anhydrous magnesium sulfate and distilled. The final identification of the 3,4,5-trimethylisoxazole was accompanied by comparing its boiling point and infrared spectrum with that of an authentic sample prepared by treating nitroethane with aqueous sodium hydroxide. The melting point of our material was found to be 3° which compares favorably with the melting point of 3–4° reported in the literature.[10]

Analysis of fraction A. The fraction was dried over phosphorus pentoxide under vacuum, at room temperature, for about 1 week. When styrene oxide was employed as the olefin oxide, the 1-(2-phenyl-2-hydroxyethyl)pyridinium nitrite (m.p. 179.6–179.9°) crystallized from the reaction mixture directly and was purified by recrystallization from absolute alcohol or dry dimethylformamide. In this case the pyridinium nitrite was analyzed directly for nitrite ion, nitrogen, carbon and hydrogen.

Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38; NO_2^-, 18.45. Found: C, 63.67; H, 5.63; N, 11.17; NO_2^-, 18.68.

When the pyridinium nitrite was obtained as an oil, it was very difficult to isolate a pure crystalline product. In these cases the amount of pyridinium nitrite in the sample was determined by titrating small portions of Fraction A with standard potassium permanganate.[13]

To obtain analytical data, the nitrite (which is very hygroscopic) was converted to the chloride, which is somewhat easier to handle, and purified in this form. The conversion and purification were carried out as follows: The crude pyridinium nitrite was taken up in water and then treated with freshly regenerated Rohm and Haas Amberlite IR-120 sulfonic acid-type ion exchange resin. When the evolution of nitrogen oxides had ceased, the solution was

(13) W. C. Pierce and E. L. Haensch, *Quantitative Analysis*, John Wiley and Sons, Inc., New York, 1945, pp. 196–197.

filtered and the resin which now contained the pyridinium salt was washed repeatedly with water and then once with acetone. The resin was then warmed with 10% hydrochloric acid to remove the pyridinium salt, and the acid solution was evaporated to 40° under vacuum. When about 10 ml. of residue remained, absolute alcohol was added and again the solution was evaporated under vacuum. This process was repeated until a viscous oil remained and all acid had been removed. The oil residue, after being dried under vacuum in the presence of phosphorus pentoxide for 1 week, was taken up in a minimum of absolutely dry dimethylformamide, sealed in a vial, then placed under refrigeration (about −10°) for 1 week. Crystals were filtered under dry nitrogen and then recrystallized from dry dimethylformamide (m.p. 127–127.4°).

Anal. Calcd. for $C_7H_{10}NOCl$: Cl, 22.22. Found: Cl, 22.06.

Analysis of fraction B. Two procedures were used in analyzing the fraction obtained from the treatment of the ether solution of the reaction mixture with anhydrous hydrogen chloride. In those cases where this fraction consisted mainly of pyridine hydrochloride, as for example from nitromethane and nitroethane, it was treated with aqueous sodium bicarbonate and the organic material was extracted into ether. Ether was removed and the residue fractionated.

The second procedure was used on those samples known to contain oxime hydrochlorides as well as pyridine hydrochloride. In this second procedure, a portion of Fraction B, which had been dried for 1 week in a vacuum desiccator over phosphorus pentoxide, was vacuum distilled. The oxime hydrochloride readily distilled as a colorless liquid which solidified in the receiver. The oximes were identified by comparing the melting points and mixed melting points of both the oxime hydrochloride and oxime with those of compounds of known structure.

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Cyclic Dienes. XXV. Synthesis of an Epoxydiene[1,2]

WILLIAM J. BAILEY AND CHARLES E. KNOX[3]

An epoxydiene, 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane, was prepared by the pyrolysis of an epoxydiacetate at 500°. The structure of the diene was proved by analysis, ultraviolet and infrared spectra, hydrolysis to a solid dihydroxydiene and conversion to two solid Diels-Alder adducts. The diene could be polymerized by a free radical mechanism to a benzene-soluble polymer of high molecular weight. Treatment of this linear polymer with a diamine produced a hard epoxy resin.

In this series of articles the preparation of a variety of cyclic dienes has been reported, but with the exception of 9,10-dimethylene-1,7-dioxacyclohendecane-2,6-dione[4] and thiophene 1-dioxide[5] all contained only carbon and hydrogen. It was of interest to extend this series to include a variety of cyclic dienes containing polar groups. Of particular interest was a cyclic diene containing an epoxy

group, since the polymers from such a monomer would combine the characteristics of a diene polymer with those of an epoxy resin. For these reasons the synthesis of the epoxydiene, 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) was undertaken.

Although Δ⁴-cyclohexene-1,2-dimethanol diacetate (I) had been prepared previously by a two-step procedure,[6] a shorter procedure was developed by use of an effectively one-step reductive acetylation with lithium aluminum hydride and acetic anhydride.[4,7] In this procedure diethyl Δ⁴-cyclohexane-1,2-dicarboxylate was reduced in the usual

(1) Previous paper in this series, *J. Am. Chem. Soc.*, **81**, 5598 (1959).

(2) Presented in part before the Division of High Polymers, 128th Meeting, ACS, Miami, Fla., April 1957.

(3) Office of Naval Research Fellow, 1955–57.

(4) W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, **78**, 2287 (1956).

(5) W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954).

(6) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

(7) W. J. Bailey and M. J. Stanek, Abstracts of the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, April 1955, p. 30N.

way with lithium aluminum hydride but, instead of the usual hydrolysis, the reaction mixture was treated directly with acetic anhydride to produce an 82% yield of the diacetate I. The epoxidation of I was accomplished in an 85% yield with perbenzoic acid. Of the methods available for the preparation of perbenzoic acid, the procedure of Kergomard and Bijou[8] was preferred. According to this simple procedure benzoyl chloride was treated with 35% hydrogen peroxide plus sodium hydroxide to give a chloroform solution of perbenzoic acid in 75 to 82% yields.
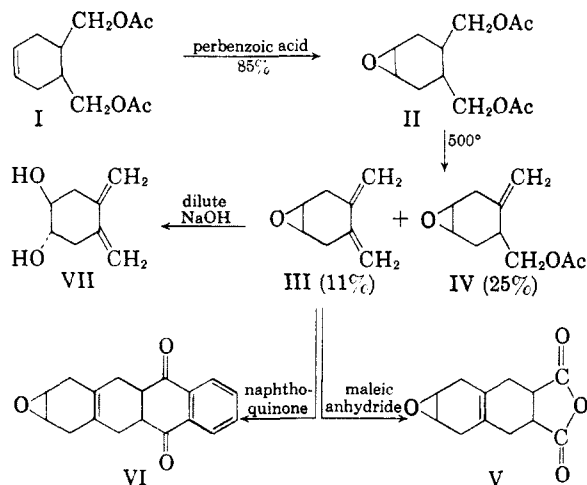
Since the pyrolysis of esters had been used successfully for the synthesis of highly unsaturated compounds, it was hoped that pyrolysis under controlled conditions would not isomerize the epoxide ring. For example, the pyrolysis of esters was used successfully to prepare 1,2-dimethylene-4-cyclohexene,[6] isomeric with o-xylene, and 1,4-dimethylene-2-cyclohexene,[9] isomeric with p-xylene. However, pyrolysis of an epoxide either in the liquid phase or over catalysts usually results in the rearrangement to an aldehyde or ketone. For example, pyrolysis of 2,3-epoxypentane gave methyl n-propyl ketone,[10] while simple distillation of 1,1-diphenyl-1,2-propylene oxide at atmospheric pressure gave α,α-diphenylacetone.[11] Pyrolysis of cyclohexene oxide in the vapor phase at high temperatures or in the presence of catalysts gave a variety of products, including cyclohexanone, water, and cyclohexadiene.[12]

The pyrolysis of the epoxydiacetate II over Pyrex helices at 500° under such conditions that very little carbonization occurred and 64% of two molar equivalents of acetic acid was liberated did

produce an 11% yield of the desired epoxydiene, 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III). At the same time, a 25% yield of the olefin acetate IV and a 7% recovery of starting material were realized. The yield of diene III, based on unrecovered II and IV, was, therefore, only 16%. However, the reason for the low yield apparently was not rearrangement of the epoxide group but rather polymerization of III either during pyrolysis or subsequent treatment. Distillation of III always gave some polymeric residue.

The structure of III was indicated by spectral data as well as conversion to several solid derivatives. The presence of conjugated double bonds exocyclic to a six-membered ring was indicated by an ε maximum of 4500 at 225 mμ in the ultraviolet spectrum of III determined in cyclohexane. Although this maximum occurs at slightly longer wave lengths than that in the spectrum of 1,2-dimethylenecyclohexane (218 mμ),[13] it occurs at a substantially shorter wave length than predicted from Woodward's rules[14] (237 mμ). This difference can be rationalized by the assumption that the attached three-membered ring changes the conformation of the six-membered ring so that the two methylene groups are more nearly planar.[15] The infrared spectrum of the epoxydiene showed a strong band at 893 cm.$^{-1}$, indicating the presence of methylene groups, and strong bands at 873, 1065, and 1232 cm.$^{-1}$, indicating the presence of an epoxide group.

Diels-Alder adducts V and VI were prepared from 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane and maleic anhydride and naphthoquinone, respectively. The structure of the maleic anhydride adduct V was indicated by analysis and by infrared spectrum; bands at 848, 1061, and 1226 cm.$^{-1}$ indicated the presence of the three-membered oxygen ring and bands at 808, 952, 1448, 1788, and 1848 cm.$^{-1}$ indicated the presence of the anhydride ring.

The hydrolysis of the epoxydiene III in very dilute sodium hydroxide gave, as the main product, polymer; however, a small amount of trans-1,2-dimethylenecyclohexane-4,5-diol (VII) was isolated from the product. The structure of the dihydroxydiene was indicated by an ε max. of 3200 at 222 mμ in the ultraviolet spectrum determined in iso-octane. The infrared spectrum of VII, determined on a Nujol mull, showed bands at 1065 and 3400 cm.$^{-1}$, indicating the presence of secondary hydroxyl groups, and a band at 905 cm.$^{-1}$, indicating the presence of methylene groups.

In a standard peroxide-catalyzed emulsion system, 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) gave solid white polymer that was completely soluble in benzene but insoluble in methanol.

(8) A. Kergomard and J. Bijou, Bull. soc. chim. France, 1956, 486.

(9) W. J. Bailey and R. Barclay, J. Am. Chem. Soc., 81, 5393 (1959).

(10) M. Favorskii, M. Chichonkin, and I. Ivanov, Compt. rend., 199, 1229 (1934).

(11) J. Levy and LaGrave, Compt. rend., 180, 1032 (1925).

(12) F. O. Rice and A. L. Stallbaumer, J. Am. Chem. Soc., 64, 1527 (1942).

(13) W. J. Bailey and H. R. Golden, J. Am. Chem. Soc., 76, 5418 (1954).

(14) R. B. Woodward, J. Am. Chem. Soc., 64, 72 (1942).

(15) W. J. Bailey and W. B. Lawson, J. Am. Chem. Soc., 79, 1444 (1957).

Although the polymer did not possess a definite softening point, it became slightly discolored and resinous between 180° and 200°, suggesting that cross linking had taken place. An infrared spectrum of the polymer showed no band at 893 cm.$^{-1}$, indicating almost complete 1,4-addition during polymerization; the strong bands corresponding to the epoxy group, 868, 1061, and 1217 cm.$^{-1}$, were, however, still present. When the epoxydiene III was polymerized in bulk with benzoyl peroxide, a rubbery polymer resulted. When this soluble polymer was cross linked with ethylenediamine, a very hard epoxy resin resulted.

It must be concluded that in the vapor state the 1,2-disubstituted three-membered epoxide ring is more stable than the ester group. It is likely that, in contrast to the noncatalyzed cyclic mechanism proposed for ester pyrolysis, the rearrangement of the epoxide ring is acid or base catalyzed. Thus, the vapor-phase pyrolysis will tend to minimize any catalyzed reaction and allow for the synthesis of a large variety of polyfunctional or strained compounds.

EXPERIMENTAL[16]

Δ^4-Cyclohexene-1,2-dimethanol diacetate (I). In a 12-l., three-necked flask, equipped with stirrer, reflux condenser, and dropping funnel, was placed 100 g. (2.63 moles) of lithium aluminum hydride in 6 l. of anhydrous ether. While the flask was externally cooled by an ice bath, 500 g. (2.22 moles) of diethyl Δ^4-cyclohexene-1,2-dicarboxylate, b.p. 103° (0.6 mm.), n_D^{25} 1.4606 [reported[17] b.p. 129–131° (5 mm.), n_D^{25} 1.4605–1.4610], in 2 l. of anhydrous ether was added dropwise over a 5-hr. period with stirring. After addition of the diester was complete, the reaction mixture was heated under reflux for 5 days. (If the reaction mixture coagulated so that the reaction mixture could not be stirred, heating was carried out without stirring until the complex could be broken—heating for 2 days usually was sufficient.)

The ether was removed by distillation and replaced with 4500 ml. of anhydrous di-n-butyl ether until a reaction temperature of 120° was reached. After the reaction mixture was cooled to 60°, 600 ml. of glacial acetic acid was added dropwise. Stirring was discontinued when the reaction mixture solidified. After the mixture was heated for 24 hr. and then cooled, the solid complex was dispersed and the stirring was continued. Acetic anhydride (2500 ml.) was added slowly to the hot mixture and the heating was continued for several days. After the reaction mixture was cooled and filtered, the solvent and excess reactants were removed in vacuo. The residue was fractionated through a 12-inch Vigreux column to give 411 g. (82%) of Δ^4-cyclohexene-1,2-dimethanol diacetate (I), b.p. 103–105° (0.2 mm.), n_D^{25} 1.4765 (reported b.p. 121–128° (1.0 mm.)).

(16) The authors are indebted to Miss Kathryn Gerdeman and Miss Jane Swan for the microanalyses and to Dr. Ellis Lippincott, Dr. Asa Leifer, Dr. Rudolph Schroeder, and Mr. Charles E. White for the infrared spectra and aid in their interpretation. The infrared spectra of the monomers were determined with a rock salt prism in a Beckman IR-4 spectrophotometer, while the spectrum of the polymer was determined on a Perkin-Elmer Model 12-C spectrophotometer modified for double-pass operation. The ultraviolet spectra were determined on a Beckman DU spectrophotometer. All melting points are corrected.

(17) A. C. Cope and E. C. Herrick, Org. Syntheses, **30**, 29 (1950).

7-Oxabicyclo[4.1.0]heptane-3,4-dimethanol diacetate (II). By a modification of the method of Kergomard and Bijou,[8] 50 g. (0.5 mole) of 35% hydrogen peroxide solution was added to a solution of 40 g. (1.0 mole) of sodium hydroxide in 300 ml. of water and 300 ml. of absolute alcohol at 0 to 4°. After the mixture was agitated for 10 min., 72 g. (0.5 mole) of benzoyl chloride was added while the temperature was maintained below 5°. Agitation was continued with external cooling until the reaction mixture became only slightly cloudy (usually 1–2 hr.), thus ensuring nearly complete reaction of the benzoyl chloride. The reaction mixture was filtered under vacuum into a cold filter flask to remove any benzoyl peroxide. The filtrate containing some sodium peroxide gave perbenzoic acid by the addition of cold 10% sulfuric acid solution to a definite acid end point (Congo red or methyl orange). Successive extractions of the acidified filtrate with 150, 75, and 50 ml. of cold chloroform gave a chloroform solution of perbenzoic acid. (It is usually advantageous to add crushed ice to the aqueous solution to avoid a temperature rise during the extraction.) The concentration of perbenzoic acid in the chloroform solution was determined by the potassium iodide titration method on an aliquot. The yield was 75 to 82% of theoretical.

To a 1-l., three-necked flask, fitted with stirrer, dropping funnel, and reflux condenser, and containing a cold chloroform solution of perbenzoic acid (0.377 mole) was added dropwise a solution of 85.2 g. (0.377 mole) of Δ^4-cyclohexene-1,2-dimethanol diacetate (I) in 200 ml. of chloroform at a rate such that the temperature of the reaction mixture did not rise above 10°. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued for an additional 18 hr. After the reaction mixture was washed with several portions of a 10% sodium carbonate solution (until all the benzoic acid was removed) and then with water, it was dried over anhydrous magnesium sulfate. After the solvent was removed by distillation in a partial vacuum, the residue was distilled through a 12-inch, helix-packed column to yield 77.2 g. (85%) of 7-oxabicyclo[4.1.0]heptane-3,4-dimethanol diacetate (II), b.p. 121–125° (0.3 mm.), n_D^{25} 1.4705.

Anal. Calcd. for $C_{12}H_{18}O_5$: C, 59.47; H, 7.49. Found: C, 59.66; H, 7.38.

3,4-Dimethylene-7-oxabicyclo[4.1.0]heptane (III). At the rate of 0.33 g. per min., 145.6 g. (0.606 mole) of 7-oxabicyclo[4.1.0]heptane-3,4-dimethanol diacetate (II) was added dropwise to a Vycor tube packed with Pyrex helices and externally heated at 500° in an apparatus described previously.[18] Charring was minimized by sweeping the system continuously with a slow stream of oxygen-free nitrogen. The yellow pyrolysate in ether was washed free of acetic acid with water and dried over anhydrous sodium carbonate. (Titration of aliquots of the aqueous washings indicated that 65% of two molar equivalents of acetic acid had been liberated.) The pyrolysate was fractionated through a 12-inch, helix-packed column to yield 7.9 g. (11%) of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III), b.p. 65–68° (10 mm.), n_D^{25} 1.4970; 27.3 g. (25%) of 3-methylene-7-oxabicyclo[4.1.0]heptane-4-methanol acetate (IV), b.p. 81–86° (0.8 mm.); and 10.4 g. (7% recovery) of unchanged 7-oxabicyclo[4.1.0]heptane-3,4-dimethanol diacetate (II). There remained 37.5 g. of a dark polymeric residue in the distilling flask. The yield of III, based on unrecovered II and IV, was 16%.

Anal. Calcd. for $C_8H_{10}O$: C, 78.62; H, 8.25. Found: C, 78.40; H, 8.50.

6,7-Epoxy-$\Delta^{9(10)}$-decalin-2,3-dicarboxylic anhydride (V). A mixture of 0.53 g. (0.0044 mole) of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) and 0.43 g. (0.0044 mole) of maleic anhydride was heated under reflux in 25 ml. of ether for 25 min. The Diels-Alder adduct, which precipi-

(18) W. J. Bailey and J. J. Hewitt, J. Org. Chem., **21**, 543 (1956).

tated from the hot mixture, was removed by filtration to give 0.9 g. (95%) of 6,7-epoxy-$\Delta^{9(10)}$-decalin-2,3-dicarboxylic anhydride (V), m.p. 190.5–191.5°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50. Found: C, 65.60; H, 5.76.

2,3-Epoxy-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (VI). To a solution of 0.52 g. (0.0033 mole) of 1,4-naphthoquinone in 25 ml. of dry toluene was added 0.60 g. (0.005 mole) of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) and the solution was heated under reflux for 2 days. The solvent was removed by distillation to give a yellow solid. Two recrystallizations from 95% ethanol gave 0.87 g. (70%) of VI as yellow needles, m.p. 165.5–170°, which became slightly discolored on exposure to air.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.00; H, 5.75.

trans-1,2-Dimethylenecyclohexane-4,5-diol (VII). Crude 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) (33 g.) was treated with a solution of 24 g. of sodium hydroxide in 800 ml. of water for 15 hr. at 40–50°. After the mixture was cooled to room temperature, 15 g. of acetic acid was added and the aqueous solution was extracted continuously with ether for 24 hr. After the ether solution was dried over anhydrous magnesium sulfate and the solvent was removed by distillation, some low boiling liquids were removed from the residue under partial vacuum. The remaining residue was a polymeric resin, which was insoluble in ether, benzene, methanol, and acetone.

Extraction of the residue in hot acetone, followed by filtration of the mixture, gave a white resin, softening point 165–167°. Evaporation of the acetone filtrate gave a white solid, which was dissolved in methanol. Addition of the solution to a large excess of benzene and concentration of this solution to one-half its original volume (essentially removing the methanol) gave 20 mg. of trans-1,2-dimethylenecyclohexane-4,5-diol (VII) as a white powder, m.p. 214–215°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.53; H, 8.63. Found: C, 68.39; H, 8.59.

Emulsion polymerization of 3,4-dimethylene-7-oxabicyclo-[4.1.0]heptane (III). In a 2-oz. screw-cap bottle were placed 2.06 g. of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III), 0.10 g. of sodium stearate, 0.02 g. of lauryl mercaptan, 0.007 g. of potassium persulfate and 3.80 g. of water. The bottle was rotated in a water bath maintained at 63° for 26 hr., at which time the emulsion had broken. After acidification of the mixture with dilute hydrochloric acid and removal of the solid by filtration, the solid was dissolved in 60 ml. of benzene and a trace of 1,3,5-trinitrobenzene was added as an inhibitor. The benzene solution was poured slowly into 250 ml. of cold methanol with stirring and the white flocculent polymer precipitated. Filtration, followed by drying, gave 0.77 g. (37% conversion) of poly-3,4-dimethylene-7-oxabicyclo[4.1.0]heptane. The polymer did not exhibit a definite softening point, although discoloration and signs of cross linking of the polymer occurred at 180°. The polymer showed signs of considerable discoloration at 230°. This decomposition probably resulted from cross linking of the epoxide groups, as the heated polymer displayed hard, brittle properties which were not present in the original polymer.

Determination of the viscosity of the polymer at 25° in a chloroform solution in an Ostwald viscometer gave an intrinsic viscosity of 0.326.

Combined peroxide-catalyzed and epoxide polymerization of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III). When 0.57 g. of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) was polymerized in bulk with a catalytic quantity of benzoyl peroxide at steam-bath temperature for 13 hr., the resulting polymer was very viscous and displayed some elasticity at room temperature. After a small amount of ethylenediamine was added to this polymer, the mixture was heated for 2 hr. on a steam bath. There resulted a very hard amber-colored resin which adhered to the walls of the glass container.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Cyclopentenes and Cyclopentanes. II. Synthesis from Isophorone[1]

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Synthesis of 1,1,3,3-tetramethylcyclopentane, 1,1,2,4-tetramethylcyclopentane and 1,1,3,4-tetramethylcyclopentane from isophorone has been accomplished. Several intermediate compounds, tetramethylcyclopentenes, trimethylcyclohexenes polymethyladipic acids, cyclohexanones cyclopentanones and cyclohexanediols were prepared and characterized. The methods described are adaptable to large scale use.

The tetramethylcyclopentanes comprise a little known group of hydrocarbons. Of the seven possible structural isomers only one (1,1,2,3-tetra-

methylcyclopentane[3]) has been reported as synthesized, and no effort was made to determine the hydrocarbon's geometrical configuration. 1-trans-2-cis-3-trans-4-Tetramethylcyclopentane and 1,1-3-trans-4-tetramethylcyclopentane have been identified in a representative petroleum.[4] If all of the geometrical isomers are counted, sixteen different tetramethylcyclopentanes are possible.

Previously,[5,6] isophorone (3,5,5-trimethyl-2-cy-

(3) J. F. Eykman, *Chem. Weekblad,* **3,** 692 (1906).

(4) F. D. Rossini and A. J. Streiff, Paper presented to Section V of the Fifth World Petroleum Congress, N. Y. (1959).