[Contribution from the Department of Chemistry, Duquesne University]

The Synthesis and Some Reactions of the *p*-Cyano Derivatives of 1,1-Diphenylethane

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Received August 25, 1955

The preparation of 1,1-diphenylethane from styrene and benzene has been improved. The iodination of 1,1-diphenylethane gave the mono- and di-*p*-iodo derivatives which were converted to the corresponding cyano compounds. The rearrangement of the iodo compounds, during oxidative degradation, was observed. The cyano compounds were subjected to various reactions including pyrolysis.

The synthesis of 1-(*p*-cyanophenyl)-1-phenylethane (**I**) and of 1,1-di-(*p*-cyanophenyl)ethane (**II**), consisted of the iodination of 1,1-diphenylethane (**III**) to the *p*-iodo and *p,p'*-diiodo derivatives, and the conversion of the iodo compounds to the desired **I** and **II** by means of cuprous cyanide.

Since **III** was needed in rather large quantities, a thorough investigation was undertaken to find the most convenient synthesis of this hydrocarbon. Of the number of synthetic procedures reported in the literature for the preparation of **III** or the closely related 1,1-di-(*p*-tolyl)ethane[1-9] several were reinvestigated. The reaction of benzene with paraldehyde in the presence of sulfuric acid[1] gave a poor yield of **III** and a considerable amount of solid, high-molecular weight byproducts. Similar results were obtained when benzene was allowed to react with acetylene in the presence of mercuric sulfate although this method is recommended for the preparation of 1,1-di-(*p*-tolyl)ethane.[2] The reaction of benzene with acetylene in the presence of mercuric sulfate and a phosphoric acid–boron trifluoride catalyst[3] gave no indication of the formation of **III** and there was formed a copious amount of black, tarry product. The procedure which gave consistently satisfactory yields of **III** (48% under optimum conditions) consisted of the addition of a mixture of styrene and benzene to a vigorously stirred mixture of benzene and sulfuric acid.[4] The use of benzene-*m*-disulfonic acid in place of sulfuric acid was also satisfactory but gave lower yields.

The iodination of **III** was carried out according to the method of Baker and Waters[10] and there was isolated a mixture of 1-(*p*-iodophenyl)-1-phenylethane and 1,1-di-(*p*-iodophenyl)ethane. The structures of these products were identified by oxidative degradation to the corresponding benzophenones. In the course of the oxidative degradations of the iodo compounds it was observed that the same batches of the mono- or di-iodo compounds gave variable yields of the expected benzophenones as well as the unexpected *p*-iodobenzoic acid. Since the formation of *p*-iodobenzoic acid could be explained if the hydrocarbon assumed to be **III** also contained some of the isomeric 1,2-diphenylethane, the absence of the latter was demonstrated by the oxidation of **III** to benzophenone and by the conversion of **III** to 1,1-diphenylethylene rather than to stilbene by means of N-bromosuccinimide.[11] The identity of the diiodo compound is also supported by the fact that the isomeric 1,2-di-(*p*-iodophenyl)ethane is a known, higher-melting solid.[12] The possibility that the iodobenzophenones are degraded to *p*-iodobenzoic acid was eliminated by the failure of an attempted oxidation of *p,p'*-diiodobenzophenone. It is concluded that the iodinated **III** is subject to a rearrangement during the oxidative degradation. A detailed investigation of this novel phenomenon will be described in a forthcoming publication from this laboratory.

The iodo compounds were cyanated by means of cuprous cyanide in pyridine or quinoline to give 64 and 83% yields of **I** and **II**, respectively. **I** was hydrolyzed to *p*-(1-phenethyl)benzoic acid which was identified by oxidation to *p*-benzoylbenzoic acid and the conversion of the latter to the methyl ester. **I** was also oxidized to *p*-cyanobenzophenone which could be hydrolyzed to the corresponding acid. The treatment of **II** with N-bromosuccinimide in the presence of benzoyl peroxide,[11] gave 1,1-di-(*p*-cyanophenyl)ethylene.

The pyrolysis of a number of 1,1-diarylethanes is

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[1] McConbrey and Lossing, U. S. Patent 2,500,369; *Chem. Abstr.*, **44**, 5393 (1950).

[2] Reichert and Nieuland, *Org. Syntheses*, Coll. Vol. I, p. 229 (1941).

[3] Vaiser, *Doklady Akad. Nauk. S.S.S.R.*, **70**, 621 (1950); *Chem. Abstr.*, **44**, 4888 (1950).

[4] Spiker and Sohade, *Ber.*, **65**, 1687 (1932).

[5] Ryuzaburo Nozu and Han-Ying Li, *J. Chem. Soc. Japan*, **60**, 695 (1939); *Chem. Abstr.*, **36**, 2843 (1942).

[6] Lynn and Fletcher, U. S. Patent 2,378,309; *Chem. Abstr.*, **39**, 3874 (1945).

[7] Balandin, Lurier, Marukhyan, *Compt. rend. acad. sci. U.R.S.S.*, **53**, 127 (1946); *Chem. Abstr.*, **41**, 3084 (1947).

[8] Malinowskiy, *J. Gen. Chem., U.S.S.R.*, **17**, 2235 (1946); *Chem. Abstr.*, **43**, 591 (1949).

[9] Sturrock, Lawe, and Kemp, U. S. Patent 2,439,228; *Chem. Abstr.*, **42**, 5052 (1948).

[10] Baker and Waters, *J. Chem. Soc.*, 150 (1952).

[11] Israelashoili and Bergmann, *J. Chem. Soc.*, 1070 (1953).

[12] *Beilsteins Handbuch der Organischen Chemie*, 4th Ed., 1st Suppl., Vol. 5, p. 282.

described in the literature[13–16a] to follow two simple paths represented by equations (a) and (b) with the formation of styrene and of 1,1-diarylethylene.

$$Ar_2CHCH_3 \longrightarrow ArCH{=}CH_2 + ArH \qquad (a)$$

$$Ar_2CHCH_3 \longrightarrow Ar_2C{=}CH_2 + H_2 \qquad (b)$$

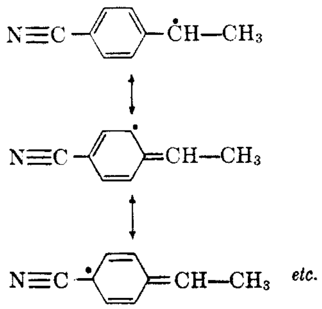
However, such products as stilbene, 9,10-dimethyl-9,10-dihydroanthracene, toluene, and ethylbenzene, resulting from more complex decomposition paths, also have been reported. Still, under controlled conditions, the pyrolysis of 1,1-diarylethanes is claimed to give practical yields of styrene or of a substituted styrene. Of theoretical as well as of practical interest is the decomposition of an asymmetrical 1,1-diarylethane according to equation (a) since two paths are possible in this case:

$$ArAr'CHCH_3 \longrightarrow ArCH{=}CH_2 + Ar'H \qquad (a\text{-}1)$$

$$ArAr'CHCH_3 \longrightarrow Ar'CH{=}CH_2 + ArH \qquad (a\text{-}2)$$

All the unsymmetrical 1,1-diarylethanes, studied so far apparently were compounds in which Ar = phenyl and Ar′ = alkylphenyl, and in these cases the decomposition follows exclusively path (a-1). If this behavior were to indicate a general pattern then the pyrolysis of **I** should produce styrene and benzonitrile rather than *p*-cyanostyrene and benzene.

The pyrolysis reactions were carried out using two types of catalysts, kaolin-coated porcelain chips and Filtrol-X-550 supplied by the Filtrol Corp., Los Angeles, California. The effect of the catalyst, as well as the temperature requirement, was tested by pyrolysis of 1,1-di-(*p*-tolyl)ethane. It was found that, for our purpose, the kaolin catalyst was superior to Filtrol-X-550 since the latter had the tendency to give the hydrogenated styrenes. Thus, from the pyrolyses of 1,1-di-(*p*-tolyl)ethane and of **I** using Filtrol-X-550 there were obtained *p*-ethyltoluene and *p*-ethylbenzonitrile, respectively. The structure of the latter was proven by hydrolysis to *p*-ethylbenzoic acid, which in turn was oxidized to terephthalic acid. The pyrolysis of **I** seemed to occur exclusively with the cleavage of the unsubstituted phenyl group and the *p*-cyanophenyl group remained attached to the aliphatic side chain. This result, while contrary to those obtained with unsymmetrical 1,1-diarylethanes, in which the aryl groups consisted of phenyl and alkylphenyls, is not entirely unexpected on theoretical grounds since it is known that electron-withdrawing substituents are more capable of stabilizing radicals than are electron-donating substituents[17,18] The contribution of resonance structures to the intermediate radical would account for the strong attachment of the *p*-cyanophenyl group to the aliphatic side chain. The above conclusion also is in agreement with the observation that the pyrolyses of **I** and of **II** required increasingly higher temperatures as compared with the temperature sufficient to cause pyrolysis of 1,1-di-(*p*-tolyl)ethane. As a matter of fact, the attempted pyrolysis of **II** under equivalent conditions to those employed for **I** and at even higher temperatures did not give any indication of the formation of either *p*-cyanostyrene or benzonitrile.



Steam is a recommended diluent in the pyrolysis of 1,1-diarylethanes[16] because of its regenerative action on the catalyst. Steam under the conditions of the pyrolysis of **I** caused a partial hydrolysis of the cyano group. Thus, from the aqueous portion of the pyrolysis mixture it was possible to isolate *p*-(1-phenethyl)benzoic acid and to detect the presence of ammonia. The distillation of the organic portion gave oily fractions boiling higher than **I**. Since these fractions could not be made to crystallize they were oxidized and *p*-benzoylbenzamide was isolated. The hydrolysis of the high-boiling fraction gave *p*-(1-phenethyl)benzoic acid and thus it appears that the pyrolysis of **I** in the presence of steam gave in addition to the low-boiling materials, such as *p*-cyanostyrene, a complex mixture of **I** and the corresponding amide and acid. This complication could be avoided when nitrogen rather than steam was used as a diluent for the pyrolysis of **I**.

EXPERIMENTAL

1,1-Diphenylethane. (A). A mixture of 1 l. of benzene and 200 ml. of 95% sulfuric acid was vigorously stirred at 30° while a solution of 170 g. of styrene in 400 ml. of benzene was added dropwise over a period of 3 hours. After an additional stirring for 5 hours, the reaction mixture was hydrolyzed, and the organic layer was washed until neutral. Upon removing unreacted benzene, the oily residue was distilled to yield 126 g. of 1,1-diphenylethane, b.p.$_8$ 126–129°, n_D^{25} 1.5719. A carefully purified sample was reported recently to have b.p.$_{20}$ 146°, n_D^{20} 1.5725.[19] The yield of 48% of theory represents an improvement over the similar procedure reported in the literature.[4]

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[13] Morton and Nickolls, *Can. J. Research*, **26B**, 581 (1948).

[14] Sheibley and Prutton, *J. Am. Chem. Soc.*, **62**, 840 (1940).

[15] Han-Ying Li, *J. Chem. Soc. Japan*, **62**, 562 (1941).

[16] Sturrock and Lawe, U. S. Patents 2,373,382; 2,420,688; 2,420,689; 2,422,318; and 2,519,719.

[16a] Dixon and Saunders, *Ind. Eng. Chem.*, **46**, 652 (1954).

[17] Dannley and Gregg, Jr., *J. Am. Chem. Soc.*, **76**, 2995 (1954).

[18] Hey, Pengilly and Williams, *J. Chem. Soc.*, 6 (1955).

[19] Corson, Dorsky, Nickels, Kutz and Thayer, *J. Org. Chem.*, **19**, 17 (1954).

(*B*). Acetylene was passed slowly for a period of 30 hours through a stirred mixture of 500 ml. of benzene, 100 g. of phosphoric acid saturated with boron trifluoride, and 5 g. of mercuric oxide.[3] The reaction mixture was filtered and the filtrate was distilled to give 170 ml. of benzene and a black tarry residue.

(*C*). A mixture of 500 g. of benzene, 100 g. of paraldehyde, and 890 g. of concentrated sulfuric acid was kept between 0–5° for 6 hours with constant stirring.[1] The reaction mixture was poured on ice and the non-aqueous layer was extracted with ether, washed, and distilled. A yield of 40 g. of 1,1-diphenylethane, b.p. 268–272°, was obtained, as well as a considerable amount of a solid polymer.

(*D*). Acetylene was bubbled into a stirred mixture of 350 g. of benzene, 50 g. of 95% sulfuric acid, and 5 g. of mercuric sulfate.[2] The reaction mixture was kept at 0–10°, and the acetylene was introduced for 4 hours. The nonaqueous layer obtained on hydrolysis of the mixture was extracted with ether to give 30 g. of III and tar.

1,1-Di-(p-iodophenyl)ethane and 1-p-iodophenyl-1-phenylethane. A mixture of 240 g. (0.132 mole) of III, 156 g. (0.15 mole) of silver sulfate, 300 ml. of conc'd sulphuric acid, and 100 ml. of water was cooled to 5° and 254 g. (1.0 mole) of iodine was added over a period of 90 minutes. The mixture was stirred rapidly for 50 hours, poured into a large volume of water and the aqueous portion and the solid were extracted with ether. The residue was distilled to give two fractions b.p.$_{1}$ 170–185° and b.p.$_{1}$ 230–240°. The lower-boiling fraction was identified as the monoiodo compound (74%) while the higher-boiling fraction (9%) was identified as the diiodo compound. The higher-boiling fraction solidified to give a white solid which upon crystallization from methanol gave a constant m.p. 87–87.5°.

Anal. Calc'd for $C_{14}H_{12}I_2$: C, 38.79; H, 2.79. Found: C, 39.15; H, 2.82.

The lower-boiling fraction was redistilled and the fraction b.p.$_{1}$ 168–170° was submitted for analysis.

Anal. Calc'd for $C_{14}H_{13}I$: C, 54.56; H, 4.25. Found: C, 54.80; H, 4.41.

1-p-Cyanophenyl-1-phenylethane (I). To a mixture of 207 g. of 1-*p*-iodophenyl-1-phenylethane and 75 ml. of pyridine there was added 70 g. of cuprous cyanide over a period of 3 hours. The reaction mixture was heated for 5 hours at 210–220°, extracted with hot dilute hydrochloric acid, and then with hot benzene. The final oily residue was distilled to give a 64% yield of the cyano compound, b.p.$_{5}$ 167–169°. The fraction solidified and upon crystallization from methanol gave a white solid, m.p. 50–51°.

Anal. Calc'd for $C_{15}H_{13}N$: C, 86.92; H, 6.34. Found: C, 87.04; H, 6.20.

1,1-Di-(p-cyanophenyl)ethane (II). Cuprous cyanide, 21 g., was added to a mixture of 36 g. of the iodo compound and 25 ml. of pyridine. The mixture was heated for five hours at 210–220°, and extracted with hot dilute hydrochloric acid, and then with hot benzene. Upon concentration of the benzene extract there was obtained an 83% yield of the cyano compound, b.p.$_{5}$ 222–225°. The cyano compound upon crystallization from benzene and petroleum ether was obtained as a white solid, m.p. 123–123.5°.

Anal. Calc'd for $C_{16}H_{12}N_2$: C, 82.74; H, 5.21. Found: C, 82.73; H, 5.39.

Oxidation experiments with the substituted 1,1-diarylethanes. The diarylethanes were heated with anhydrous chromic acid in glacial acetic acid and the reaction mixtures were poured into large volumes of ice-water. The mixtures were filtered when a solid was present and the filtrates were extracted with benzene. The benzene extracts were in turn extracted with dilute alkali. The acidic oxidation products were obtained by acidification of the alkaline extract while the neutral oxidation products were obtained by concentration of the benzene solution.

The oxidation of 3 g. of the above monoiodo compound with 5 g. of chromic acid gave in one experiment 1.2 g. of *p*-iodobenzoic acid, m.p. 266–267°, while another experiment using 4.5 g. of the iodo compound and 6 g. of chromic acid gave 2.6 g. of *p*-iodobenzophenone, m.p. 100–101°.

The oxidation of 3 g. of the above diiodo compound with 5 g. of chromic acid gave in one experiment 0.1 g. of *p,p'*-diiodobenzophenone, m.p. 237–238° and 1.7 g. of *p*-iodobenzoic acid, m.p. 266–267°, while in another experiment using 2.9 g. of diiodo compound and 4 g. of chromic acid there was obtained only 2.7 g. of *p,p'*-diiodobenzophenone, m.p. 237–238°.

The oxidation of 1 g. of I with 1.5 g. of chromic acid gave 0.7 g. of *p*-cyanobenzophenone, m.p. 110–111°.

Several oxidation reactions of III gave exclusively benzophenone.

The preparation and identification of p-1-phenethylbenzoic acid. A mixture of 0.5 g. of I and 50 cc. of dilute sodium hydroxide was refluxed until the evolution of ammonia ceased. The solution on cooling, filtration and acidification gave an acid, m.p. 124–125°.

Anal. Calc'd for $C_{15}H_{14}O_2$: C, 79.60; H, 6.23; Neut. equiv., 226. Found: C, 79.79; H, 6.15; Neut. equiv., 218.

The oxidation of 0.1 g. of the above acid with 0.3 g. of chromic acid in acetic acid gave *p*-benzoylbenzoic acid, m.p. 196–197°, which was converted to the corresponding methyl ester, m.p. 105–108°,[20] by heating for 24 hours with methanol and a few drops of sulfuric acid.

The preparation and identification of p-benzoylbenzamide. From a number of pyrolyses experiments of I in the presence of steam there were obtained fractions boiling 20–30° higher than unreacted I. These oily fractions could not be made to crystallize, and they were subjected to oxidation with anhydrous chromic acid in glacial acetic acid. Variable amounts of a solid m.p. 169–170° were obtained.

Anal. Calc'd for $C_{14}H_{11}NO_2$: C, 74.68; H, 4.89; N, 6.23; M. W., 225. Found: C, 74.67; H, 5.18; N, 6.49; (Rast) 224.

The hydrolysis of this solid by means of dilute sodium hydroxide gave *p*-benzoylbenzoic acid, m.p. 196–197°, and heating of 0.2 g. the amide with 10 cc. of thionyl chloride for two hours gave *p*-cyanobenzophenone (m.p. and mixed m.p. 106–107°).

THE PREPARATION OF 1,1-DIARYLETHYLENES

1,1-Diphenylethylene. A mixture of 2 g. of III, 4 g. of N-bromosuccinimide, 0.1 g. of benzoyl peroxide, and 50 cc. of carbon tetrachloride was refluxed for 1 hour. The mixture was filtered, and the filtrate was concentrated and heated for 1 hour with 20 cc. of pyridine. The reaction mixture was poured into water and extracted with benzene. The benzene layer was distilled and the fraction b.p.$_{4}$ 118–135° was collected. Redistillation gave 0.8 g. of liquid b.p.$_{3}$ 116–118° (n_D^{22} 1.6117), the physical properties of which agree with those reported for 1,1-diphenylethylene.[21]

1,1-Di-(p-cyanophenyl)ethylene. II, 1 g., was treated as described for the preceding experiment and there was obtained 0.8 g. of product m.p. 158–158.5° (in agreement with the literature m.p.).[22]

Construction and calibration of the pyrolysis tube. The pyrolysis tube was constructed from a stainless steel pipe 1 inch in diameter and 20 inches in length. The tube was covered with a thin layer of asbestos tape and chromel wire was wound over the entire length with $^1/_4$ inch intervals between coils. The entire tube then was covered with wet asbestos tape, smoothed to form a continuous pad, and left to dry. Ground glass joints were provided at the top and bottom of the tube for the attachment of a dropping-funnel and condenser. The pyrolysis tube was filled with the catalyst and a calibrated 400°-thermometer was inserted

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(20) Smith, *J. Am. Chem. Soc.*, **43**, 1920 (1921).

(21) Heilbron, *Dictionary of Organic Compounds*, Vol. 1, p. 415, London, 1953.

(22) Ashley, Grove, and Henshall, *J. Chem. Soc.*, 261 (1948).

into the tube. The voltage readings across a variable resistance were plotted against the observed temperature in the apparatus and the voltage values were extrapolated into the 500° range.

Catalysts. (*A*). Porcelain boiling chips were broken into 1–5 mm. particles and mixed in a 1:1 ratio with kaolin. Water was added and the resulting paste was dried first at 110° and finally baked at 650° for two hours. The baked solid was screened before use to remove the powdery particles.

(*B*). Filtrol X-550 was obtained through the courtesy of the Filtrol Corp., Los Angeles, California.

PYROLYSIS OF 1,1-DI-(*p*-TOLYL)ETHANE

Using catalyst (*A*). The pyrolysis of 14.3 g. of the hydrocarbon at 450° was carried out using a 20-fold quantity of steam as diluent. The nonaqueous portion of the reaction mixture was separated and titration[23] of an aliquot indicated a 30% yield of unsaturated material. The reaction product was distilled to give 3.4 g. of low-boiling fraction, b.p.$_{70}$ 75–80°, and 9 g. of unreacted starting material, b.p.$_{70}$ 194–210°. The low-boiling fraction was titrated for unsaturation and contained 72% *p*-methylstyrene.

Using catalyst (*B*). The pyrolysis of 29 g. of the hydrocarbon at 420° using nitrogen gas as diluent gave, upon distillation of the reaction mixture, 0.8 g. of material b.p. 127–130° (n_D^{20} 1.5043), 4 g. of material b.p. 140–157° (n_D^{20} 1.5106), and a high-boiling residue. The second fraction was redistilled and material b.p. 150–152° (n_D^{20} 1.5072) was obtained. This liquid gave a negligible titer for unsaturation and in view of the close agreement with the $n_D^{22.8}$ 1.4950 reported for *p*-ethyltoluene[24] was believed to be the latter rather than *p*-methylstyrene [reported[25] n_D^{18} 1.5306].

PYROLYSIS OF I

Using catalyst (*A*). In a typical experiment 19 g. of I in 200 cc. of benzene was introduced into the apparatus maintained at 500° simultaneously with a three-fold amount of steam. The nonaqueous portion of the reaction mixture was separated and distilled, and in addition to biphenyl there were two fractions. The first consisted of 2.5 g. of *p*-cyanostyrene, b.p.$_9$ 104–107° (n_D^{23} 1.5778) in agreement with the b.p.$_9$ 102–104° (n_D^{20} 1.5787) reported in the literature.[26] The second fraction consisted of 8 g. of recovered starting material, b.p.$_9$ 170–175°.

Using catalyst (*B*). In a typical experiment 35 g. of I in 200 cc. of benzene was introduced into the apparatus maintained at 480–500° simultaneously with an 11-fold amount of water. The organic layer upon distillation gave 1 g. of liquid b.p.$_{10}$ 105–112° (n_D^{25} 1.5323). This liquid was shown to be *p*-ethylbenzonitrile (reported[27] to have b.p.$_{12}$ 103–104° and n_D^{20} 1.5274) by hydrolysis to *p*-ethylbenzoic acid, m.p. 112–113°,[27] and the oxidation of the latter to terephthalic acid (m.p. with sublimation at 300°, di-*p*-nitrobenzyl ester m.p. 265°). The distillation of the organic portion of the reaction mixture also gave 11 g. of material b.p.$_1$ 148–160° which consisted of impure I. The aqueous layer of the reaction mixture was concentrated by distillation (the presence of ammonia was noticed during this operation) and the residue gave an acid m.p. 124–125° identical with the sample of *p*-(1-phenethyl)benzoic acid prepared by the hydrolysis of I.

Pyrolysis of II. When the pyrolysis of II employing catalyst (*A*) was attempted at temperatures below 500° the starting material was recovered unchanged. Two pyrolyses at 550° gave no indication of the formation of either *p*-cyanostyrene or benzonitrile. From the complex mixture of solid materials obtained in the first experiment it was possible to isolate a small amount of unidentified product m.p. 166–166.5° (C, 80.69; H, 3.24). The second experiment gave an unidentified solid m.p. 208–209° (C, 90.34; H, 5.98).

Acknowledgment. The financial support of this project by The Koppers Co. is greatfully acknowledged. We wish to thank Mr. John Deffner for assistance in some of the experimental work.

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[23] D'Alelio, *Experimental Plastics and Synthetic Resins*, John Wiley and Sons, Inc., New York, 1946, p. 177.

[24] Ref. (21), Vol. 2, p. 524.

[25] Ref. (21), Vol. 3, p. 507.

[26] Marvel and Overberger, *J. Am. Chem. Soc.*, **67**, 2250 (1945).

[27] Birch, Dean, Fidler, and Lowry, *J. Am. Chem. Soc.*, **71**, 1362 (1949).