**oxybutane Hydrochloride-N-methyl-$C^{14}$.**—One-half of the crude radioactive α-*dl*-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol hydrochloride was converted to its propionyl ester. A reaction mixture containing 272 mg. (0.85 mmole.) of the radioactive carbinol hydrochloride, 1 ml. of propionic anhydride and 0.5 ml. of triethylamine was heated under nitrogen at 82° for 8 hours. To the cooled reaction mixture was added 30 ml. of ether, 10 ml. of water and 700 mg. of sodium bicarbonate. The ether layer was removed and treated with charcoal and anhydrous magnesium sulfate in a centrifuge cone. The solids were removed by centrifugation and the supernatant solution evaporated to dryness. The residue was stored in a vacuum overnight to ensure volatilization of any residual triethylamine. The crude base was then dissolved in 25 ml. of ether and the solution saturated with dry hydrogen chloride. The solution was evaporated to dryness and the residue recrystallized three times from ethyl acetate–ether solution. The yield was 137 mg., m.p. 168–170°, and the specific activity 1.9 mc./mg. The radiochemical yield from formaldehyde-$C^{14}$ was 40%.

INDIANAPOLIS, INDIANA

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

# Cyclic Dienes. XIX. 2,3-Dimethylenebicyclo[2.2.2]octane[1]

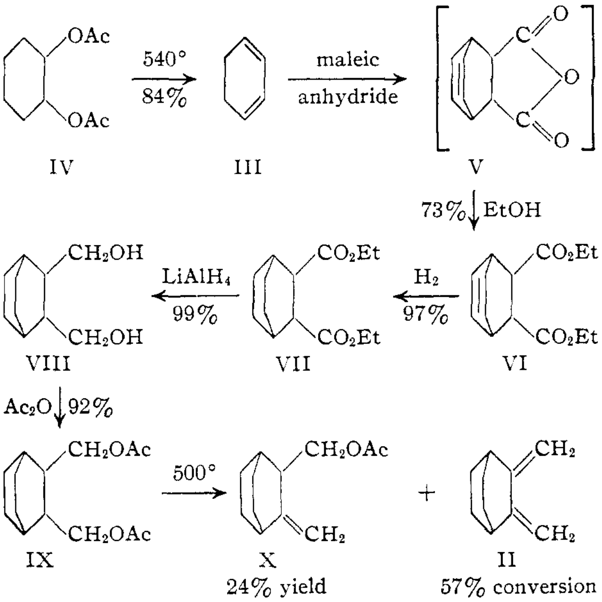
BY WILLIAM J. BAILEY AND WILLIAM B. LAWSON[2]

RECEIVED SEPTEMBER 5, 1956

A convenient synthesis of 1,3-cyclohexadiene in an 84% yield was developed by the pyrolysis of a mixture of *cis*- and *trans*-1,2-diacetoxycyclohexane. The cyclohexadiene was then used as a starting material for a five-step synthesis of 2,3-dimethylenebicyclo[2.2.2]octane. The final step in the preparation of the latter diene was a pyrolysis of a diacetate, which produced the desired diene in a 78% yield. The structure of this diene was proved by ultraviolet and infrared absorption spectra and by conversion to two solid derivatives through Diels–Alder reactions.

In a research program designed to determine the correlation between the structure and the physical properties of all-*cis* polymers related in structure to natural rubber, a series of cyclic dienes have been prepared. In order to determine the effect of a bulky, yet compact, side group containing a bicyclic structure, 2,3-dimethylenebicyclo[2.2.1]heptane (I) was prepared.[3] However, since the diene I contained a very rigid bicyclic system that would not stabilize an endocyclic double bond in the same manner as a cyclohexane ring,[4] the polymer derived from the diene I consisted of at least 30% 1,2-addition. Since this polymer differed substantially in structure from the all-*cis* all-1,4 poly-1,2-dimethylenecyclohexane, it was difficult to determine the exact effect of the bicyclo ring system on the properties of an all-*cis* polymer. For this reason the synthesis of the more flexible and more symmetrical 2,3-dimethylenebicyclo[2.2.2]octane (II) was undertaken. It was hoped that the fused six-membered rings would permit some stabilization of an endocyclic double bond.

The most convenient starting material for the synthesis of II appeared to be 1,3-cyclohexadiene (III). No wholly satisfactory method of synthesis has been reported for this very simple and common cyclic diene. Hine and co-workers[5] recently reviewed many of the previously reported syntheses of III and concluded that either a highly impure product was produced or the method was extremely tedious. They did conclude, however, that the most convenient preparation involved the treatment of cyclohexene dibromide with sodium hydroxide in ethylene glycol solution to give a 60% yield of 1,3-cyclohexadiene (III) (80% purity) contaminated with benzene and cyclohexene. Since the pyrolysis of esters had been so successful for the synthesis of other cyclic dienes,[6,7] the synthesis of III by this procedure was investigated. Rice and Stallbaumer[8] previously had prepared III in a 50% yield by the pyrolysis of 1,2-diacetoxycyclohexane (IV) in a quartz tube at 750° and 6 mm. pressure. Even at this relatively high temperature, their product contained less than 5% benzene. Stork, van Tamelen, Friedman and Burgstahler[9] also pyrolyzed the distearate of 1,2-cyclohexanediol in the liquid phase to produce III, which was not isolated but was converted directly to its maleic anhydride adduct in a 42% over-all yield.



When a mixture of *cis*- and *trans*-1,2-diacetoxy-

---

[1] Previous paper in this series, THIS JOURNAL, **78**, 2806 (1956).

[2] Office of Naval Research Fellow, 1951–1955.

[3] W. J. Bailey and W. B. Lawson, THIS JOURNAL, **77**, 1606 (1955).

[4] W. J. Bailey and H. R. Golden, *ibid.*, **76**, 5418 (1954).

[5] J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, *ibid.*, **77**, 594 (1955).

[6] W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

[7] W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

[8] F. O. Rice and A. C. Stallbaumer, *ibid.*, **64**, 1527 (1942).

[9] G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgstahler, *ibid.*, **75**, 384 (1953).

cyclohexane (IV) was pyrolyzed at 540° in a Vycor tube packed with glass helices, an 84% yield of 1,3-cyclohexadiene (III) was obtained. Since the physical properties of the diene agreed very well with those reported by Henri and Pickett,[10] it appeared that the III produced in this manner was quite pure. In fact the ultraviolet absorption curve was somewhat smoother in the aromatic region than that previously reported.[10] The fact that there was very little, if any, of the enol acetate, 1-acetoxycyclohexene, produced in the pyrolysis agrees with the previously observed influence of an acetoxy group on the direction of elimination during pyrolysis.[11]

Since Hurd[12] indicated that the pyrolysis of cyclohexanone at 700° over clay produced some 1,3-cyclohexadiene (III), the dehydration of cyclohexanone over alumina was investigated. At 600° cyclohexanone was converted to a complex mixture of materials containing a 6% yield of III. The major by-products were cyclohexene and phenol with some benzene and *o*-phenylphenol as minor constituents. When the lower boiling hydrocarbon fraction (shown by absorption at 285 mμ to contain approximately 20% of III) was treated with maleic anhydride, a 5.5% yield (based on cyclohexanone) of the adduct V was obtained. Although this procedure was not satisfactory for the production of III, the availability of cyclohexanone may make this procedure acceptable for the preparation of V.

Since it was found previously that reduction of a liquid ester proceeded much more easily than that of a solid anhydride,[3] a method was worked out for the preparation of the ester, *endo*-2,3-dicarbethoxy-5-bicyclo[2.2.2]octene (VI), from 1,3-cyclohexadiene (III) without the isolation of the intermediate adduct V. Thus III was treated with an excess of maleic anhydride and the crude reaction mixture was esterified with ethanol by removal of the water formed in the reaction by an azeotropic distillation. With this procedure a 73% over-all yield of VI was obtained for the two steps. Catalytic hydrogenation of VI produced a 97% yield of the saturated diester VII, which on reduction with lithium aluminum hydride produced nearly a quantitative yield of the crude glycol VIII. Treatment of the glycol VIII with an excess of acetic anhydride produced a 92% yield of *endo*-2,3-di-(acetoxymethyl)-bicyclo[2.2.2]octane (IX).

Pyrolysis of the diacetate IX through a Vycor tube packed with glass helices at 500°, as described previously,[3,6] produced a 57% conversion to 2,3-dimethylenebicyclo[2.2.2]octane (II). In addition there was obtained a 24% yield of the intermediate olefin acetate, 2-methylene-3-acetoxymethylbicyclo[2.2.2]octane (X). The yield of II, based on unrecovered X, was 78%. Some impure starting diacetate IX was recovered, but the high refractive index of the material indicated that some aromatization had occurred. The over-all yield of the diene II for the eight-step procedure from catechol was 33%.

The ultraviolet absorption spectrum of II, which possessed an ε maximum of 8280 at 247 mμ, indicated the presence of two coplanar conjugated exocyclic double bonds. Woodward's rules[13] would have predicted a maximum absorption at 237 mμ, but almost all the cyclic dienes in this present series violate these rules. The closely related 2,3-dimethylenebicyclo[2.2.1]heptane (I) possessed an ε maximum at 248 mμ.[3]

1,2-Dimethylenecyclohexane,[6] which has its methylene groups somewhat askew, had a maximum absorption at 218 mμ.[14]

The infrared absorption spectrum of 2,3-dimethylenebicyclo[2.2.2]octane (II) was consistent with the assigned structure of II and was very similar to the spectrum of the closely related 2,3-dimethylenebicyclo[2.2.1]heptane (I).

The diene II was characterized further by conversion to two solid Diels–Alder adducts. Treatment of II with maleic anhydride produced a 50% yield of 5,8-endoethylene-$\Delta^{9(10)}$-octalin-2,3-dicarboxylic anhydride (XI), while treatment with 1,4-naphthoquinone produced a 59% yield of 1,4-endoethylene-6,11-diketo-$\Delta^{4a(12a),6a(10a),7,9}$-dodecahydronaphthacene (XII).

The polymerization and dimerization of this interesting diene will be reported separately.

## Experimental[15]

**1,2-Diacetoxycyclohexane (IV).**—Catalytic hydrogenation of catechol in the presence of W-7 Raney nickel catalyst by a modification of the procedure of Palfray[16] produced a 90% yield of a mixture of *cis*- and *trans*-1,2-cyclohexanediols, b.p. 120–130° (14 mm.) [reported[17] for the *cis* isomer, b.p. 118° (14 mm.); *trans* isomer, b.p. 120° (14 mm.)]. After 1998 g. (16.4 moles) of this mixture of glycols had been heated under reflux for 3 days with 4900 ml. (49.2 moles) of acetic anhydride, the reaction mixture was fractionated through a 15-inch Vigreux column to yield 3045 g. (89%) of a mixture of *cis*- and *trans*-1,2-diacetoxycyclohexanes (IV), b.p. 97–104° (2.0–3.5 mm.), $n^{25}\text{D}$ 1.4477 [reported[17] for the *cis* isomer, b.p. 120° (14 mm.), $n^{20.5}$ He 1.4497; *trans* isomer, b.p. 123° (15 mm.), $n^{20}$ He 1.4465].

**1,3-Cyclohexadiene (III).**—By use of the general procedure described previously,[18] 200 g. (1 mole) of a mixture of *cis*- and *trans*-1,2-diacetoxycyclohexanes (IV) was dropped at the rate of 2 g. per minute through a vertical Vycor tube packed with $^1/_8$-inch Pyrex helices and externally heated at 540°. A slow stream of oxygen-free nitrogen was continuously passed through the tube to help prevent any charring. The pyrolysate was condensed in a 6-inch coil condenser and collected in a side-inlet flask cooled in a Dry Ice–chloroform–carbon tetrachloride bath. Distillation of the pyrolysate through a 6-inch, helix-packed column gave the crude diene, b.p. 78–110°. This crude material was extracted with a saturated sodium bicarbonate solution and dried over anhydrous potassium carbonate. Fractionation of this dried

---

[10] V. Henri and L. W. Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

[11] W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 648 (1956).

[12] C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, N. Y., 1929, p. 258.

[13] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

[14] Although 1,2-dimethylenecyclopentane was erroneously reported [W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 2287 (1956)] to absorb below 220 mμ, it actually has a maximum absorption at 243 mμ since its methylene groups are nearly planar.

[15] The authors are grateful to Dr. Mary Aldridge and Kathryn Gerdeman for the microanalyses and to Dr. Robert A. Spurr and Kathryn Gerdeman for the infrared absorption spectrum. The infrared spectrum was determined on the pure liquid with a Perkin–Elmer model 12-C infrared spectrometer modified for double-pass operation and equipped with a sodium chloride prism. The ultraviolet absorption spectra were determined with a Beckman model DU spectrophotometer by use of cyclohexane as the solvent. All melting points are corrected.

[16] L. Palfray, *Bull. soc. chim. France*, **7**, 407 (1940).

[17] K. von Auwers and F. Dersch, *J. prakt. Chem.*, **124**, 227 (1930).

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

material through the same column produced 67 g. (84%) of 1,3-cyclohexadiene (III), b.p. 80°, $n^{25}$D 1.4723, log $\epsilon_{max}$ 3.64 at 257 mμ (reported[10] b.p. 80.1°, $n^{20}$D 1.4739, log $\epsilon_{max}$ 3.90 at 256 mμ).

**Pyrolysis of Cyclohexanone.**—At the rate of 6 g. per minute 100 g. of cyclohexanone was dropped into a preheater consisting of a vertical Vycor tube packed with 1/8-inch Pyrex helices and externally heated at 400°. The vapors from the preheater were passed directly into a second Vycor tube packed with Harshaw alumina catalyst (Al-4) and heated at 600–610°. The vapors were then condensed in a spiral condenser and collected in a 300-ml., side-inlet flask cooled in a Dry Ice–chloroform–carbon tetrachloride bath. A slow stream of oxygen-free nitrogen was continuously introduced at the top of the apparatus.

The pyrolysate (93 g.) was mixed with 100 ml. of ether and the aqueous layer (11 g.) was removed. After the ether solution was dried over Drierite, it was fractionated through a 6-inch, helix-packed column to produce 24 g. of a hydrocarbon fraction, b.p. 75–81°, $n^{25}$D 1.4420–1.4522. Analysis of the ultraviolet absorption spectrum at 280 and 285 mμ indicated that this hydrocarbon fraction contained 20–21% 1,3-cyclohexadiene. Treatment of 20 g. of this fraction (presumably containing 4 g. or 0.05 mole of cyclohexadiene) with 5.1 g. (0.052 mole) of maleic anhydride in 100 ml. of benzene produced 8.7 g. of *endo*-5-bicyclo[2.2.2]octene-2,3-dicarboxylic anhydride (V), m.p. 146–147° (reported[19] m.p. 147°).

Further analysis of the ultraviolet spectrum indicated that only a trace of benzene was present in the hydrocarbon fraction. The major component was cyclohexene, identified as its dibromide, b.p. 90–91° (3 mm.), $n^{25}$D 1.5509 [reported[20] b.p. 124–125° (36 mm.), $n^{16}$D 1.5540].

The distillation residue contained, in addition to some recovered cyclohexanone, a substantial amount of phenol, identified as its tribromo derivative, m.p. 95° (reported[21] m.p. 95–96°). A small amount of *o*-phenylphenol, m.p. 56–57° (reported[22] m.p. 56°), also was isolated. A mixed melting point determination with an authentic sample showed no depression.

***endo*-2,3-Dicarbethoxy-5-bicyclo[2.2.2]octene (VI).**—To a solution of 515 g. (5.25 moles) of maleic anhydride in 2.5 liters of benzene contained in a 5-liter, three-necked flask was added over a period of 1 hour with vigorous stirring and occasional cooling 403 g. (5.03 moles) of 1,3-cyclohexadiene (III). After the reaction mixture had been stirred for an additional hour, 875 ml. (15.8 moles) of absolute ethanol and 25 g. of *p*-toluenesulfonic acid monohydrate were added. After the stirrer had been removed and a Dean–Stark trap had been inserted between the condenser and the flask, the mixture was heated under reflux for 8 days until no more aqueous phase separated. Most of the solvent (about 1.5 liters) was then removed by distillation. The residue was extracted with two 500-ml. portions of a 5% sodium carbonate solution and dried over anhydrous magnesium sulfate. After the remaining solvent had been removed by flash distillation, the residue was fractionated through a 15-inch Vigreux column to yield 923 g. (73%) of *endo*-2,3-dicarbethoxy-5-bicyclo[2.2.2]octene (VI), b.p. 142–145° (4 mm.), $n^{25}$D 1.4808.

*Anal.* Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.90; H, 7.78.

**2,3-Dicarbethoxybicyclo[2.2.2]octane (VII).**—At room temperature, 808 g. (3.21 moles) of *endo*-2,3-dicarbethoxy-5-bicyclo[2.2.2]octene (VI) was hydrogenated at 1000 lb./sq. inch pressure in the presence of 80 g. of Raney nickel catalyst. After the catalyst was removed by filtration, the filtrate was fractionated through a 15-inch Vigreux column to yield 788 g. (97%) of 2,3-dicarbethoxybicyclo[2.2.2]-octane (VII), b.p. 134–137° (2.5 mm.), $n^{25}$D 1.4728.

*Anal.* Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.18; H, 8.55.

**2,3-Dimethylolbicyclo[2.2.2]octane (VIII).**—To a suspension of 46 g. (1.2 moles) of lithium aluminum hydride in 1.5 liters of absolute ether contained in a 5-liter, three-necked flask cooled in an ice-bath was added as rapidly as possible, with vigorous stirring, 252 g. (1 mole) of 2,3-dicarbethoxybicyclo[2.2.2]octane (VII). After the reaction mixture had been heated under reflux for 2 days, 100 ml. of water was added to decompose the excess hydride and then 1 liter of 10% hydrochloric acid was added very slowly over a period of 3 hours in order to dissolve the complex. Then after the ether layer was dried over anhydrous magnesium sulfate, the ether was removed by evaporation to yield 171 g. (99%) of crude 2,3-dimethylolbicyclo[2.2.2]octane (VIII). This crude material usually was not purified but was used as such for the subsequent acetylation. However, in one experiment, a small quantity of the crude glycol VIII was recrystallized three times from cyclohexane to give analytically pure 2,3-dimethylolbicyclo[2.2.2]octane (VIII), m.p. 87–88°.

*Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.56; H, 10.66. Found: C, 70.41; H, 10.44.

**2,3-Di-(acetoxymethyl)-bicyclo[2.2.2]octane (IX).**—A mixture of 263 g. (1.54 moles) of crude 2,3-dimethylolbicyclo[2.2.2]octane (VIII), 865 ml. (9.23 moles) of acetic anhydride and 25 ml. of acetic acid was heated under reflux for 2 days. The excess acetic anhydride and acetic acid were removed by distillation and the residue was fractionated through a 15-inch Vigreux column to yield 356 g. (92%) of 2,3-di-(acetoxymethyl)-bicyclo[2.2.2]octane (IX), b.p. 146–150° (3 mm.), $n^{25}$D 1.4802.

*Anal.* Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.88; H, 8.57.

**2,3-Dimethylenebicyclo[2.2.2]octane (II) and 2-Methylene-3-acetoxymethylbicyclo[2.2.2]octane (X).**—At a rate of 1.4 g. per minute, 100 g. (0.745 mole) of 2,3-di-(acetoxymethyl)-bicyclo[2.2.2]octane (IX) was dropped through a vertical Vycor tube packed with 1/8-inch Pyrex helices and heated externally at 500° as previously described.[18] In order to minimize charring the pyrolysis apparatus was continuously flushed with a slow stream of oxygen-free nitrogen. The pyrolysate was collected in a 200-ml., side-inlet flask which contained 0.1 g. of *p*-*t*-butylcatechol in 25 ml. of ether and which was cooled in a Dry Ice–methyl cellosolve bath. After the ether solution of the pyrolysate had been extracted with seven 50-ml. portions of water and finally with 50 ml. of saturated sodium bicarbonate solution, it was dried over anhydrous potassium carbonate. (Titration of an aliquot of the aqueous extracts indicated that 78% of two molar equivalents of acetic acid had been liberated.) Fractionation of the ether solution of the pyrolysate through a 6-inch, helix-packed column gave 30 g. (57%) of 2,3-dimethylenebicyclo[2.2.2]octane (II), b.p. 39–41° (4.5 mm.), $n^{25}$D 1.5118; 18 g. (24%) of 2-methylene-3-acetoxymethylbicyclo[2.2.2]octane (X), b.p. 66–79° (1 mm.); and 9.0 g. of a high refracting diacetate fraction, b.p. 135–140° (1.5 mm.), $n^{25}$D 1.4994. (Presumably the diacetate was partially aromatized.) The yield of the diene II, based on unrecovered material, was 78%.

*Anal.* Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.76; H, 10.39.

The infrared absorption spectrum of 2,3-dimethylenebicyclo[2.2.2]octane (II) possessed strong bands at 847, 865–898, 1400, 1440, 1610, 2790, 2880 and 3000 cm.$^{-1}$ and medium or weak bands at 718, 795, 810, 1030, 1072, 1135, 1190, 1245, 1270, 1330, 1760 and 2300 cm.$^{-1}$.

The crude 2-methylene-3-acetoxymethylbicyclo[2.2.2]-octane (X) was refractionated through a 6-inch, helix-packed column to produce an analytically pure sample, b.p. 79° (1.5 mm.), $n^{25}$D 1.4868.

*Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.57; H, 8.67. Found: C, 74.59; H, 8.70.

**5,8-Endoethylene-$\Delta^{9(10)}$-octalin-2,3-dicarboxylic Anhydride (XI).**—A solution of 2.6 g. (0.019 mole) of 2,3-dimethylenebicyclo[2.2.2]octane (II), 2.0 g. (0.020 mole) of maleic anhydride and 0.1 g. of *p*-*t*-butylcatechol in 20 ml. of benzene was allowed to stand at 0° for 2 hours. The benzene was removed by evaporation and the solid residue was recrystallized from cyclohexane to give 2.3 g. (50%) of slightly impure XI, m.p. 132–135°. An additional recrystallization from cyclohexane produced white needles of analytically pure 5,8-endoethylene-$\Delta^{9(10)}$-octalin-2,3-dicarboxylic anhydride (XI), m.p. 132.2–133.2°.

*Anal.* Calcd. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.95. Found: C, 72.12; H, 6.87.

---

(19) O. Diels and K. Alder, *Ann.*, **478**, 138 (1930).

(20) S. Coffey, *Rec. trav. chim.*, **42**, 398 (1923).

(21) Lassar-Cohn and F. Schultz, *Ber.*, **38**, 3297 (1905).

(22) P. Jacobson and F. Hönigsberger, *ibid.*, **36**, 4080 (1903).

**1,4-Endoethylene-6,11-diketo-$\Delta^{4a(12a),6a(10a),7,9}$-dodecahydronaphthacene (XII).**—A mixture of 2.0 g. (0.015 mole) of 2,3-dimethylenebicyclo[2.2.2]octane (II), 2.4 g. (0.015 mole) of 1,4-naphthoquinone, 0.1 g. of *p-t*-butylcatechol and 30 ml. of benzene was allowed to stand for 3 days at room temperature. The benzene was removed by evaporation and the residue was crystallized from cyclohexane to give 2.6 g. (59%) of a slightly impure adduct XII, m.p. 148–151°. Recrystallization from cyclohexane produced white flakes of analytically pure 1,4-endoethylene-6,11-diketo - $\Delta^{4a(12a),6a(10a),7,9}$ - dodecahydronaphthacene (XII), m.p. 150–151°.

*Anal.* Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.29; H, 6.86.

COLLEGE PARK, MARYLAND

---

[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

# Autoxidation of 2,3-Dimethylbutadiene-1,3

BY FRED K. KAWAHARA

RECEIVED SEPTEMBER 6, 1956

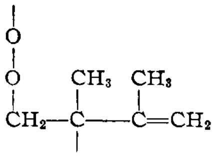
Autoxidation of 2,3-dimethylbutadiene-1,3 yields polymeric peroxides. The 1,2-addition of oxygen to 2,3-dimethylbutadiene-1,3 has been confirmed by the isolation of formaldehyde and isopropenyl methyl ketone. However, isolation of two additional volatile products, dimethyl glyoxal and α-isopropenylacrolein, points to a more complex reaction. Presence of dialkyl peroxidic linkages of at least two types is demonstrated by reductive cleavage. In addition, the presence of ether groups is shown in the polymeric peroxides, as well as that of carbonyls, hydroperoxides, acidic, ester and hydroxyl groups.

## Introduction

An important problem in the storage of cracked gasoline is the development of undesirable polymeric material called gum. Gum formation is retarded through use of antioxidants and metal deactivators, and by proper choice of refining procedures. Valuable ways of further reducing gum might be discerned from the mechanism of formation and the structure of the polymeric gum.

Unfortunately, little is known about either. However, the catalytic action of oxygen on conjugated diolefins in gasoline is known to be an important factor in deterioration.[1] Structural studies of the peroxides formed by autoxidation of acyclic conjugated dienes have been limited because of the complexity of the products. Addition of oxygen to the double bonds has been assumed to occur at either the 1,2- or 1,4-position.[2] Only in the case of the cyclic diolefins has the 1,4-addition of oxygen to the diene system been structurally established; Hoch and Depke[3] have isolated 1,3-diols after the catalytic reduction of the polymeric peroxide of cyclopentadiene.

For reasons of convenience and availability, 2,3-dimethylbutadiene-1,3 has received particular attention. Bodendorf[2] hydrogenated the polymeric peroxide and identified formaldehyde among the cleavage products. Kern[4] thermally decomposed the same material and obtained, in addition to formaldehyde, isopropenyl methyl ketone. Isolation of these products led Kern to propose as the structure of the monomer of the polymeric peroxide of dimethylbutadiene



$$-O-O-CH_2-\underset{|}{\overset{CH_3}{\overset{|}{C}}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

A polymer of this monomer is formed by interpolymerization of oxygen with the diene at the 1,2-position.

An investigation of the products of the autoxidation of 2,3-dimethylbutadiene-1,3 has been carried out. One objective of the work was to determine whether 1,2-interpolymerization with oxygen was the sole mechanism or whether polymer was also formed by reaction at the 1,4-position, by carbon-to-carbon polymerization or by addition of RO· radicals to double bonds. A second objective was to isolate additional volatile products of the autoxidation and thus cast light upon the mechanism of polymer formation. The polymer was subjected to reductive procedures of varying severity to determine whether the peroxide linkages were of uniform strength, and thus of one type, or whether peroxide bonds of varying ease of reduction, and hence of different structure, were present. An additional aim was to determine the effect of different products of autoxidation upon the formation of others.

## Experimental

Freshly distilled 2,3-dimethylbutadiene-1,3 (2.5 g.) was added to 100 ml. of *n*-heptane in a 450-ml. bottle. The *n*-heptane had been purified by treatment with acid and percolation through silica gel. The bottle was sealed and placed in dark storage at 110°F. for 28 days. After 14 days it was cooled to ice temperature and the air was changed before sealing again. Eighty such bottles were prepared for the study of three fractions: volatile products, heptane-soluble material and heptane-insoluble material.

**Isolation and Identification of Volatile Products.**—The volatile distillate obtained by distillation of total autoxidized product at 40° (20 mm.) with a nitrogen bubbler gave a positive peroxide test with glacial acetic acid and potassium iodide. Absence of peroxides in the aqueous extract of the volatile distillate was shown by a negative test with ferrous thiocyanate.[5]

Four volatile products were isolated and identified: formaldehyde, isopropenyl methyl ketone, α-isopropenylacrolein and dimethyl glyoxal. These compounds were identified by the melting points of the appropriate derivatives.[6]

**Formaldehyde.**—At the end of the storage period, four samples (originally totalling 10.0 g. of dimethylbutadiene) were combined and extracted with 100 ml. of water. The aqueous extract was then treated with a saturated solution of

---

[1] R. H. Rosenwald, "The Chemistry of Petroleum Hydrocarbons," Coll. Vol. II, Reinhold Publ. Corp., New York, N. Y. 1955, p. 345.

[2] W. Kern and J. Stallman, *Makromol. Chem.*, **7**, 199 (1951); K. Bodendorf, *Arch. Pharm.*, **271**, 1 (1933).

[3] H. Hoch and F. Depke, *Ber.*, **84**, 349 (1951).

[4] W. Kern and A. R. Heinz, *Makrom. Chem.*, **16**, 81 (1955).

[5] R. F. Robey and H. K. Wise, *Anal. Chem.*, **17**, 425 (1945).

[6] Melting points were not corrected.