The samples[2] were redistilled prior to being observed as the pure liquids at room temperature. The reported relative intensities are based on the apparent per cent. transmission at a constant sample thickness of 0.025 mm. Thinner samples were used occasionally to resolve the keto and ester C=O absorption bands.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

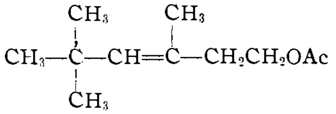
2-Neopentyl-1,3-butadiene. Preparation and Proof of Structure[1]

BY A. T. BLOMQUIST AND JEROME C. WESTFAHL[2]

RECEIVED MARCH 7, 1952

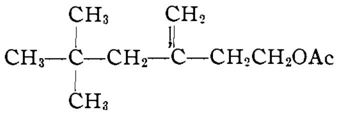
The isomeric nonenyl acetates obtained by the condensation of diisobutylene, paraformaldehyde and glacial acetic acid when pyrolyzed yield 2-neopentyl-1,3-butadiene, diisobutylene, acetic acid and formaldehyde. The structure of 2-neopentyl-1,3-butadiene was established. Its formation of an adduct with maleic anhydride, which on aromatization and degradation gave trimellitic acid, demonstrated the presence of one alkyl group in the 2-position of the 1,3-butadiene chain. Oxidation of the diene to *t*-butylacetic acid showed that the alkyl group is a neopentyl group.

Recent studies in this Laboratory of the condensation of olefins with paraformaldehyde and glacial acetic acid had shown that the principal products are acetates of unsaturated alcohols having one more carbon atom than the original olefins and having the same degree of unsaturation. The structure of individual isomers in the mixture of acetates obtained from commercial diisobutylene (80% 2,4,4-trimethyl-1-pentene and 20% 2,4,4-trimethyl-2-pentene) has been studied by means of ozonolysis and the isomeric acetates I and II are believed to be present.[3]



$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CH{=}\overset{\displaystyle CH_3}{C}{-}CH_2CH_2OAc}$$

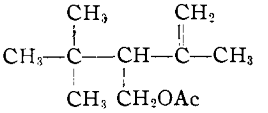
I



$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CH_2{-}\overset{\displaystyle CH_2}{\overset{\|}{C}}{-}CH_2CH_2OAc}$$

II

The structures of I and II indicate that they are both formed from the major isomer of diisobutylene. Since the condensation of pure 2,4,4-trimethyl-2-pentene with paraformaldehyde and glacial acetic acid has been shown to produce a nonenyl acetate,[4] an isomer such as III may be assumed to be present in the mixture of isomeric acetates prepared from diisobutylene. The compounds I, II and III each contain the $\mathrm{{-}CH{=}\underset{|}{C}{-}\underset{|}{C}H{-}CH_2OAc}$ group



$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}\underset{\displaystyle CH_2OAc}{CH}{-}\overset{\displaystyle CH_2}{\overset{\|}{C}}{-}CH_3}$$

III

and, accordingly, pyrolysis of the mixture of nonenyl acetates should yield a mixture of alkyl substituted 1,3-butadienes.

Pyrolysis at 475° of the nonenyl acetate fraction of b.p. 78–85.5° (10 mm.) and $n^{20}\mathrm{D}$ 1.442–1.444 gave a mixture of 2-neopentyl-1,3-butadiene (IV), diisobutylene, acetic acid, paraformaldehyde and unpyrolyzed nonenyl acetate. Repyrolysis of the recovered nonenyl acetate under the same conditions produced IV and acetic acid with only traces of diisobutylene and paraformaldehyde. This indicated that the more thermolabile nonenyl acetates responsible for the production of diisobutylene and formaldehyde were almost completely decomposed in the first pyrolysis.

The structure of IV was established by the series of reactions shown in the chart. Reaction of the diene (IV) with maleic anhydride in benzene solution gave 4-neopentyl-4-cyclohexene-1,2-dicarboxylic anhydride (V). Aromatization of V, carried out with a 30% palladium-on-norit catalyst[5] by the method of Fieser[6] or by heating with sulfur at 200–250°, produced VI. Oxidation of the sodium salt of VII, obtained from VI, by refluxing with an excess of aqueous potassium permanganate failed to give trimellitic acid (XII) but produced instead the stable intermediate oxidation product pivalophenone-3,4-dicarboxylic acid (VIII).

The possibility of establishing the position and structure of the acyl group in VIII by means of a Beckmann rearrangement of the oxime of VIII was investigated. The keto acid (VIII) was converted to the N-phenyl imide (IX) by a modification of the method of Tingle and Cram[7] in order to simplify the preparation of an oxime. The oxime X was prepared by a standard method.[8] In studying the Beckmann rearrangement of pivalophenone ketoxime Schroeter[9] observed that treatment with phosphorus pentachloride gave benzonitrile. However, treatment of the oxime with anhydrous hydrogen chloride in acetic acid effected rearrangement to trimethylacetanilide. When Schroeter's anhy-

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[1] The work reported here was done as part of a research project at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Company.

[2] Abstracted from the dissertation submitted by Jerome C. Westfahl in September, 1950, to the Graduate Faculty of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. T. Blomquist, L. I. Diuguid, M. Passer and C. S. Schollenberger, unpublished; M. Passer, Thesis, Cornell University, 1948; C. S. Schollenberger, Thesis, Cornell University, 1947.

[4] Private communication from Dr. Fred T. Fiedorek, Research Center, The B. F. Goodrich Co., Brecksville, Ohio.

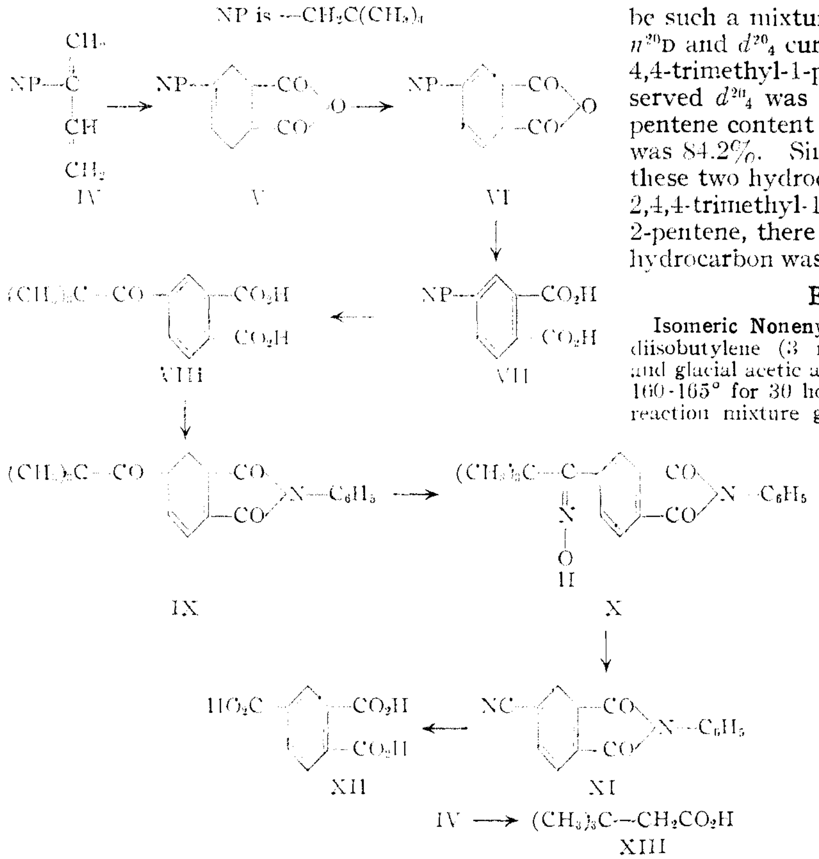
[5] R. P. Linstead and S. L. C. Thomas, *J. Chem. Soc.*, 1127 (1940).

[6] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, pp. 461–462.

[7] J. B. Tingle and M. P. Cram, *Am. Chem. J.*, **37**, 596 (1907).

[8] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 198.

[9] G. Schroeter, *Ber.*, **44**, 1201 (1911).



drous hydrogen chloride procedure was applied to the oxime X no rearrangement occurred and only unchanged oxime was isolated. Treatment of X with phosphorus pentachloride in benzene gave N-phenyl 4-cyano-1,2-benzenedicarboximide (XI). Hydrolysis of XI, effected by heating with alcoholic potassium hydroxide for 24 hours at 150°, produced aniline, ammonia and trimellitic acid (XII). The latter was characterized by comparison with an authentic sample of XII and by conversion to its anhydride.[10]

Since a normal Beckmann rearrangement of the oxime X did not occur the structure of the alkyl group was elucidated by the oxidation of the diene (IV) with aqueous potassium permanganate at room temperature to give *t*-butylacetic acid (XIII). XIII was characterized by conversion to its amide,[11] anilide[11] and *p*-bromophenacyl ester.[12]

The diisobutylene formed in the first pyrolysis was identified as follows. After careful purification, its physical properties were determined. From the molecular weight (Victor Meyer method) and the results of semi-micro quantitative hydrogenation, the formula C_8H_{16} was deduced. Comparison of the observed b.p., $n^{20}D$ and d^{20}_4 with those for the known C_8H_{16} hydrocarbons[13] showed that the properties found agreed best with those of a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. Assuming the hydrocarbon to be such a mixture and that the composition *versus* $n^{20}D$ and d^{20}_4 curves were linear, the content of 2,-4,4-trimethyl-1-pentene calculated using the observed d^{20}_4 was 83.3% and the 2,4,4-trimethyl-1-pentene content calculated using the observed $n^{20}D$ was 84.2%. Since the equilibrium composition of these two hydrocarbons[14] is known to contain 80% 2,4,4-trimethyl-1-pentene and 20% 2,4,4-trimethyl-2-pentene, there seemed little doubt that the C_8H_{16} hydrocarbon was diisobutylene.

Experimental Part[15]

Isomeric Nonenyl Acetates.[3]—A mixture of commercial diisobutylene (3 moles), paraformaldehyde (1.5 moles) and glacial acetic acid (1.5 moles) was heated in a bomb at 160-165° for 30 hours with agitation. Distillation of the reaction mixture gave 60–70% of a mixture of isomeric nonenyl acetates; b.p. 199–210°, $n^{20}D$ 1.442–1.444. A redistilled fraction of b.p. 78–85.5° (10 mm.) was used for pyrolysis.

2-Neopentyl-1,3-butadiene (IV).—Through a vertical Pyrex tube (25 mm. inside diameter) packed with a 220-mm. layer of carborundum chips and heated to 475° there was passed 500 g. of the isomeric nonenyl acetates (b.p. 78–85.5° (10 mm.)) at a rate of approximately 50 g. per hour. A slow stream of carbon dioxide was passed through the apparatus throughout the pyrolysis. In an ice-cooled receiver attached to the lower end of the pyrolysis tube 478 g. of a pale yellow liquid containing suspended paraformaldehyde was collected. After filtering the formaldehyde and adding hydroquinone the liquid was fractionated at 50 mm. giving 198 g. (b.p. up to 52° (50 mm.)) of a mixture of acetic acid and hydrocarbons. Fractional distillation of the residue at 10 mm. gave 207 g. of recovered nonenyl acetates, b.p. 78–85.5°. The acetic acid–hydrocarbon fraction after washing with cold dilute sodium hydroxide, drying, and fractional distillation at 87 mm. gave 40.4 g. of a forerun, consisting largely of diisobutylene, and 66.4 g. (33.6%) of IV; b.p. 60.5–64.5° (87 mm.). On refractionation the major portion boiling at 61–63° (87 mm.) showed b.p. 123–125° (743.7 mm.), $n^{20}D$ 1.4431, d^{20}_4 0.755.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.23, 87.02; H, 12.61, 12.75.

Repyrolysis of the recovered nonenyl acetates (207 g.) under the same conditions described above gave 204 g. of a pale yellow liquid product free of suspended paraformaldehyde. From this product there was obtained 118 g. of nonenyl acetates and 25.1 g. (42%) of IV: b.p. 60.5–64.5° (87 mm.). Practically no diisobutylene was obtained in this second pyrolysis.

The lower boiling hydrocarbon produced in the first pyrolysis of the nonenyl acetates was treated with molten maleic anhydride on the steam-bath to remove yellow color and any IV present. The colorless hydrocarbon was decanted, steam distilled, dried, and fractionated at atmospheric pressure. The major fraction had the following properties: b.p. 99–99.6° (746.2 mm.), $n^{20}D$ 1.4100, d^{20}_4 0.717.

Anal. Calcd. for C_8H_{16}: mol. wt., 112.21; M_D, 38.69. Found: mol. wt., 110.5, 114.4 (Victor Meyer method); M_D, 38.79 (using *m*, 112.21). Quantitative reduction in ethanol using Adams catalyst required 105% of one molar equivalent of hydrogen.

4-Neopentyl-4-cyclohexene-1,2-dicarboxylic Anhydride (V).—A solution of 33.1 g. (0.338 mole) of maleic anhydride in 120 ml. of benzene was added to 42.07 g. (0.338 mole) of IV. There was immediate evolution of heat and within ten minutes cooling was required to prevent boiling. After

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(10) W. Schultze, *Ann.*, **359**, 143 (1908).

(11) A. H. Homeyer, F. C. Whitmore and V. H. Wallingford, THIS JOURNAL, **55**, 4209 (1933).

(12) I. L. Ozanne and C. S. Marvel, *ibid.*, **52**, 5267 (1930).

(13) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., pp. 214–234.

(14) W. S. Gallaway and M. J. Murray, THIS JOURNAL, **70**, 2584 (1948).

(15) All melting points are corrected unless otherwise noted. All boiling points are uncorrected.

20 minutes the solution was refluxed for two hours. After removal of the benzene *in vacuo* there was obtained 75.0 g. (99.7%) of crude crystalline adduct; m.p. after recrystallization from benzene–hexane 114.4–114.9°.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.23, 70.26; H, 8.37, 8.46.

4-Neopentyl-4-cyclohexene-1,2-dicarboxylic Acid.—The adduct V and four times its weight of water, containing two equivalents of sodium hydroxide, were heated slowly to boiling. After filtering and acidifying the crude acid precipitated and was recrystallized from acetic acid–water; m.p. 150.4–151.5°.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39; neut. equiv., 120. Found: C, 65.01, 64.93; H, 8.29, 8.33; neut. equiv., 121, 121.

The dicarboxylic acid was characterized as its N-phenyl imide which was prepared using a modification of the procedure of Tingle and Cram[7] for phthalanil. The crystalline imide showed m.p. 129.1–130.1° from ethanol–water.

Anal. Calcd. for $C_{13}H_{22}O_2N$: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.72, 76.62; H, 7.96, 7.77; N, 4.77, 4.74.

4-Neopentyl-1,2-benzenedicarboxylic Acid (VII). A. Quantitative Catalytic Dehydrogenation.—Using an apparatus similar to that described by Fieser[6] a solution of 2 g. of V in 20 ml. of *p*-cymene (Eastman Kodak Co. White Label) was refluxed with 80 mg. of a 30% palladium-on-norit catalyst, prepared according to the procedure of Linstead and Thomas.[5] After 7.5 hours 86.6% of two molar equivalents of hydrogen was evolved. The filtered *p*-cymene solution was refluxed for one hour with 25 ml. of water containing 1 g. of sodium hydroxide and steam distilled until free of *p*-cymene. Acidification of the aqueous alkaline solution with hydrochloric acid gave crude liquid VII. After extraction with ether there was obtained 2.1 g. (98.6%) of crude liquid VII which crystallized after long standing. Four recrystallizations from benzene–hexane gave colorless needles; m.p. 153.2–154.7°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83; neut. equiv., 118. Found: C, 66.23, 66.29; H, 7.19, 7.27; neut. equiv., 119, 119.

A small quantity of a less soluble acid of m.p. 206.1–206.6° was isolated from the crude VII. This acid was shown by mixed melting point determination to be identical with 4-neopentyl-1,2-cyclohexanedicarboxylic acid (m.p. 204.1–205.6°) prepared by hydrogenating 4-neopentyl-4-cyclohexene-1,2-dicarboxylic acid (m.p. 150.4–151.5°).

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.29, 64.49; H, 9.00, 9.08.

The formation of completely saturated compounds in the catalytic aromatization of cyclohexene derivatives has been previously observed.[16]

The saturated dicarboxylic acid was characterized as its N-phenyl imide and as its anhydride. N-Phenyl 4-neopentyl-1,2-cyclohexanedicarboximide; m.p. 124.4–124.9°. *Anal.* Calcd. for $C_{19}H_{25}O_2N$: C, 76.21; H, 8.42; N, 4.68. Found: C, 76.38, 76.35; H, 8.38, 8.42; N, 4.74, 4.85; 4-Neopentyl-1,2-cyclohexanedicarboxylic anhydride; m.p. 75.8–76.3°.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.72, 69.80; H, 9.22, 9.27.

B. Sulfur Dehydrogenation.—Using an apparatus similar to that described by Fieser for the distillation of solids[17] a mixture of 20.00 g. (0.08998 mole) of V and 5.76 g. (0.1797 mole) of powdered sulfur (flowers) was heated from 210 to 250° over a period of 1.5 hours, during which hydrogen sulfide was evolved vigorously. Distillation of the mixture at a bath temperature of 165–170° and a pressure of 0.1–1.0 mm. gave 17.51 g. (89%) of impure VI as a viscous yellow liquid which solidified completely when seeded. One recrystallization from petroleum ether (b.p. 30–60°) gave 13.84 g. (70%) of yellow needles still contaminated with sulfur. This impure anhydride (13.84 g.) after dissolving in hot aqueous potassium hydroxide (7.12 g. in 100 ml.), filtering and separating from insoluble oil was treated at room temperature with small portions of a saturated aqueous potassium permanganate solution until the permanganate color persisted for 15 minutes. The excess permanganate was destroyed with sodium bisulfite, the solution filtered, acidified with sulfuric acid, and extracted with ether. There was obtained 14.5 g. (68%) of colorless liquid VII which crystallized readily when scratched or seeded.

4-Neopentyl-1,2-benzenedicarboxylic Anhydride (VI).—The acid VII when refluxed for one hour with acetyl chloride gave 90% of colorless, odorless crystalline VI when distilled at a bath temperature of 160–175° at 10 mm.; m.p. 62.7–63.7° from petroleum ether (b.p. 30–60°). The m.p. of pure VI prepared by the catalytic method and by sulfur aromatization was not depressed.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.37, 71.48; H, 6.44, 6.41.

N-Phenyl-4-neopentyl-1,2-benzenedicarboximide was prepared as described previously; m.p. 174.2–175°. *Anal.* Calcd. for $C_{19}H_{19}O_2N$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.78, 77.93; H, 6.93, 6.94; N, 4.79, 4.85.

Pivalophenone-3,4-dicarboxylic Acid (VIII).—To a solution of 2 g. (0.00846 mole) of VII in 80 ml. of water containing a 1-ml. excess of 10% sodium hydroxide there was added 1.79 g. (0.01698 equiv.) of potassium permanganate. The mixture was refluxed three hours, cooled and the faint permanganate color discharged with a few drops of aqueous sodium bisulfite. The filtered mixture was acidified and extracted with ether. From the ether extracts there was obtained 2.53 g. of colorless liquid acid which was dissolved in a minimum amount of boiling benzene. Boiling hexane was added to the hot benzene solution to incipient cloudiness. Upon slow cooling to room temperature colorless needles separated: 1.80 g. (86%) of keto acid showing m.p. 108.5–111.7°. After several recrystallizations the m.p. was raised to 113.8–115.4°. This keto acid contained solvent of recrystallization which was removed by crystallization from boiling water. The acid thus obtained showed m.p. 101.9–102.9°, determined by inserting m.p. tubes as the bath temperature was raised as the acid formed its anhydride very readily.

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64; neut. equiv., 125. Found: C, 62.29, 62.58; H, 5.54, 5.54; neut. equiv., 127, 128.

The N-phenyl imide (IX) of VIII was prepared by the method previously described. When IX was recrystallized from ethanol–water it showed m.p. 152.2–152.7°.

Anal. Calcd. for $C_{19}H_{17}O_3N$: C, 74.25; H, 5.58; N, 4.55. Found: C, 74.32, 74.49; H, 5.79, 5.67; N, 4.83, 4.65.

The oxime of IX was prepared by refluxing IX and an alcoholic solution of hydroxylamine hydrochloride and pyridine for 2 hours.[8] The crude oxime (X) was recrystallized three times from ethanol–water; m.p. 191.6–192.1°. Further recrystallizations raised the m.p. to 198.3°.

Anal. Calcd. for $C_{19}H_{18}O_3N_2$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.63, 70.74; H, 5.46, 5.54; N, 8.63, 8.79.

N-Phenyl-4-cyano-1,2-benzenedicarboximide (XI).—A solution of 2.52 g. (0.00781 mole) of X, 7.00 g. (0.0336 mole) of phosphorus pentachloride in 77 ml. of benzene was refluxed for 2 hours and then permitted to stand at room temperature overnight. The solution diluted with an additional 80 ml. of benzene was treated cautiously with 200 ml. of water and the benzene layer subsequently washed with aqueous potassium carbonate and dried. After most of the benzene had been removed petroleum ether (b.p. 90–100°) was added and the solution allowed to cool slowly to yield 1.56 g. of yellow crystals. Concentration of the mother liquor gave an additional crop of 0.13 g. Recrystallization of the combined crops from petroleum ether (b.p. 90–100°) plus a little benzene gave 1.52 g. (60%) of pale yellow XI; m.p. 215.5–216° (uncor.).

Anal. Calcd. for $C_{15}H_8O_2N_2$: C, 72.74; H, 3.25; N, 11.29. Found: C, 72.49; H, 3.16; N, 11.31, 11.29.

Hydrolysis of XI.—A solution of 1.52 g. (0.0061 mole) of XI, 1.79 g. (0.0319 mole) of potassium hydroxide, and 13.4 ml. of 95% ethanol was heated for 24 hours at 150° in a sealed heavy-walled Pyrex tube. On cooling to room temperature the contents of the tube consisted of a lower layer of colorless crystalline solid and an upper layer of colorless alcoholic solution. The solution was decanted and the solid

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(16) R. P. Linstead, *Annual Reports*, 294 (1936).

(17) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 250.

washed with 15 ml. of ethanol. The combined ethanol solutions were distilled through a short column until ammonia ceased to collect in the distillate. The distillate was acidified and the alcohol removed by distillation. From the residual solution the benzoyl and benzenesulfonyl derivatives of ammonia were prepared by the Schotten–Baumann reaction.[18] The derivatives were identical with authentic samples of benzamide and benzenesulfonamide.

The alcoholic distillation residue was diluted with water and distilled until the b.p. of water was reached. From the distillate the benzoyl and benzenesulfonyl derivatives of aniline were prepared.[18]

An aqueous solution of the colorless crystalline solid product was distilled to remove alcohol, ammonia and aniline. Acidification of the residue with sulfuric acid and extraction with ether gave trimellitic acid (XII), m.p. 211–214° (uncor.).[19] Sublimation of XII at 12 mm. and 200–220° converted it to its anhydride[10]; m.p. 166.8–167.9° from toluene. A mixed m.p. determination with an authentic specimen of XII anhydride, m.p. 166.8–167.9° from toluene, showed no depression. The reported m.p. of XII anhydride is 162.5–163°.[10]

Oxidation of IV.—A solution of 90.6 g. (0.860 equiv.) of potassium permanganate in 1750 ml. of water was added portionwise with shaking over a 4-hour period to 10.7 g. (0.0861 mole) of IV and 1 l. of water. The resulting mixture was allowed to stand at room temperature for 21 hours. After destroying excess permanganate with bisulfite and adding aqueous potassium carbonate until the mixture was definitely basic, it was filtered. The concentrated filtrate (500 ml.) was acidified and steam distilled until 130 ml. of distillate had collected. This distillate, after being made basic, was steam distilled to remove neutral insoluble material. Ether extraction of the acidified distillate gave 1.52 g. (15%) of crude *t*-butylacetic acid; b.p. 170–185°. The acid was characterized as its amide[11] (m.p. 129.6–130.6°), its anilide[11] (m.p. 130.7–131.7°) and its *p*-bromophenacyl ester[12] (m.p. 81.6–82.1°).

ITHACA, N. Y.

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(18) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 47.

(19) Beilstein, "Handbuch der organischen Chemie," IX, 977 (428). The reported m.ps. of trimellitic acid range from 215–221°.

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL CO., INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

The Condensation of 2-Hydroxyethyl Sulfides with Alcohols and Phenols[1]

BY FREDERICK RICHTER, FREDERICK B. AUGUSTINE, EMIL KOFT, JR., AND E. EMMET REID

RECEIVED NOVEMBER 19, 1951

The high rate of reaction of thiodiglycol with aqueous hydrochloric acid suggests that it will readily condense with alcohols in the presence of an acid catalyst to form ethers. This anticipated activation of the hydroxyl group is demonstrated for thiodiglycol and for several other compounds containing the 2-hydroxyethyl sulfide grouping. The reaction appears to be general and when extended to glycols is useful for the preparation of linear and cross-linked polyethers. A mechanism for the condensation reaction is suggested.

In his study of the reactivity of atoms and groups in organic compounds Norris[2] demonstrated that a definite correlation exists between the reactivity of an alcohol with aqueous hydrochloric acid and its tendency to condense with ethyl alcohol to form a mixed ether. Thus, *t*-butyl alcohol, which "reacts with concentrated aqueous hydrochloric acid over 200,000 times as rapidly as *n*-butyl alcohol," could be condensed with ethyl alcohol in the presence of 15% aqueous sulfuric acid to produce *t*-butyl ethyl ether in 95% yield. *n*-Butyl alcohol under the same conditions yielded no mixed ether at all. *s*-Butyl alcohol, which is intermediate in its reactivity with aqueous hydrochloric acid, required a much higher sulfuric acid concentration to effect condensation with ethyl alcohol and since all three possible ethers were formed in this case the yield of mixed ether was much lower than that obtained in the condensation of *t*-butyl alcohol with ethyl alcohol.

On the basis of this correlation it seemed that thiodiglycol, $(HOCH_2CH_2)_2S$, which is known to react readily with hydrochloric acid according to equation 1, should condense with alcohols in the presence of an acid catalyst to form ethers according to equation 2.

$$HOCH_2CH_2SCH_2CH_2OH + 2HCl \longrightarrow ClCH_2CH_2SCH_2CH_2Cl + 2H_2O \quad (1)$$

$$HOCH_2CH_2SCH_2CH_2OH + 2ROH \longrightarrow ROCH_2CH_2SCH_2CH_2OR + 2H_2O \quad (2)$$

The reaction suggested by equation 2 was studied, using all the normal alcohols from methyl to octadecyl alcohol, and condensation was found to proceed smoothly in each case to form the corresponding diether in good yield. Dilute aqueous sulfuric acid, *p*-toluenesulfonic acid and phosphoric acid served as effective catalysts. The physical properties of the diethers of thiodiglycol are listed in Table I. An interesting alternation of melting point with chain length is apparent.

The use of glycols or polyols such as pentaerythritol instead of the simple alcohols in equation 2 leads to the formation of polymeric ethers. The glycols yield linear polymers of which the average chain length (viscosity) may be regulated by introducing a monofunctional alcohol. Pentaerythritol when condensed with thiodiglycol rapidly forms a highly cross-linked polyether.

The condensation of thiodiglycol with glycols was found to proceed somewhat more slowly than in the case of the simple alcohols and required a higher reaction temperature. Under these conditions the formation of dithiane (m.p. 112° with sublimation) in minor amounts was observed in several instances. The mechanism of its formation prob-

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(1) F. P. Richter and E. E. Reid (to Socony-Vacuum Oil Co., Inc.), U. S. Patent 2,582,605, January 15, 1952.

(2) J. F. Norris and G. W. Rigby, THIS JOURNAL, **54**, 2088 (1932).