. Secondly, the oxidation reaction itself depends upon the sulphuric acid concentration, because the oxidizing property of the acid diminishes considerably upon dilution. In 85% sulphuric acid the occurrence of this oxidation could still be concluded from the course of the reaction (Fig. 4) and from the evolution of sulphur dioxide.

The direct oxidation of an alcohol to a ketone by means of sulphuric acid alone appears to be an exceptional reaction and—as far as we know—has not been reported previously. It may well be restricted to those secondary alcohols, which are not transformed into olefinic products and in which skeletal rearrangements are unlikely.

4. *Oxidation of adamantane to* 1-*hydroxyadamantane by means of sulphuric acid*

Adamantane that had separated from a 0·8 molar solution of 1-hydroxyadamantane owing to disproportionation in 96% sulphuric acid, disappeared fairly rapidly at elevated temperature. When the reaction mixture was stirred at 75° the precipitate of adamantane was completely dissolved again after about 5 hr. The course of this reaction is illustrated by Fig. 5. A considerable evolution of sulphur dioxide was observed, indicating the occurrence of an oxidation reaction by means of sulphuric acid. The adamantanone yield rose to an average of 73%, based on the initial 1-hydroxyadamantane, after a total reaction time of 5 to 6 hr at 75°.

---

* See footnote at page 5363.

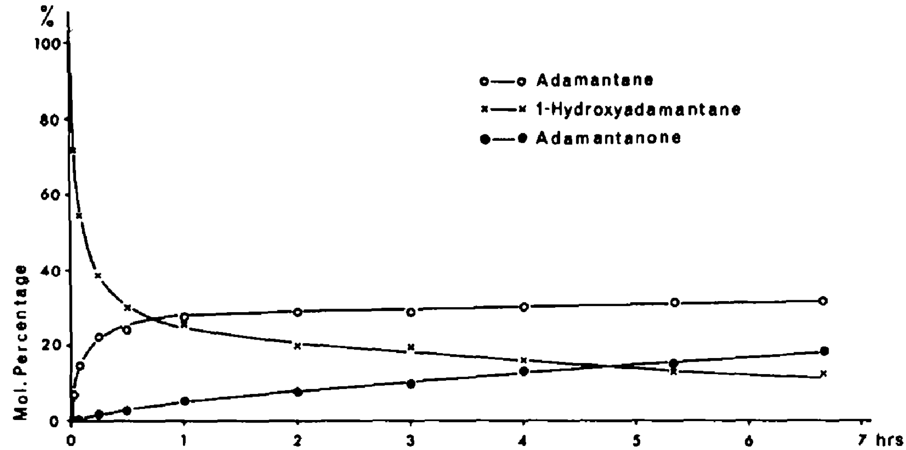

FIG. 4 Reaction of 1-hydroxyadamantane (0·8M) in 85% sulphuric acid at 75°C.

NOTE. The rapid formation of adamantane at the beginning of the reaction is due to disproportionation of 1-hydroxyadamantane into adamantane and 1,3-dihydroxyadamantane.[1,10] The latter is not indicated in the figure.

These observations prompted us to start the synthesis of adamantanone directly from adamantane. We found that analogous reactions take place, resulting in the formation of 50–60% of adamantanone. The course of the reaction is represented by Fig. 6. The figure illustrates the initial formation of 1-hydroxyadamantane, which concentration reached a level that proved to be constant as long as adamantane was present. 1-Hydroxyadamantane itself gives rise to adamantanone formation by secondary reactions as mentioned before.

The straight line which represents the adamantane content is striking. It suggests an oxidation reaction governed by a constant concentration of dissolved adamantane. Consequently the rate of dissolution of adamantane is much higher than the rate of oxidation. Little information about the mechanism of oxidation of hydrocarbons by means of concentrated sulphuric acid proved to be available in the literature.[14,15]

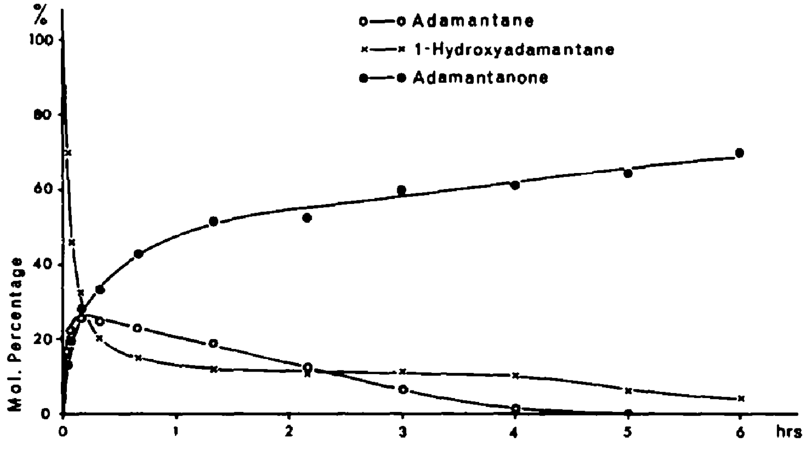

FIG. 5 Reaction of 1-hydroxyadamantane (0·8M) in 96% sulphuric acid at 75°C.

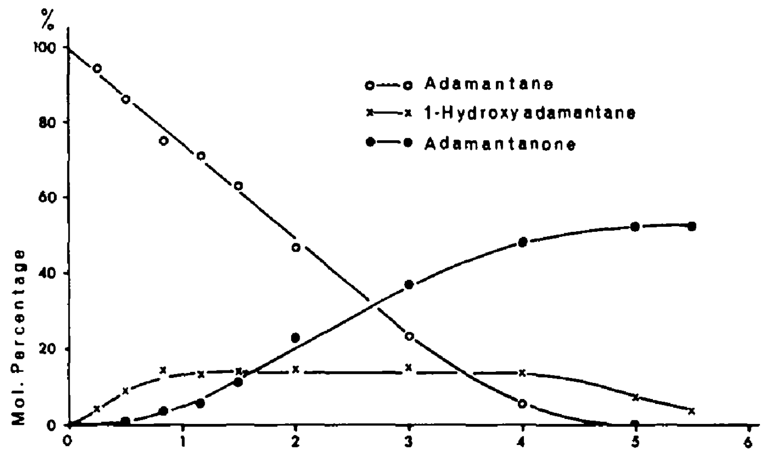

FIG. 6 Reaction of adamantane (0·4M) in 96% sulphuric acid at 77°C.

The oxidation reaction rate was found to depend critically upon the sulphuric acid concentration. Convenient results were obtained in the range of 94–100% sulphuric acid. Adamantane reacts slowly in sulphuric acid having a concentration less than 90%. The oxidation reaction is also strongly influenced by the reaction temperature. In 96% sulphuric acid the reaction rate becomes very slow at temperatures below 60°.

At higher sulphuric acid concentrations (98–100%) the oxidation of adamantane is very fast. In contrast to this the conversion of 1-hydroxyadamantane into adamantanone proceeds slowly, resulting in the accumulation of 1-hydroxyadamantane during the reaction. Thus, when adamantane (0·8 molar) was stirred in 100% sulphuric acid at 40°, 40% of 1-hydroxyadamantane, 15% of adamantanone and 30% of unchanged starting material were found after 4 hr.

The favourable results of the oxidation of adamantane to 1-hydroxyadamantane by sulphuric acid may well be due to the resistance of the adamantane skeleton to form double bonds (Bredt's rule) and consequently to its failure to be rearranged or polymerized via olefinic products.*

EXPERIMENTAL

Analytical data. M.ps were measured in closed capillary tubes totally immersed in an electrically heated aluminium block. Temp indication was given by a chromel-alumel couple on a Philips G.M. 6020 tube voltmeter. GLC was carried out on a Becker Model 1473 instrument, equipped with a 1 m, ϕ 3 mm Cu column, filled with 80/100 mesh chromosorb W, silanised with DDS, and impregnated with 3% apiezon L, 1% Epon 1001 and 1% PEG 4000-monostearate, at 115° with FID. NMR spectra were measured on a Varian HA spectrometer, solvent $CDCl_3$; chemical shifts are reported in ppm from TMS used as internal reference. IR spectra were recorded on a Perkin–Elmer Model 337. Mass spectral data were obtained from an AEI-MS 9 double focusing mass spectrometer. Elemental micro analyses were done by A. Bernhardt, Micro analytical Lab., Max-Planck-Institut für Kohlenforschung, Müllheim, (W-Germany).

General procedure. In a 100 ml glass-stoppered conical flask H_2SO_4 (50 ml) of a specified concentration

---

* A brown to black coloured tar is obtained as a by-product from the adamantanone preparation in concentrated sulphuric acid. The amount of this polymeric substance varies mainly with the sulphuric acid concentration and the reaction temperature. It proved to consist of partially sulphated adamantylpolyethers. The polymer probably arises from dihydroxyadamantanes, which are formed in turn by disproportionation reactions of 1- and 2-hydroxyadamantane in concentrated sulphuric acid.[10]

was heated in a glycerine bath and maintained at the desired temp thermostatically (±0·5°). The desired amount of finely divided starting material was added by dispersing the substance quickly into the H_2SO_4 under vigorous magnetic stirring. The flask had been closed lightly by a glass stopper so that SO_2, when formed, could escape. The reaction mixture was shaken thoroughly at regular intervals in order to introduce sublimed material into the H_2SO_4 again. Samples of the reaction mixture, having been previously homogenized as well as possible by shaking and stirring, were taken with a small glass spoon (0·61 ml) fitted on a thin glass rod. The samples were immediately poured into ice water and were extracted twice with ether. The extracts were diluted with ether to a specified volume. A measured quantity of an internal standard (e.g. menthol) dissolved in ether, was added. Specimens of these solns were introduced into the gas chromatograph.

1-Hydroxyadamantane. The hydrolysis of 1-bromoadamantane[16] could be appreciably simplified in the following way. 1-bromoadamantane[16, 17] (10 g) was stirred and heated in a mixture of 0·67N HCl (15 ml) and dimethylformamide (13 ml) at 105° for ½ hr. The reaction mixture was diluted with water (100 ml) and filtered under suction. The solid was washed several times with water and dried *in vacuo*, yield: 95% of pure 1-hydroxyadamantane, m.p. 283–285°. (Lit. m.p. 287·2–288·5[4]; 277·0–278·0[7]; 282[16]; 288·5–290.[17]

Adamantanone from 1-hydroxyadamantane. 1-hydroxyadamantane (7·6 g) was dissolved in 96% H_2SO_4 (60 ml) and stirred at 75°. Adamantane precipitated immediately. Sublimed material was regularly brought back into the liquid by shaking the flask vigorously. After the adamantane had dissolved completely (4–5 hr) stirring was continued for another hr. The reaction mixture was poured on to ice and extracted twice with ether. Polymeric material which had separated from the soln was collected and extracted several times with ether. The extracts were combined, washed with 10% NaClaq and dried over Na_2SO_4. After evaporation of the solvent, crude adamantanone (6·3 g, 84%) was obtained. The adamantanone could also be isolated by steam-distillation after quenching the reaction mixture. In this case pure adamantanone in a colourless crystalline state was obtained (5·4 g, 72%, m.p. 280–282°). An analytical sample of adamantanone was prepared by chromatography through alumina (eluent ether), m.p. 285–286° (Lit. m.p. 281·2–282·8[4]; 283[5]; 224·0–225·0[7]; 283·4–284·4[9]). Found: C, 80·1; H, 9·5; O, 10·7. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·4; O, 10·7%; NMR ($CDCl_3$): Signals at δ 2·05 (12H) and 2·53 (2H); in benzene at δ 1·53 (4H), 1·68 (8H) and 2·47 (2H). The 2H signal at about δ 2·5, that does not show a solvent shift in benzene, must therefore indeed be attributed to the two protons α to the carbonyl group.[18, 19] Apparently the protons at C-6 are not influenced by the C=O group. IR (KBr): 2920(vs), 2855(s) (CH), 1720(vs) (C=O, main peak with minor peaks or shoulders at 1655, 1675, 1695, 1730 and 1750 cm^{-1}), 1450(s), 1350(m), 1312(m), 1293(m), 1236(m), 1058(s), 875(m), and 466(s) cm^{-1}. In CH_2Cl_2 soln a similar complicated C=O stretching band with five distinct side peaks or shoulders was found, this being characteristic for the adamantanone carbonyl vibration.

Oxime m.p. 164–165·5° (lit. 162·8–163·6[7]; 162·5–163.[8]) 2,4-dinitrophenylhydrazone: m.p. 220·5–221·5° (lit. m.p. 221–221·5;[4] 221;[5] 213·5–214·5[7]).

Adamantanone from adamantane. Finely divided adamantane (8·2 g) was added to 96% H_2SO_4 (150 ml) and heated at 77°. The mixture was stirred vigorously and shaken thoroughly at regular intervals. After a reaction period of 4–5 hr the solid had dissolved completely. Stirring was continued for another hr and the soln was then poured on ice. After extraction with ether as described above, the yield of crude material (6·0 g) was 66%. When the substance was isolated by steam-distillation 54% of adamantanone was obtained (4·8 g, m.p. 278–282°).

The disproportionation of 2-hydroxyadamantane in 70% sulphuric acid will be reported in the following paper.[10]

Acknowledgements—We gratefully acknowledge the assistance of colleagues and co-workers. We are particularly indebted to Mr. A. de Heer for the gaschromatographic analyses and to Mr. F. W. van Deursen amd Dr. P. K. Korver for the IR, NMR, and mass spectral analyses as well as for helpful discussions about their interpretation.

REFERENCES

[1] H. W. Geluk and J. L. M. A. Schlatmann, *Chem. Comm.* 426 (1967).
[2] N. V. Philips'Gloeilampenfabrieken, Neth. Appl. 6,509,139; *Chem. Abstr.* 73246c (1967).
[3] A. C. Udding, J. Strating, H. Wijnberg and J. L. M. A. Schlatmann, *Chem. Comm.* 657 (1966).
[4] P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.* **83**, 182 (1961).
[5] H. Stetter, H. Held and J. Mayer, *Liebigs Ann.* **658**, 151 (1962).

[6] R. C. Fort, Jr. and P. von R. Schleyer, *Chem. Rev.* **64**, 277 (1964).

[7] G. W. Smith and H. D. Williams, *J. Org. Chem.* **26**, 2207 (1961).

[8] E. Müller and G. Fiedler, *Chem. Ber.* **98**, 3493 (1965).

[9] S. Landa, J. Vais and J. Burkhard, *Coll. Czech. Chem. Comm.* **32**, 570 (1967).

[10] H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*

[11] Sun Oil Co., Neth. Appl. 6,511,851; *Chem. Abstr.* **65**, 3768^b (1966).

[12] P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.* **78**, 1441 (1956).

[13] N. C. Deno, H. J. Peterson and G. S. Saines, *Chem. Rev.* **60**, 7 (1960).

[14] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *J. Am. Chem. Soc.* **73**, 5741 (1951).

[15] G. M. Kramer, *J. Org. Chem.* **32**, 1916 (1967).

[16] H. Stetter, M. Schwarz and A. Hirschhorn, *Chem. Ber.* **92**, 1629 (1959).

[17] S. Landa, S. Kriebel and E. Knobloch, *Chem. Listy* **48**, 61 (1954), *Chem. Abstr.* **49**, 1598^b (1955)

[18] M. Fétizon, J. Goré, P. Laszlo, B. Waegell, *J. Org. Chem.* **31**, 4047 (1966).

[19] R. C. Fort, Jr. and P. von R. Schleyer, *Ibid.* **30**, 789 (1965).