[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Chemistry of Spiropentane. I. An Improved Synthesis of Spiropentane

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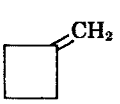
It has been found that nearly pure spiropentane can be obtained from the reaction of pentaerythrityl tetrabromide with zinc by inclusion of ethylenediaminetetraacetate in the reaction mixture. It is concluded that the rearranged product, methylenecyclobutane, which normally predominates in the product, is probably formed by a carbonium ion rearrangement of an intermediate dibromide.

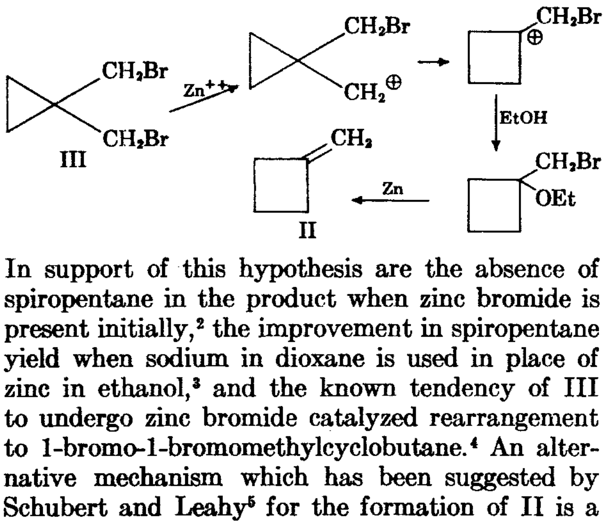
The extensive literature[1] on the synthesis of spiropentane (I) by the reaction of pentaerythrityl tetrabromide with zinc has failed to reveal a satisfactory method for the prevention of extensive simultaneous formation of methylenecyclobutane (II). There is suggestive evidence that II is formed by way of an electrophilically induced rearrangement of the intermediate 1,1-bis(bromomethyl)-cyclopropane (III), perhaps as shown in Chart I.


I



II

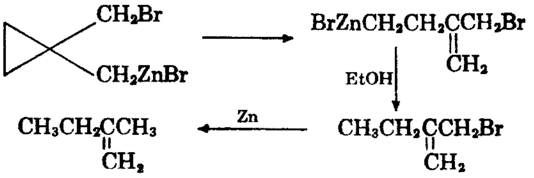
CHART I



In support of this hypothesis are the absence of spiropentane in the product when zinc bromide is present initially,[2] the improvement in spiropentane yield when sodium in dioxane is used in place of zinc in ethanol,[3] and the known tendency of III to undergo zinc bromide catalyzed rearrangement to 1-bromo-1-bromomethylcyclobutane.[4] An alternative mechanism which has been suggested by Schubert and Leahy[5] for the formation of II is a "base-induced" rearrangement of III with zinc metal acting as the base. Strong confirmation of the former hypothesis and a much improved synthesis of spiropentane have now been obtained by the discovery that the formation of methylenecyclobutane as a product of the reaction of pentaerythrityl tetrabromide with zinc in aqueous ethanol may under optimum conditions be reduced to less than one per cent of the hydrocarbon product by inclusion of tetrasodium ethylenediaminetetraacetate in the reaction mixture to remove free zinc ion. Under the conditions specified in the Experimental section, an 81% yield of hydrocarbon, consisting of 94% spiropentane, 4.2% 2-methyl-1-butene, 0.7% 1,1-dimethylcyclopropane, and 0.6% methylenecyclobutane, was obtained.

The persistence of 2-methyl-1-butene as an important impurity in the spiropentane in spite of the sequestering agent suggests that this olefin is not entirely, if at all, a product of an anionotropic rearrangement of III, as had been suggested.[1h] A reasonable alternative explanation for its formation is a rearrangement of an intermediate organozinc compound (Chart II), analogous to the rearrangement which would account for the allylcarbinyl derivatives obtained from Grignard reactions of cyclopropylcarbinyl chloride.[6]

CHART II



EXPERIMENTAL

Pentaerythrityl tetrabromide was prepared from phosphorus tribromide and pentaerythritol (Heyden Chemical, technical grade) according to Murray and Stevenson's modification[1d] of the *Organic Syntheses* preparation.[7] The melting point was approximately 158–160° in three separate runs.

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[1] (a) Gustavson, *J. Prakt. Chem.*, **54**, 97 (1896); (b) N. D. Zelinskii and V. P. Kraevich, *J. Russ. Phys. Chem. Soc.*, **44**, 1870, 1873 (1912); *Chem. Abstr.*, **7**, 1175 (1913); (c) F. Rogowski, *Ber.*, **72B**, 2021 (1939); (d) M. J. Murray and E. H. Stevenson, *J. Am. Chem. Soc.*, **66**, 314, 812 (1944); (e) V. A. Slabey, *J. Am. Chem. Soc.*, **68**, 1335 (1946); (f) V. A. Slabey, *Natl. Advisory Comm. Aeronautics Tech. Note No.* 1023 (1946); *Chem. Abstr.*, **40**, 3729 (1946); (g) Y. M. Slobodin and I. N. Shokhor, *Zhur. Obshchei Khim.*, **21**, 2005 (1951); *Chem. Abstr.*, **46**, 6598 (1952); (h) Y. M. Slobodin and I. N. Shokhor, *Zhur. Obshchei Khim.*, **23**, 42 (1953); *Chem. Abstr.*, **48**, 543 (1954).

[2] J. D. Roberts and C. W. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).

[3] H. O. House, R. C. Lord, and H. S. Rao, *J. Org. Chem.*, **21**, 1487 (1956).

[4] D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 874 (1956).

[5] W. M. Schubert and S. M. Leahy, *J. Am. Chem. Soc.*, **79**, 381 (1957).

[6] (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (b) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

[7] H. B. Schurink, *Org. Syntheses*, Coll. Vol. II, 476 (1943).

Spiropentane (I). In a 5-l. three-necked creased flask fitted with a high-speed stirrer, a solids-addition apparatus, and a water-cooled reflux condenser in series with a spiral condenser (arranged for distillation) and two Dry Ice traps, was placed 852 g. (2.57 moles) of disodium dihydrogen ethylene diaminetetraacetate, 297 g. (7.43 moles) of sodium hydroxide dissolved in 510 ml. of water, 1470 ml. of 95% ethanol, and 20.7 g. (0.138 mole) of sodium iodide. The mixture was heated to reflux, and 214.5 g. (3.28 g.-atoms) of zinc dust was then added. A slow stream of nitrogen was passed through the system to carry volatile products to the cold traps, and 321 g. (0.828 mole) of pentaerythrityl tetrabromide was added slowly to the stirred, refluxing mixture. After the addition was complete, the mixture was stirred at reflux temperature for 1 hr. The condensate in the cold traps was washed with two 150-ml. portions of a cold, saturated solution of sodium chloride in water and then dried over Drierite to give 45.5 g. (81%) of crude spiropentane.

Vapor chromatography (Perkin-Elmer Model 154B; column B, di-2-ethylhexyl sebacate as stationary phase) of a sample of crude spiropentane showed five other components to be present besides spiropentane. Collection of three of these in pure form by vapor chromatography of a sample of crude hydrocarbon, which had been enriched in the low-boiling impurities by fractional distillation, and comparison of their infrared spectra with those of known compounds permitted identification of 2-methyl-1-butene,[8] 1,1-dimethylcyclopropane,[9] and ethanol. Methylenecyclobutane was identified by comparison of its retention time on the column with that of a known sample. The major component was identified as spiropentane by comparison of the infrared spectrum of the crude hydrocarbon with the published spectrum.[9] The crude hydrocarbon from one run was found to be 94% spiropentane, 4.2% 2-methyl-1-butene, 0.7% 1,1-dimethylcyclopropane, 0.6% methylenecyclobutane, 0.2% ethanol, and 0.3% of an unidentified low-boiling material (possibly neopentane).

Spiropentane was obtained free of unsaturated impurities by rough titration of a 20% (by volume) solution of the hydrocarbon in ethylene dibromide with bromine, followed by distillation through a 4.5-ft. spiral-wire column. The product (b.p. 36.5–37.5°) had an infrared spectrum in agreement with the published spectrum[9] of spiropentane.

Acetylacetone was tried as a sequestering agent also and was found to be less satisfactory than ethylenediaminetetraacetate. When the theoretical amounts of acetylacetone and sodium carbonate were used to chelate the zinc ion generated in the reaction, a 60% yield of hydrocarbon containing 76% spiropentane (by base-line infrared analysis) was obtained. Smaller amounts of acetylacetone and sodium carbonate gave much smaller yields of spiropentane.

Methylenecyclobutane (II) in pure form for infrared and vapor chromatographic analysis was prepared by the method of Roberts and Sauer.[2] The reaction of 6 g. of zinc bromide, 18 ml. of ethanol, 700 ml. of water, 225.6 g. of zinc, and 406.8 g. of pentaerythrityl tetrabromide gave methylenecyclobutane in 19% yield. The product, b.p. 40.5°, was purified by distillation through a 4-ft. spinning-band column, and its infrared spectrum agreed with the published spectrum.[2]

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URBANA, ILL.

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[8] American Petroleum Institute, Research Project 44 at National Bureau of Standards, *Infrared Absorption Spectrograms, Vol. I*, No. 196.

[9] F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *J. Chem. Phys.*, **15**, 742 (1947).

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Chlorination of Cellulose with Thionyl Chloride in a Pyridine Medium

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Activated cotton linters were treated with thionyl chloride in anhydrous pyridine to form cellulose derivatives containing up to 1.3 stable chlorine atoms per anhydroglucose unit. Unstable sulfur groupings, presumably in the form of sulfurous acid esters, were also introduced. Chlorocelluloses were hydrolyzed in aqueous sulfuric acid solution without loss of chlorine, but resistance to hydrolysis was encountered as the degree of chlorine substitution was increased. A hydrolyzate was fractionated chromatographically; glucose was isolated from one fraction and a monochloroglucose from another.

The chemical literature contains very little information concerning the halogen derivatives of cellulose. Past investigations revealed that halogens had been introduced into cellulose during the preparation of the tosyl and mesyl esters,[1] but the presence of halogens was generally considered to be of only secondary importance. The tosylation of carbohydrates in general and accompanying chlorination has been extensively reviewed by Tipson.[2] Pacsu and Schwenker[3] have recently prepared 6-mesyl chloro, 6-mesyl bromo, and 6-mesyl iodocelluloses by partial replacement of the 6-mesyl group by the appropriate halogen.

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[1] K. Hess and N. Ljubitsch, *Ann.*, **507**, 62 (1933); F. B. Cramer and C. B. Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939); A. L. Bernoulli and H. Stauffer, *Helv. Chim. Acta*, **23**, 627 (1940); M. L. Wolfrom, J. C. Sowden, and E. A. Metcalfe, *J. Am. Chem. Soc.*, **63**, 1688 (1941); J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942); C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Am. Chem. Soc.*, **70**, 2740 (1948); E. Heuser, M. Heath, and W. H. Shockley, *J. Am. Chem. Soc.*, **72**, 670 (1950); R. Roberts, *J. Am. Chem. Soc.*, **79**, 1175 (1957).

[2] R. S. Tipson, *Advances in Carbohydrate Chemistry*, Academic Press, New York, Volume 8, p. 107.

[3] E. Pacsu and R. F. Schwenker, Jr., *Textile Research J.*, **27**, 173 (1957)