

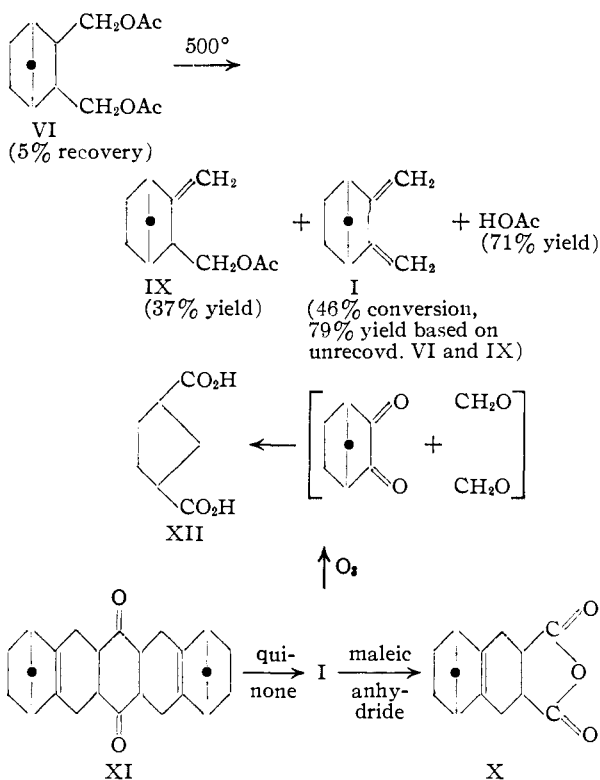
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. XIV. 2,3-Dimethylenebicyclo[2.2.1]heptane<sup>1</sup>BY WILLIAM J. BAILEY AND WILLIAM B. LAWSON<sup>2</sup>

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The cyclic diene, 2,3-dimethylenebicyclo[2.2.1]heptane, was synthesized in five steps from the Diels-Alder adduct of cyclopentadiene and maleic anhydride in an over-all yield of 44%. The crucial step was the pyrolysis of a diacetate in a 79% yield. The structure of the diene was proved by analysis, infrared and ultraviolet absorption, ozonization to a known derivative and conversion to solid Diels-Alder adducts.

A series of cyclic 2,3-disubstituted butadienes<sup>3</sup> were prepared because they produce not only all-*cis*-diene polymers but also multicyclic Diels-Alder adducts. For example, 1,2-dimethylenecyclohexane<sup>3</sup> with a peroxide catalyst produces a high molecular weight all-*cis*-diene polymer<sup>4</sup> that is very similar in structure to natural rubber. In contrast to



natural rubber, the synthetic all-*cis* poly-1,2-dimethylenecyclohexane was a highly crystalline solid, melting at 165°. To determine the reason for this striking difference, a series of related cyclic dienes with various substituents were synthesized. One cyclic diene of interest was 2,3-dimethylenebicyclo[2.2.1]heptane (I). The polymer prepared from I should allow determination of the effect of the very rigid bicyclo ring system and the asymmetry due to the random orientation of the endomethylene group on either side of the symmetrical ring on the properties of an all-*cis* diene polymer. The bicyclic diene I also will form unusual multicyclic Diels-Alder adducts.

The Diels-Alder adduct of cyclopentadiene and maleic anhydride, *endo*-5-bicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride (II), was converted to its diethyl ester III by azeotropic distillation in 75% yield. III was catalytically reduced to the *endo*-2,3-diacetate IV in 92% yield. When IV was further reduced with lithium aluminum hydride, crude *endo*-2,3-dimethylolbicyclo[2.2.1]heptane (V), which could be purified by recrystallization, was obtained. (Alder and Roth<sup>5</sup> very recently prepared this same glycol by a slightly different route.) The crude glycol V usually was not purified but was directly acetylated with acetic anhydride to form *endo*-2,3-di-(acetoxymethyl)-bicyclo[2.2.1]heptane (VI) in an 81% over-all yield for the two steps.

An alternative route from the adduct II to the saturated diacetate VI was investigated but proved to be inferior to the above sequence both in yield and ease of handling. The adduct II was reduced with lithium aluminum hydride directly to the unsaturated glycol, *endo*-2,3-dimethylol-5-bicyclo[2.2.1]heptene (VII), in a 43% yield. Because of the limited solubility of the anhydride II, the addition to the hydride solution was carried out by means of an exhaustive ether extractor. Even so, the low solubility of II and its intermediate reduction products restricted the yield of the glycol VII. A considerable amount of base-soluble material was isolated from the crude reaction product. VII was esterified with acetic anhydride to the solid *endo*-2,3-di-(acetoxymethyl)-5-bicyclo[2.2.1]heptene (VIII) in only a 62% yield. Apparently the unsaturation promotes some side reaction such as internal ether formation. Reduction of the double bond in VIII gave a mixture of products from which a 68% yield of the desired saturated diacetate VI could be obtained. The difficulty of working with the solids and occurrence of mixtures make this sequence of reactions less desirable than the first synthesis.

The diacetate VI was pyrolyzed at 500° under such conditions that only 71% of two molar equivalents of acetic acid was liberated. Under these mild conditions no carbonization that might cause rearrangement occurred.<sup>3,6</sup> From the pyrolysis was obtained a 46% conversion to 2,3-dimethylenebicyclo[2.2.1]heptane (I). In addition to the desired diene I, there was obtained a 37% yield of the olefin acetate, 2-methylene-3-acetoxymethylbicyclo[2.2.1]heptane (IX) and a 5% recovery of the starting material VI. The yield of diene I, based on unrecovered VI and IX, was 79%.

(1) Previous paper in this series, *THIS JOURNAL*, **77**, 1163 (1955).  
 (2) Office of Naval Research Fellow, 1951-1954.  
 (3) W. J. Bailey, *et al.*, *THIS JOURNAL*, **75**, 4780 (1953); **76**, 2251, 5421 (1954), **77**, 992 (1955).  
 (4) W. J. Bailey and H. R. Golden, *ibid.*, **76**, 5418 (1954).

(5) K. Alder and W. Roth, *Ber.*, **87**, 161 (1954).  
 (6) W. J. Bailey and J. Rosenberg, *THIS JOURNAL*, **77**, 73 (1955).

The structure of the diene I was proved by analysis, ultraviolet and infrared absorption, ozonization to a known derivative and conversion to solid Diels-Alder adducts. The presence of conjugated double bonds was indicated by the fact that the diene I possessed an  $\epsilon$  maximum of 10,800 at 248  $m\mu$  in its ultraviolet absorption spectrum. [1,2-Dimethylenecyclohexane has an  $\epsilon$  maximum at 220  $m\mu$ .<sup>3</sup>]

It is rather surprising that both of these dienes violate Woodward's rules<sup>7</sup>; 1,2-dimethylenecyclohexane has an  $\epsilon$  maximum at a lower wave length than would be predicted while 2,3-dimethylenebicyclo[2.2.1]heptane (I) has a maximum at a higher wave length. However, one can explain the difference in the position of the maxima by the fact that in the diene I the double bonds are held rigidly in one plane while in 1,2-dimethylenecyclohexane the puckering in the ring may force the double bonds out of the same plane. The infrared spectrum of I was similar to that of 1,2-dimethylenecyclohexane in several respects, showing strong absorption peaks at 720, 890, 1115, 1240, 1390, 1415, 1438, 1622 and 2810  $cm^{-1}$ . The 2,3-dimethylenebicyclo[2.2.1]heptane (I) reacted with maleic anhydride to produce a 62% yield of the adduct, 5,8-endomethylene- $\Delta^9(10)$ -octalin-2,3-dicarboxylic anhydride (X). The bicyclic diene I did not react as rapidly as previous simple cyclic dienes, indicating that the double bond in the adduct X is somewhat strained. Treatment of the diene I with a half-molar quantity of benzoquinone produced a mixture of stereoisomeric Diels-Alder adducts from which a pure isomer XI could be obtained by fractional crystallization. Ozonization of the diene I produced formaldehyde, identified as its dimethone derivative. Hydrolysis and oxidation of the ozonide produced *cis*-cyclopentane-1,3-dicarboxylic acid (XII), which was purified through the corresponding anhydride. The polymerization of the diene I will be reported later.

**Acknowledgment.**—The authors wish to thank Richard A. Mikulec and Richard Skonieczny, who prepared several of the starting materials for this research.

### Experimental<sup>8</sup>

**endo-2,3-Dicarbethoxybicyclo[2.2.1]heptane (IV).**—*endo*-2,3-Dicarbethoxy-5-bicyclo[2.2.1]heptene (III), b.p. 122–127° (2.5 mm.),  $n_D^{25}$  1.4742 [reported<sup>9</sup> b.p. 138–140° (8 mm.),  $n_D^{25}$  1.4761], was prepared in a 75% yield by esterification of *endo*-5-bicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride (II). When 700 g. (2.91 moles) of *endo*-2,3-dicarbethoxy-5-bicyclo[2.2.1]heptene (III) was hydrogenated at 1800 pounds per square inch pressure and room temperature in the presence of 70 g. of Raney nickel catalyst, a quantitative amount of hydrogen was absorbed. The hydrogenation product plus a small amount of ethanol were filtered and fractionated through a 15-inch Vigreux column to yield 645 g. (92%) of *endo*-2,3-dicarbethoxybicyclo[2.2.1]heptane (IV), b.p. 122–126° (2.3 mm.),  $n_D^{25}$  1.4676.

*Anal.* Calcd. for  $C_{13}H_{20}O_4$ : C, 64.98; H, 8.39. Found: C, 65.02; H, 8.34.

**endo-2,3-Di-(acetoxymethyl)-bicyclo[2.2.1]heptane (VI).**  
A. From *endo*-2,3-Dimethylolbicyclo[2.2.1]heptane (V).—

(7) R. B. Woodward, *THIS JOURNAL*, **65**, 1123 (1941).

(8) All melting points are corrected. The authors are grateful to Mary Aldrich and Kathryn Gerdeman for the analyses and the infrared spectrum.

(9) M. S. Morgan, R. S. Tipson, A. Lowry and W. E. Baldwin, *THIS JOURNAL*, **66**, 404 (1944).

In a 5-liter, three-necked flask, equipped with a reflux condenser, a Hershberg stirrer and a dropping funnel, were placed 2 liters of absolute ether and 57 g. (1.5 moles) of lithium aluminum hydride. While the flask was cooled in ice, 300 g. (1.25 moles) of *endo*-2,3-dicarbethoxybicyclo[2.2.1]heptane (IV) was added as rapidly as possible. After the reaction mixture had been heated under reflux for 2 days, the complex was carefully decomposed with about 1 liter of 10% hydrochloric acid so that the pH of the solution was never below 2. The ether layer was separated and the aqueous layer was extracted with two 500-ml. portions of ether. The combined ether layers were dried over magnesium sulfate and the ether was removed by distillation. This crude glycol V was mixed with 1000 ml. of acetic anhydride and 50 ml. of acetic acid. After the mixture was heated under reflux for 3 days, it was fractionated through a 15-inch Vigreux column to yield 242 g. (81%) of *endo*-2,3-di-(acetoxymethyl)-bicyclo[2.2.1]heptane (VI), b.p. 145° (4 mm.),  $n_D^{25}$  1.4728.

*Anal.* Calcd. for  $C_{13}H_{20}O_4$ : C, 64.98; H, 8.39. Found: C, 64.68; H, 8.28.

A small sample of the crude glycol was recrystallized from cyclohexane to give white micron-crystalline *endo*-2,3-dimethylolbicyclo[2.2.1]heptane (V), m.p. 60–61° (reported<sup>5</sup> m.p. 62°).

*Anal.* Calcd. for  $C_9H_{16}O_2$ : C, 69.19; H, 10.33. Found: C, 69.50; H, 10.16.

Treatment of the glycol V with 3,5-dinitrobenzoyl chloride produced the *endo*-2,3-di-(3,5-dinitrobenzoxymethyl)-bicyclo[2.2.1]heptane, m.p. 178–181° (reported<sup>5</sup> m.p. 180°).

*Anal.* Calcd. for  $C_{23}H_{20}N_4O_{12}$ : C, 50.75; H, 3.70. Found: C, 50.72; H, 3.76.

B. From *endo*-2,3-Di-(acetoxymethyl)-5-bicyclo[2.2.1]heptene (VIII).—The *endo*-2,3-di-(acetoxymethyl)-5-bicyclo[2.2.1]heptene (VIII) (140 g., 0.59 mole) was hydrogenated with Raney nickel at 1500 pounds per square inch pressure and 50° in a cyclohexane solution. The solution was filtered and distilled through a 15-inch Vigreux column to yield 96 g. (68%) of *endo*-2,3-di-(acetoxymethyl)-bicyclo[2.2.1]heptane (VI), b.p. 142–143° (4.5 mm.),  $n_D^{25}$  1.4734, identical with the product obtained above. Several unidentified lower boiling substances also were obtained from this distillation.

The *endo*-2,3-Di-(acetoxymethyl)-5-bicyclo[2.2.1]heptene (VIII).—The *endo*-2,3-dimethylol-5-bicyclo[2.2.1]heptene (VII), b.p. 144–162° (6.5 mm.), m.p. 82.8–83.4° (reported<sup>6</sup> m.p. 82° was prepared in a 43% yield by reduction of *endo*-5-bicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride (II) with lithium aluminum hydride. A mixture of 154 g. (1.0 mole) of *endo*-2,3-dimethylol-5-bicyclo[2.2.1]heptene (VII), 470 ml. of acetic anhydride and 100 ml. of acetic acid was heated under reflux for 24 hours. The mixture was distilled through a 12-inch, helix-packed column to yield 147 g. (62%) of *endo*-2,3-di-(acetoxymethyl)-5-bicyclo[2.2.1]heptene (VIII), b.p. 159–160° (11 mm.). The distillate solidified immediately and a small portion was recrystallized from dilute ethanol to obtain pure VIII, m.p. 65.8–67.2°.

*Anal.* Calcd. for  $C_{13}H_{18}O_4$ : C, 65.53; H, 7.61; sapn. equiv., 119. Found: C, 65.64; H, 7.48; sapn. equiv., 116.

**2,3-Dimethylenebicyclo[2.2.1]heptane (I).**—At a rate of 1.6 g. per minute 150 g. (0.625 mole) of *endo*-2,3-di-(acetoxymethyl)-bicyclo[2.2.1]heptane (VI) was dropped through a Vycor pyrolysis tube packed with 1/8-inch, Pyrex helices, as previously described.<sup>3</sup> The tube was externally heated at 500–505° and was continuously flushed out with a slow stream of oxygen-free nitrogen. The pyrolysate was condensed in a 6-inch spiral condenser and collected in a flask cooled with Dry Ice. Approximately 50 ml. of ether containing 0.1 g. of *p*-*t*-butylcatechol was added to the pyrolysate, and the resulting solution was extracted with seven 50-ml. portions of water. (Titration of an aliquot of the aqueous extracts indicated that 71% of two molar equivalents of acetic acid had been liberated.) The ether solution was extracted further with a saturated sodium bicarbonate solution and a saturated sodium chloride solution. After the ether solution was dried over anhydrous sodium sulfate, it was fractionally distilled through a 6-inch, helix-packed column to give 34.3 g. (46%) of 2,3-dimethylenebi-

cyclo[2.2.1]heptane (I), b.p. 52.5–54° (25 mm.),  $n_D^{25}$  1.5007; 42 g. (37%) of 2-methylene-3-acetoxymethylbicyclo[2.2.1]heptane (IX), b.p. 75–83° (4.0 mm.),  $n_D^{25}$  1.4767; and 7.2 g. (5% recovery) of the starting diacetate VI. There was a small fraction of high refracting material that distilled at a temperature intermediate between that of the olefin acetate IX and the diacetate VI. The total recovery of material was 88% and the yield of the diene I was 79%, based on unrecovered VI and IX.

*Anal.* Calcd. for  $C_9H_{12}$ : C, 89.93; H, 10.07. Found: C, 90.06; H, 10.10.

**5,8-Endomethylene- $\Delta^9(10)$ -octalin-2,3-dicarboxylic Anhydride (X).**—A solution of 0.816 g. (0.00834 mole) of maleic anhydride and 1.00 g. (0.00834 mole) of 2,3-dimethylenebicyclo[2.2.1]heptane (I) in 7 ml. of anhydrous benzene was allowed to stand overnight at 0°. The benzene was removed by evaporation and the residue was recrystallized three times from cyclohexane to yield 1.05 g. (62%) of 5,8-endomethylene- $\Delta^9(10)$ -octalin-2,3-dicarboxylic anhydride (X), m.p. 118.2–120.2°.

*Anal.* Calcd. for  $C_{13}H_{14}O_3$ : C, 71.54; H, 6.47. Found: C, 71.37; H, 6.70.

**1,4,8,11-Di-endomethylene-6,13-diketo- $\Delta^{4a(14a),7a(11a)}$ -octadecahydropentacene (XI).**—A solution of 2.0 g. (0.017 mole) of 2,3-dimethylenebicyclo[2.2.1]heptane (I) and 0.90 g. (0.0083 mole) of 1,4-benzoquinone in 20 ml. of ethanol was heated under reflux for 12 hours. After the solution was cooled to 0°, 0.89 g. of light yellowish crystals, m.p. 182–202° dec., was removed by filtration. This solid was undoubtedly a mixture of isomeric forms of XI. Several recrystallizations of this solid from methyl ethyl ketone produced white needles of 1,4,8,11-diendomethylene-6,13-diketo- $\Delta^{4a(14a),7a(11a)}$ -octadecahydropentacene (XI), m.p. 219–227° dec. (evacuated capillary), whose m.p. range did not change on repeated

recrystallization. A small amount of a higher melting form also was obtained.

*Anal.* Calcd. for  $C_{24}H_{28}O_2$ : C, 82.72; H, 8.10. Found: C, 82.55; H, 7.86.

**Ozonolysis of 2,3-Dimethylenebicyclo[2.2.1]heptane (I).** A solution of 2.0 g. (0.017 mole) of 2,3-dimethylenebicyclo[2.2.1]heptane (I) in 75 ml. of ethyl acetate was ozonized at 0°. Formaldehyde that was evolved during the ozonization was collected in a water trap and identified by odor and conversion to its dimethone derivative, m.p. 190° (reported<sup>10</sup> m.p. 191–191.5°).

The ethyl acetate was removed under reduced pressure and the residual ozonide was decomposed by heating for 2 hours on a steam-bath with 25 ml. of 30% hydrogen peroxide and 40 ml. of glacial acetic acid. The excess peroxide was decomposed and the reaction mixture was evaporated to dryness under reduced pressure. Since the *cis*-cyclopentane-1,3-dicarboxylic acid (XII) could not be easily purified from the reaction product, the residue was heated under reflux for 12 hours with acetic anhydride. Removal of the acetic anhydride under reduced pressure, followed by recrystallization from a mixture of ethyl acetate and cyclohexanone, gave 0.40 g. (17%) of *cis*-cyclopentane-1,3-dicarboxylic anhydride, m.p. 163–164° (reported<sup>11</sup> 160–161.5°). A small portion of the anhydride was heated with water and the water removed by evaporation to give the *cis*-cyclopentane-1,3-dicarboxylic acid (XII), m.p. 120.5–123° (reported<sup>11</sup> m.p. 120–121.5°). Heating a small sample of the anhydride for 12 hours with aniline followed by recrystallization from methanol produced the corresponding dianilide, m.p. 223–225° (reported<sup>11</sup> m.p. 222–224°).

(10) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(11) K. T. Pospischil, *Ber.*, **31**, 1950 (1898).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

## Radioactive Anthracene- $C^{14}$ and Acridine- $C^{14}$ from the Neutron Irradiation of Acridine<sup>1</sup>

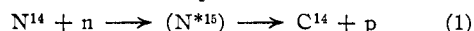
BY ALFRED P. WOLF AND R. CHRISTIAN ANDERSON

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Anthracene- $C^{14}$  has been produced by neutron irradiation of the nitrogen analog, acridine. The recoiling carbon-14 entities produced by the  $N^{14}(n,p)C^{14}$  reaction also were found in acridine molecules, where the nitrogen had not undergone neutron capture during the course of irradiation. The ratio of activity as acridine to the activity as anthracene was about 19/1. Of the total activity produced in the samples, 3.5% was found as acridine and 0.2% was found as anthracene.

Prior to the advent of nuclear reactors, production of carbon-14 was severely limited by the lack of adequate sources of neutrons. The high neutron fluxes available from nuclear reactors allow the production of carbon 14 on a much larger scale.

Equation 1 represents the nuclear transformation taking place in carbon-14 production.



The ejection of a proton from the compound nucleus,  $N^{*15}$ , imparts a recoil energy<sup>2</sup> of 45,000 e.v.<sup>3</sup> to the carbon-14 as it is formed.

The chemical consequences of such an act afford a novel approach to the reactivity of organic molecules. It seems certain that the tremendous energy (with respect to bond energies) imparted to

carbon-14 would result in bond rupture in every event. The recoiling fragment can lose energy by various means such as elastic and inelastic collisions and dissipation as vibrational energy in the crystal lattice. The fate of the carbon-14 when it has lost most of its recoil energy then becomes of chemical interest. The mechanism of entry into a molecular species whether by physical or chemical means depends on the precise nature of the carbon-14 fragment just prior to reaction. The question may only be resolved by knowing its energy and structure at this point.

The present work is the first part of a systematic study of the nature of the recoil processes occurring in organic compounds *via* the  $N^{14}(n,p)C^{14}$  reaction. A consequence of exploring the recoil processes may be the development of useful techniques for labeling organic compounds without involving organic synthesis.

Acridine was irradiated in the Brookhaven nuclear reactor. This compound was chosen for study because of its high chemical and thermal stability, and its resistance to radiation decomposition, which

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission. Presented before the Organic Division at the 123rd National Meeting, Los Angeles, Calif., March, 1953. This paper is the first of a series on the chemical consequences of a recoiling  $C^{14}$  fragment in organic compounds.

(2) H. Huber and A. Stebler, *Phys. Rev.*, **II 73**, 85 (1948).

(3) 1 e.v. =  $1.602 \times 10^{-12}$  erg. A value of  $6.02 \times 10^{23}$  e.v./mole is equivalent to 23.1 kcal./mole. Normal bond energies are in the 3–5 e.v. region.