mmoles, 76%) of white needles, m.p. 251–252°, infrared spectrum C=O (5.96 μ in $CHCl_3$).

Anal. Calcd. for $C_{20}H_{22}N_2O_2$: C, 74.50; H, 6.88; N, 8.69; mol. wt., 322.4. Found: C, 74.66; H, 6.76; N, 8.54; mol. wt., 330 (Rast).

Isoquinoline Dimer (VII).—1,3-Diacetamido-2,4-diphenylcyclobutane (0.95 g., 2.95 mmoles) was dissolved in 50 ml. of redistilled tetralin and 7.4 g. (52.8 mmoles) of P_2O_5 was added. The mixture was heated slowly to 160° with stirring. After heating at 160° for ten minutes, the mixture was cooled and a second 7.4-g. portion of P_2O_5 was added. The flask was reheated and kept at 160° for 30 minutes, then allowed to cool to room temperature. The tetralin was decanted and the residue was cautiously decomposed with water (*ca.* 250 ml.). The remaining tetralin was removed by steam distillation, and the aqueous phase was filtered and neutralized. The white precipitate was filtered and dried (0.640 g., 2.24 mmoles, 77%). Recrystallization from benzene yielded crystals melting between 190 and 205°, depending on the rate of heating; λ_{max} 221 mμ (log ε 4.59) and 248 mμ (log ε 4.13) in 95% ethanol.

Anal. Calcd. for $C_{20}H_{18}N_2$; C, 83.88; H, 6.34; N, 9.78; mol. wt., 286.4. Found: C, 83.84; H, 6.07; N, 9.88; mol. wt., 280 (Rast).

When the dimer VII was heated in a sublimator at *ca.* 185° and 60 mm., 1-methylisoquinoline distilled as a clear oil, m.p. 10–12°. The ultraviolet absorption spectrum in 95% ethanol had maxima at the following wave lengths (mμ, log ε in parentheses): 217 (4.79), 263 (360), 271 (3.66), 283 (3.55), 309 (3.43), 318 (3.40), 322 (3.55). The infrared spectrum of this material and that of a sample prepared from 1-methyl-3,4-dihydroisoquinoline were superimposable in detail.

The 1-methylisoquinoline from the thermal cleavage of 24.5 mg. (0.086 mmole) of the dimer, was converted into the picrate (51.8 mg., 0.139 mmole, 81%), m.p. 225–226° (lit.[20] 225–226°).

1-Methyl-3,4-dihydroisoquinoline (IX).—N-(2-Phenylethyl)-acetamide[21] (X) was converted into 1-methyl-3,4-dihydroisoquinoline in 79% yield by the method of Späth[20]; λ_{max} 210 mμ (log ε 4.27), 250 mμ (log ε 3.81) in 95% ethanol.

The picrate prepared in and recrystallized from ethanol melted at 191–194° (lit.[20] 188–190°).

1-Methylisoquinoline (VIII).—A mixture of the dihydroisoquinoline IX (0.51 g., 3.51 mmoles) and 0.122 g. of palladium black in redistilled *p*-xylene (3.5 ml.) was refluxed for three hours. The properties of the product at this point indicated only partial dehydrogenation. Fresh catalyst (0.12 g.) and xylene (4 ml.) were added to the organic material and the mixture was refluxed for another 18 hours. The catalyst was filtered, the xylene removed and the product distilled to yield 0.45 g. of a clear oil (3.12 mmole, 89%), m.p. 10–12° (lit.[22] 10.1–10.4°). The ultraviolet absorption spectrum in 95% ethanol of a sample purified *via* the picrate, had the following maxima (mμ, log ε in parentheses): 217 (4.80), 262 (3.61), 270 (3.66), 307 (3.45), 283 (3.56), 316 (3.41), 320 (3.57). The picrate melted at 224–227° (lit.[20] 225–226°).

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[20] E. Späth, F. Berger and W. Kuntara, *Ber.*, **63**, 137 (1930).

[21] A. Michaelis and E. Linow, *ibid.*, **26**, 2167 (1893).

[22] E. Jantzen, Dechema-Monographie, No. 48, Berlin, 1932, p. 135.

NEW HAVEN, CONNECTICUT

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

1,2-Dimethylenecyclopentane and 1,2-Dimethylene-3-methylcyclopentane[1]

BY A. T. BLOMQUIST, JOSEPH WOLINSKY, Y. C. MEINWALD AND D. T. LONGONE

RECEIVED MAY 29, 1956

1,2-Dimethylenecyclopentane and its 3-methyl homolog have been obtained by the thermal decomposition of 1,2-bis-(dimethylaminomethyl)-cyclopentane dimethohydroxide and the like 3-methyl derivative, respectively. These dienes were also obtained, but less satisfactorily, by pyrolysis of the requisite 1,2-bis-(acetoxymethyl)-cyclopentanes. The syntheses of the precursors for the dienes involved standard classical transformations starting with the appropriate 1,2-cyclopentanedicarboxylic acids. The structures of the two dienes were confirmed by all of their observed chemical and physical properties, including their infrared and ultraviolet spectra. Both dienes formed Diels–Alder adducts with great ease and those obtained with maleic anhydride could be degraded to 2,3-hydrindene and 1-methyl-2,3-hydrindene. Persulfate initiated polymerization of the dienes at 50° for 24 hr. gave rubber-like soluble polymers comprising essentially only 1,4-addition polymerization units as indicated by their infrared spectra.

The observation that persulfate-initiated polymerization of 1,2-dimethylenecyclobutane affords a soluble, tough, elastic, rubber-like polymer[2] encouraged us to examine the properties of certain conjugated exocyclic dienes of larger carbocycles. In particular, it seemed pertinent to make a careful study of 1,2-dimethylenecyclopentane (I) and its 3-methyl homolog II. Since structural studies of 1,2-dimethylenecyclobutane polymer indicated that it comprised *ca.* 80% *cis*-1,4-units, it might be expected that under comparable polymerization conditions the dimethylenecyclopentanes should give polymers having a higher content of *cis*-1,4-units as there is considerably less "steric strain" attendant in a five-membered ring than in a four-membered ring.

In this study it also seemed desirable to examine the methods of acetate pyrolysis and Hofmann elimination with the object of determining which is better for obtaining dienes of highest purity. Inasmuch as it had been observed earlier that pyrolysis of 1,2-bis-(acetoxymethyl)-cyclobutane proceeded abnormally, possibly *via* 1,4-transannular elimination with resulting ring cleavage to form 2-vinyl-1,3-butadiene,[2,3] it was of interest to observe whether pyrolysis of the bis-acetoxymethyl cyclopentanes might also result in the formation of undesirable accessory products and hence be inferior to the Hofmann method as a route to pure exocyclic conjugated dienes.

1,2-Dimethylenecyclopentane (I).—The synthesis of I by pyrolysis of 1,2-bis-(acetoxymethyl)-cyclopentane has been described by Bailey and Sorenson,[4] but some of the properties reported for it, notably the b.p. and ultraviolet absorption spectrum, are at variance with what might be expected

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[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by the B. F. Goodrich Co.

[2] A. T. Blomquist and J. A. Verdol, THIS JOURNAL, **77**, 1806 (1955).

[3] W. J. Bailey, C. H. Curov and L. Nicholas, *ibid.*, **77**, 2787 (1955).

[4] W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 5421 (1954).

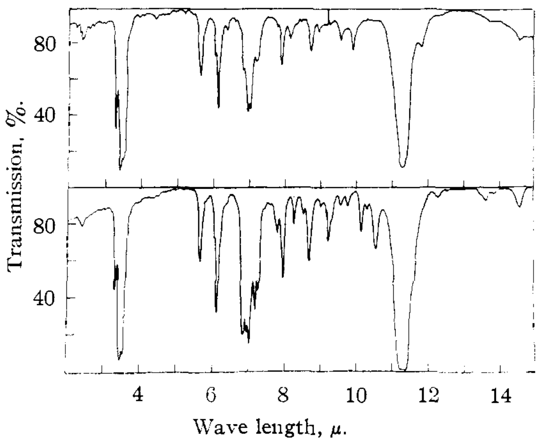
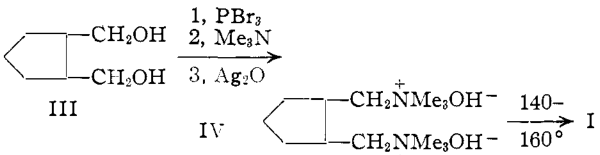


Fig. 1.—Infrared spectra: upper curve, 1,2-dimethylenecyclopentane; lower curve, 3-methyl-1,2-dimethylenecyclopentane.

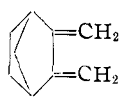
for a homolog of 1,2-dimethylenecyclobutane. Our best synthesis of I was achieved as indicated in the diagram below.



The glycol *trans*-1,2-bis-(hydroxymethyl)-cyclopentane (III) used for these studies showed n^{25}_{D} 1.4773, in good agreement with the value n^{25}_{D} 1.4771 reported by Bailey.[4] Our III was obtained by lithium aluminum hydride reduction of diethyl *trans*-1,2-cyclopentanedicarboxylate which in turn had been synthesized from pimelic acid according to the method of Fuson.[5,6] The over-all yield of III from pimelic acid was 48%. Treatment of III with phosphorus tribromide gave 1,2-bis-(bromomethyl)-cyclopentane in 85% yield. Conversion of the dibromide to the bis-quaternary ammonium hydroxide IV was effected in essentially quantitative yield by treatment with methanolic trimethylamine followed by reaction with freshly prepared moist silver oxide.

Thermal decomposition of IV at 140–160° gave I (62%) showing n^{25}_{D} 1.4738. Upon distillation, under nitrogen, the diene I showed b.p. 45° (100 mm.), n^{25}_{D} 1.4732, d^{25}_{4} 0.8210 (Bailey reported[4] b.p. 80–82° (130 mm.), n^{25}_{D} 1.4694, d^{25}_{4} 0.8553). The observed molar refractivity is 0.63 greater than the calcd. value and may be attributed to the exaltation due to conjugation. Conjugated unsaturation of I involving two exocyclic double bonds was supported by the absorption spectra data. In the infrared (Fig. 1) compound I showed strong absorption at 3.26, 3.45, 3.50 and 11.35 μ, medium absorption at 5.66, 6.15, 6.98 and 7.03 μ and weak absorption at 6.08 and 7.95 μ. The ultraviolet spectrum of I in isoöctane showed a maximum at λ 248 mμ, log ε 4.02.

It is of interest here that for I Bailey reported no maxima in the ultraviolet region above 220 mμ.[4] However, the ultraviolet spectrum of a closely related model compound, 2,3-dimethylenebicyclo[2.2.1]heptane (V), shows $\lambda_{\max}$ 249 mμ, log ε 4.06 and $\lambda_{\max}$ 240 mμ, log ε 3.99 as reported by Alder,[7] while Bailey reported for this $\lambda_{\max}$ 248, ε 10800.[8] Thus the ultraviolet absorption reported for V is in good agreement with that found for our sample of I.



V

Pyrolysis of III-diacetate (n^{25}_{D} 1.4468) at 525–535° also afforded the diene I but in lower yield and contaminated with other hydrocarbons. Distillation of the pyrolysate always gave a substantial amount of forerun, b.p. 32–45° (100 mm.), n^{25}_{D} 1.4553, as well as the desired hydrocarbon I having b.p. 46–49° (100 mm.), n^{25}_{D} 1.4700–1.4713. This sample of I showed a broad plateau of absorption in the ultraviolet with $\lambda_{\max}$ *ca.* 246–248 mμ, log ε 3.89. The infrared spectrum of this I was essentially identical with that of I obtained *via* the Hofmann elimination. The only significant differences were in the intensities of certain of the absorption peaks. The diene I obtained by acetate pyrolysis thus appeared to be less pure than I formed in the thermal decomposition of the bis-quaternary ammonium hydroxide IV.

All chemical characterization of the diene I was done using diene obtained *via* the Hofmann method. It was impossible to distil I at atmospheric pressure because of its great tendency to undergo thermal dimerization and/or polymerization. In all such attempted distillations rapid dimerization ensued at 97° to give a product having n^{25}_{D} 1.5160.[9]

Attempted purification of crude I, n^{25}_{D} 1.4738, by chromatographing on silica gel was also unsuccessful. The colorless crude I became deeply colored (orange-brown) and evolved heat when it came in contact with the adsorbent. Elution of the column with methanol gave a small amount of a yellow liquid, n^{25}_{D} 1.4940, which appeared to be mainly I-dimer. The main portion remained on the column as a sticky polymer. The greater ease of dimerization and polymerization of I as compared with 1,2-dimethylenecyclobutane under comparable conditions may be attributed to the fact that in the latter diene "strain" is increased in the four-membered ring with the introduction of an endocyclic double bond required by dimerization or 1,4-polymerization.

The diene I absorbed 100.7 mole per cent. of the amount of hydrogen required for two ethylenic

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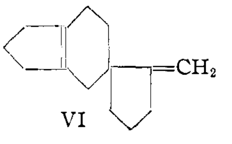
(5) R. C. Fuson and W. Cole, THIS JOURNAL, **60**, 1238 (1938).

(6) R. C. Fuson, C. L. Flemming, P. F. Warfield and D. E. Wolf, *J. Org. Chem.*, **10**, 126 (1945).

(7) K. Alder and W. Roth, *Chem. Ber.*, **88**, 407 (1955).

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

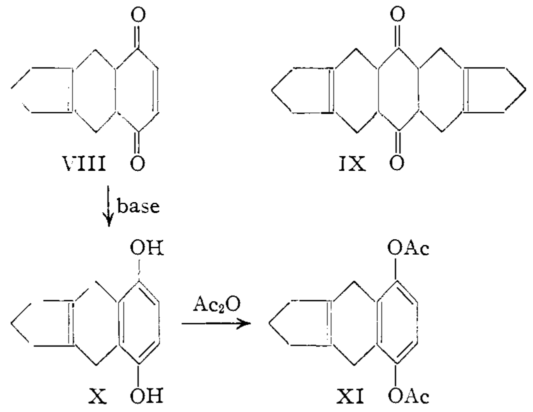
(9) This dimer (VI) is considered to be a self Diels–Alder adduct solely on the basis of spectral evidence. The infrared spectrum of the product showed strong absorption at 3.44, 3.50 and 11.35 μ and medium absorption at 6.04, 6.90 and 6.97 μ. Thus, there was observed absorption characteristic of the olefinic link, including the terminal methylene group and no absorption for a conjugated diene system.



VI

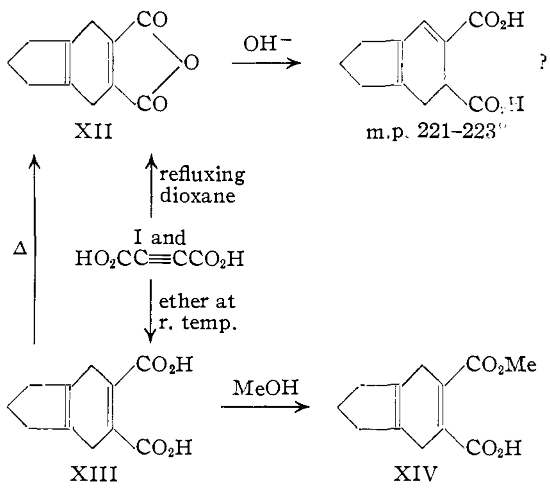
bonds when hydrogenated quantitatively. Reductive ozonolysis of I gave formaldehyde, characterized as its dimedone derivative. Potassium permanganate oxidation of I yielded succinic acid, in low yield, and polymeric products.[10]

With benzoquinone compound I formed a mono-adduct VIII, m.p. 133–135°, and a di-adduct IX, m.p. 227–228°. In the presence of a trace of base VIII enolizes readily to X, m.p. 206–207°. X was characterized as its diacetate XI, m.p. 144–145°.



VIII IX X XI

Contrary to expectation and to the previous report of Bailey,[4] the Diels–Alder adduct of I with acetylenedicarboxylic acid, obtained by refluxing in dioxane for 6 hr., was the anhydride XII, m.p. 145–146°, rather than the acid XIII, m.p. 164–166°. This anhydride XII showed strong infrared absorption at 5.43 and 5.63 μ. Authentic dicarboxylic acid XIII was obtained by effecting addition of I to acetylenedicarboxylic acid in ether solution at room temperature.



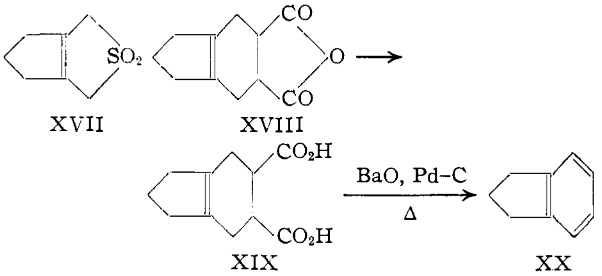
XII XIII XIV

On heating, XIII slowly converted to XII. Alkaline hydrolysis of XII gave an isomeric dicarboxylic acid, m.p. 221–223°, which appears to be a double bond isomer of XIII. This isomeric acid was not investigated further.[12] Because of its tendency to dehydrate to XII, the acid XIII was not analyzed. Recrystallization of XIII from methanol gave the monomethyl ester derivative XIV, m.p. 103–105°, presumably *via* XII as an intermediate.

XV XVI

The cyclic sulfone XVII was obtained from I in 60% yield, together with polymeric material. XVII did not possess a definite m.p. but dissociated slowly at *ca.* 150°. Under similar conditions 1,2-dimethylenecyclobutane gave only polymeric material.[2] These observations demonstrate the greater ease with which a five–five ring fusion may be achieved as compared to a five–four fusion.

The diene I with maleic anhydride gave the adduct XVIII, m.p. 87–88°, in quantitative yield. The latter affords the dicarboxylic acid XIX, m.p. 212–214°, on hydrolysis. Only a 91% yield of XIX was realized when compound I obtained *via* acetate pyrolysis was used. Heating XIX with barium oxide and palladium-on-charcoal gave the well known hydrocarbon 2,3-hydrindene (XX). All of the properties of this hydrindene, including its infrared and ultraviolet spectra, were in agreement with the properties reported for 2,3-hydrindene.[15]



XVII XVIII XIX XX

1,2-Dimethylene-3-methylcyclopentane (II).—Synthesis of II was realized as shown by the chart which follows.

Tetraethyl 2-methyl-1,1,5,5-pentanetetracarboxylate (IIIa) was obtained by alkylation of malonic ester with 1,3-dibromobutane in *ca.* 40% yield. This malonic ester condensation proved to be rather complex and was studied in some detail. The results of this special study will be presented separately. Perkin cyclization[16] of IIIa gave tetraethyl 3-methyl-1,1,2,2-cyclopentanetetracarboxylate (IVa), m.p. 51–53°, in *ca.* 87% yield. The latter after saponification and decarboxylation gave a 94% yield of crude 3-methyl-1,2-cyclopentanedicarboxylic acid (Va) which was esterified azeotropically to afford diethyl 3-methyl-1,2-cyclopentanedicarboxylate (VIa), (79% from IIIa).

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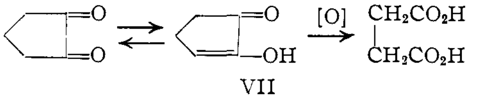
(10) Succinic acid probably arises from oxidation of the unstable intermediate oxidation product 1,2-cyclopentanedione. The latter has been shown to exist as a mono-enol VII and to give succinic acid on permanganate oxidation.[11]



VII

(11) W. Dieckmann, *Ber.*, **35**, 3208 (1902).

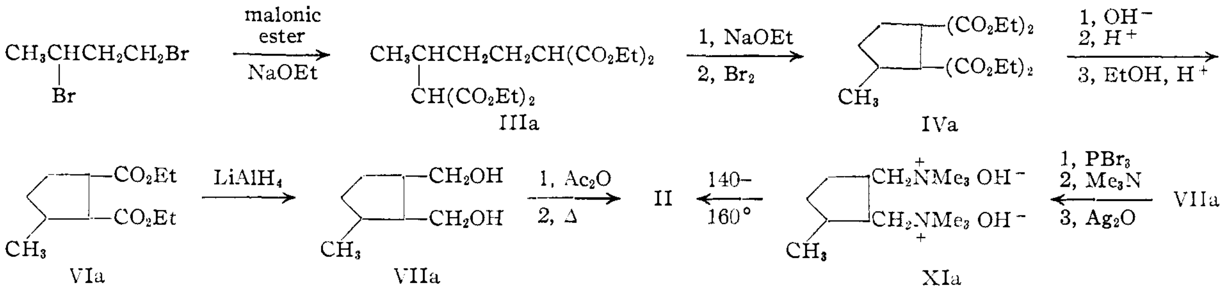
(12) The behavior of XIII corresponds to behavior observed for 3,6-dihydrophthalic acid (XV). The latter converts to its anhydride at temperature above 100°.[13] Further, alkaline hydrolysis of the adduct XVI rearranges it to isomeric dihydrophthalic acids of unknown structure.[14]

(13) A. von Baeyer, *Ann.*, **269**, 204 (1892).

(14) O. Diels and K. Alder, *ibid.*, **490**, 236 (1931).

(15) A. Plattner and J. Wyss, *Helv. Chim. Acta*, **24**, 486 (1941).

(16) N. H. Perkin, *J. Chem. Soc.*, **51**, 540 (1887).



Lithium aluminum hydride reduction of VIa gave (VIIa) 1,2-bis-(hydroxymethyl)-3-methylcyclopentane which was acetylated quantitatively with acetic anhydride and pyridine to its diacetate VIIIa.

The glycol VIIa with phosphorus tribromide afforded the dibromide IXa (81%) and treatment of the latter with trimethylamine gave the bis-quaternary ammonium bromide Xa in essentially quantitative yield. Finally, the bis-quaternary base XIa was obtained from Xa by treatment with moist silver oxide.

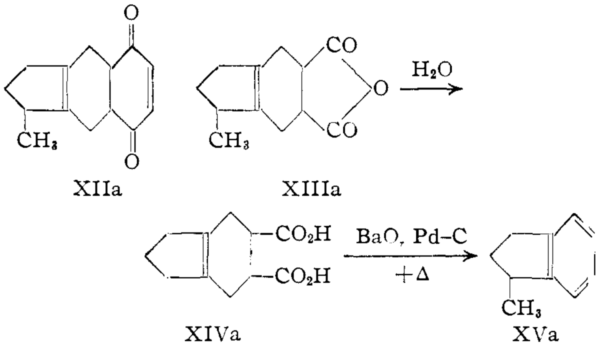
The diene II was obtained by two methods. Thermal decomposition of XIa at 140–160° gave crude II (37% from VIIa) having n^{25}_{D} 1.4731. Redistillation of II under nitrogen *in vacuo* gave pure II having b.p. 50° (60 mm.), n^{25}_{D} 1.4692 and d^{25}_{4} 0.8163. The observed molar refractivity was 0.70 greater than the calculated value, a consequence of the exaltation due to conjugation. The ultraviolet spectrum of II in isoöctane showed an absorption maximum at λ_{248} mμ, log ε 3.93 in close agreement with that found for I. The infrared absorption of II (Fig. 1) was very similar to that of I with additional strong absorption at 6.9 and 7.29 μ due to the presence of the C-methyl group.

Pyrolysis of 30 g. of the diacetate VIIIa at 515–525° gave 1.3 g. of diene II having b.p. 75–78° (120 mm.), n^{20}_{D} 1.4690. Substantial amounts, 15 g., of unpyrolyzed VIIIa and its partially pyrolyzed product, unsaturated monoacetate, were recovered.

Essentially all characterization studies of the diene II were done using II obtained *via* the Hofmann elimination.

The diene II absorbed 98.8 mole per cent. of the amount of hydrogen required for two double bonds. The rate of hydrogenation was greatly reduced after half the required hydrogen had been absorbed. This presumably is a steric effect arising from the presence of the branching methyl group attached to the cyclopentane ring.

The diene II formed a mono-adduct XIIa, m.p. 114.5–116°, with *p*-benzoquinone. The possibility here of forming a di-adduct and the ease of enolization of XIIa were not investigated. Presumably one would observe here behavior similar to that noted for the diene I. From the diene II and maleic anhydride the adduct XIIIa, m.p. 72–74°, was obtained. Hydrolysis of this gave the dicarboxylic acid XIVa, m.p. 180–182°, in quantitative yield from II. Degradation of XIVa by heating with barium oxide and palladium-on-charcoal afforded 1-methyl-2,3-hydrindene (XVa). The physical properties of XVa were in close agreement with those reported for 1-methyl-2,3-hydrindene.[15] Direct comparison of this XVa with a synthetic sample of 1-methyl-2,3-hydrindene *via* ultraviolet and infrared spectra confirmed this structural assignment.



Polymerization of I and II.—Emulsion polymerizations of I and II, prepared *via* the Hofmann method, were carried out using the same conditions and recipe described for the polymerization of 1,2-dimethylenecyclobutane.[2] In each instance conversion was quantitative and gave a rubber-like, elastic polymer.[17] It was noted also that the polymers were still elastic and gummy at low temperature when reprecipitated from chloroform solutions by addition to ethanol at −78°. The homopolymers of I and II obtained here appear to differ markedly from the polymer of 1,2-dimethylenecyclohexane described by Bailey and also from the polymer of I described recently in a preliminary report.[18,19] Since this earlier report did not describe the method used to polymerize I nor present any extensive characterization of the polymer, it is difficult to make much of a comparison. It is possible that the differences in properties noted may be a consequence of the purity of the diene I used.

Evaluation of the homopolymers of I and II included determination of percentage *cis*-1,4-units by the perbenzoic acid method,[20] static solubilities and intrinsic viscosities in benzene at 25.0° according to Frank, *et al.*,[21] and examination of the

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[17] Persulfate initiated polymerization of our best sample of I obtained by acetate pyrolysis also gave a soluble, rubber-like polymer qualitatively similar to the polymer derived from I prepared by the Hofmann procedure.

[18] W. J. Bailey and H. R. Golden, This Journal, **76**, 5418 (1954).

[19] W. J. Bailey, Proceedings Joint Conference on Elastomer Research and Development, National Academy of Sciences–National Research Council, Publication 370, Jan. 12 and 13, 1954.

[20] I. M. Kolthoff, M. A. Mairs and T. S. Lee, *J. Polymer Sci.*, **2**, 206 (1947).

[21] R. L. Frank, E. C. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *Ind. Eng. Chem.*, **39**, 887 (1947).

infrared absorption spectra of the polymer films. The results are presented in Table I.

TABLE I

CHARACTERIZATION OF HOMOPOLYMERS

Polymer	*cis*-1,4-Units %[a]	Static solubility in benzene, %	Intrinsic viscosity in benzene, 25.0°
From I	94	58	0.05
From II	72	98	.98

[a] On the basis of 100% unsaturation.

Infrared spectra of the two polymers were obtained on films deposited on a sodium chloride window. Neither polymer showed absorption in the region 11.0 to 11.4 μ, characteristic of a terminal methylene group. This observation suggests that both polymers probably comprised only *cis*-1,4-units. The low value for the percentage of *cis*-1,4-units in the homopolymer of II, as indicated by the perbenzoic acid method, cannot be attributed to extensive crosslinking either by a 1,2- and 3,4-addition or radical attack on internal double bonds. The solubility of the polymer and steric factors involving the cyclopentane ring exclude this possibility. Polymer degradation in solution may be a factor in the low unsaturation value as viscosities of benzene solutions of both homopolymers were observed to decrease on solution aging. Considerably more study is required to clarify this anomaly.

As no chain modifiers were used in the polymerization recipe, the low viscosities observed indicate that the polymers are "self-modifying" as noted previously for the polymers of 2-alkyl- and 3-methyl-2-alkylbutadienes.[22,23]

Summary.—The study which has been presented suggests that the Hofmann elimination method is the procedure of choice for synthesis of conjugated exocyclic dienes in the cyclopentane series as well as the cyclobutane series. This method affords dienes of the highest purity with least contamination from various undesirable accessory products which are difficult to remove.

The two dimethylenecyclopentanes are highly reactive dienes which are prone to undergo thermal dimerization and/or polymerization with great ease. Their physical and chemical properties are in complete accord with the assigned conjugated 1,2-dimethylene structure.

The homopolymers of these dienes, obtained on persulfate initiation, are soluble, rubber-like and qualitatively similar to the polymer of 1,2-dimethylenecyclobutane. It is likely though that the polymers derived from the cyclopentane dienes are largely all-*cis* elastomers.

Experimental Part

Diethyl *trans*-1,2-Cyclopentanedicarboxylate.—The crude *trans*-1,2-cyclopentanedicarboxylic acid obtained from 511 g. of diethyl 1-cyano-1,2-cyclopentanedicarboxylate, $n^{20}\mathrm{D}$ 1.4560, prepared as described by Fuson[6] was esterified azeotropically with ethanol using *p*-toluenesulfonic acid as a catalyst. There was obtained 375.3 g. (82% from cyanoester) of the diethyl ester having b.p. 80–88° (0.5–0.7 mm.), $n^{14}\mathrm{D}$ 1.4463–1.4468 (Owen[24] reported b.p. 133° (17 mm.), $n^{16}\mathrm{D}$ 1.4451; Birch[25] reported b.p. 111–113° (7.0 mm.), $n^{20}\mathrm{D}$ 1.4435.

1,2-Bis-(hydroxymethyl)-cyclopentane (III).—Lithium aluminum hydride reduction of 623 g. of diethyl 1,2-cyclopentanedicarboxylate carried out in the usual way gave 305 g. (81%) of III, b.p. 117–119° (2.1 mm.), $n^{25}\mathrm{D}$ 1.4773 [Halford[26] reported b.p. 117–118° (0.6 mm.), $n^{25}\mathrm{D}$ 1.4480; Bailey[4] found b.p. 127–129° (2.4 mm.), $n^{25}\mathrm{D}$ 1.4771; Owen[24] reported b.p. 147° (11 mm.), $n^{22}\mathrm{D}$ 1.4760; Birch[25] reported b.p. 102–106° (0.6 mm.), $n^{25}\mathrm{D}$ 1.4798].

The bis-phenylurethan derivative of III had m.p. 109.5–111.5° after recrystallization from benzene–hexane.

Anal. Calcd. for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57. Found: C, 68.37, 68.38; H, 6.76, 6.46.

The glycol III was acetylated with acetic anhydride–pyridine. From *ca.* 90 g. of III there was obtained 128 g. of the diacetate having b.p. 95–100° (0.5–1.0 mm.), $n^{25}\mathrm{D}$ 1.4468 [Bailey[4] reported b.p. 116° (2 mm.), $n^{25}\mathrm{D}$ 1.4471; Owen[24] reported b.p. 104° (1 mm.), $n^{24}\mathrm{D}$ 1.4522].

1,2-Bis-(bromomethyl)-cyclopentane.—Using the procedure described for the preparation of 1,2-bis-(bromomethyl)-cyclobutane,[2] from 26 g. of III there was obtained 42.1 g. (85%) of the dibromide, b.p. 102° (3.2 mm.), $n^{25}\mathrm{D}$ 1.5343.

Anal. Calcd. for $C_7H_{12}Br_2$: C, 32.84; H, 4.73; Br, 62.44. Found: C, 32.84; H, 4.69; Br, 62.22.

1,2-Bis-(dimethylaminomethyl)-cyclopentane Dimethobromide.—A mixture of 45 g. (0.76 mole) of trimethylamine, 22 g. (0.086 mole) of 1,2-bis-(bromomethyl)-cyclopentane and 15 ml. of methanol was kept in a sealed Pyrex bomb at room temperature for 5 days or until the separation of solid precipitate was complete. Evaporation of the reaction mixture to dryness *in vacuo* gave 32 g. (100%) of the bis-quaternary ammonium bromide, m.p. *ca.* 270°. This product could not be recrystallized from ethanol. It was characterized as its quaternary ammonium picrate, m.p. 199–200° from ethanol.

Anal. Calcd. for $C_{25}H_{34}O_{14}N_2$: C, 44.77; H, 5.11; N, 16.72. Found: C, 44.70; H, 5.14; N, 16.89.

1,2-Dimethylenecyclopentane (I). (A) **From IV.**—To a cooled aqueous solution of 68 g. of the crude bis-quaternary ammonium bromide described above freshly prepared silver oxide (from 68 g. of silver nitrate and 25 g. of potassium hydroxide) was added carefully in small portions with stirring and cooling. The addition of silver oxide was continued until the formation of silver bromide ceased. The reaction mixture was filtered and the filtrate placed in an evaporating dish with a stream of dry air blowing on the surface overnight. The concentrated solution was placed in a distillation flask containing hydroquinone and pyrolyzed using essentially the same procedure given for the preparation of 1,2-dimethylenecyclobutane.[2] Rapid pyrolysis commenced at 150° with the organic products co-distilling with water at 95–97°. The crude pyrolysate was separated from water and washed with dil. hydrochloric acid and water until neutral to litmus. There was obtained 9.8 g. (62%) of I having $n^{25}\mathrm{D}$ 1.4738. The diene was evaporatedly distilled at room temperature under a nitrogen atmosphere at 100 mm. pressure into two successive Dry Ice traps. All fractions showed $n^{25}\mathrm{D}$ 1.4732, $d^{25}{}_4$ 0.8210.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71; $M\mathrm{D}$, 31.56. Found: C, 89.23; H, 10.51; $M\mathrm{D}$, 32.18.

(B) **From III-Diacetate.**—The diacetate of III (74.5 g.) was dropped slowly under a nitrogen atmosphere into a vertically arranged 16-in. Pyrex tube packed with carborundum chips and heated to 525–540°. The pyrolysate (72.5 g.), collected in a receiver cooled with Dry-Ice, was washed with water, sodium carbonate solution and finally with water. After brief drying over Drierite the pyrolysate was distilled *in vacuo* under nitrogen to give 2.5 g. of very impure diene having b.p. 32–45° (100 mm.), $n^{28}\mathrm{D}$ 1.4543; 6.0 g. of I having b.p. 45–48° (100 mm.), $n^{28}\mathrm{D}$ 1.4680 [Bailey[4] reported b.p. 80–82° (130 mm.), $n^{25}\mathrm{D}$ 1.4694] and 34.0 g. of mono- and diacetates, b.p. 70–100° (0.5–8.0 mm.). Redistillation of the second fraction gave 0.3 g. of forerun, b.p. 33–46° (110 mm.), $n^{25}\mathrm{D}$ 1.4609, and 4.45 g. of relatively pure I, b.p. 46–49° (110 mm.), $n^{25}\mathrm{D}$ 1.4700–1.4713.

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The infrared and ultraviolet absorption spectra data for the two preparations of I were presented in the Discussion.

Reduction and Oxidation of I.—The diene I (73.6 mg., 0.782 mmole) was hydrogenated in ethyl acetate using Adams catalyst. It absorbed 40.8 ml. of hydrogen at 26° and 739 mm. (1.007 molar equivalents for two double bonds).

Ozonized oxygen was passed through a solution of 0.18 g. (0.002 mole) of I in 10 ml. of methylene chloride cooled to Dry Ice temperature. After 0.5 hr. the solution was added to a stirred mixture of 0.2 g. of zinc dust in 10 ml. of acetic acid. After stirring (0.5 hr.) the methylene chloride was distilled into a receiver containing 1.1 g. (0.008 mole) of dimedone and one drop of piperidine in ethanol. The mixture collected in the receiver was heated until all methylene chloride had been removed. Upon cooling, colorless crystals of m.p. 140–189° separated. Recrystallization of the crude solid from 75% ethanol gave 0.35 g. (30%) of the dimedone derivative of formaldehyde having m.p. 190–191° and which did not depress the m.p. of an authentic sample of the dimedone derivative of formaldehyde.

To a solution of 0.6 g. of I in 10 ml. of acetone (freshly distilled over potassium permanganate) there was added gradually a 5% potassium permanganate solution until the permanganate color persisted (*ca.* 150 ml.). The reaction mixture was then heated on a steam-bath for 10 min., decolorized with sulfur dioxide and extracted thoroughly with ether. From the ether extracts there was obtained a small amount of crude acid of m.p. 165–180°. One crystallization of this crude acid from benzene–acetone gave an acid which had m.p. 189–190°. This product did not depress the m.p. of authentic succinic acid.

Reaction of I with Maleic Anhydride. (A).—The diene I (1.88 g., 0.02 mole) was added slowly to a solution of 1.94 g. (0.02 mole) of maleic anhydride in benzene. An immediate exothermic reaction occurred. After keeping the mixture at room temperature for two days, or refluxing for 2 hr., the solvent was removed to give 3.8 g. (100%) of the crude anhydride XVIII, m.p. 82–87°. This showed m.p. 87–88° after one crystallization from hexane.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.71; H, 6.35.

Alkaline hydrolysis of 3.8 g. of XVIII followed by acidification gave 4.1 g. (98%) of the dicarboxylic acid XIX, m.p. 208–210°. One recrystallization from 30% aq. ethanol gave 4.05 g. of prisms of m.p. 212–214°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.94; H, 6.67.

(B).—From 0.5 g. of I obtained *via* acetate pyrolysis and 0.052 g. of maleic anhydride, there was obtained 0.93 g. (91%) of XIX, m.p. 210–212°.

Reaction of I with *p*-Benzquinonoe. (A) In the Presence of a Trace of Base.—A solution of 0.5 g. (0.0053 mole) of I and 0.6 g. (0.0053 mole) of *p*-benzoquinone in 30 ml. of benzene containing a trace of trimethylamine was refluxed 6 hr. After evaporation of the solvent, 1 g. (90%) of the crystalline adduct (X), m.p. 206–207° dec., was obtained. This adduct darkened on exposure to air and was difficult to purify. In the infrared it showed maxima at 3.10, 6.15 and 6.25 μ.

Acetylation of X (0.5 g.) with acetic anhydride–pyridine gave 0.65 g. (93%) of a stable, colorless crystalline diacetate (XI) having m.p. 144–145° from hexane.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.34; H, 6.38.

(B) **In the Absence of Base.**—Using the same procedure as described in (A) above but excluding the trace of trimethylamine, 1.5 g. (0.016 mole) of I and 1.2 g. (0.011 mole) of *p*-benzoquinone gave 2.2 g. of a mixture having m.p. 132–230°. Thorough extraction of this mixture with boiling hexane left a colorless residue comprising the diadduct IX which, after crystallization from benzene, showed m.p. 227.5–228° and infrared abs., $\lambda_{\max}$ 5.88 μ.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.97; H, 8.08.

The hexane extract gave very faintly yellow needles of m.p. 133–135° and infrared abs., $\lambda_{\max}$ 5.98 and 6.15 μ. This is the monoadduct VIII (Bailey[4] reported m.p. 135–136°).

Reaction of I with Acetylenedicarboxylic Acid. (A) In Refluxing Dioxane.—The diene I (0.25 g., 0.0025 mole) and acetylenedicarboxylic acid (0.3 g., 0.0026 mole) were refluxed in 15 ml. of dioxane for 6 hr. Removal of solvent *in vacuo* left a slightly moist residue which after one washing with cold pentane weighed 0.35 g. (67%) and had m.p. 138–142°. After one recrystallization from ether–pentane the anhydride XII was obtained as long needles, m.p. 145–146°, infrared abs. $\lambda_{\max}$ 5.40 and 5.63 μ.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.35; H, 5.43.

(B) **In Ether at Room Temperature.**—The above addition was repeated using 0.5 g. (0.0053 mole) of I and 0.6 g. (0.0053 mole) of acetylenedicarboxylic acid dissolved in ether. After standing at room temperature for 2 days, during which time crystals slowly deposited, the solvent was removed giving 1.1 g. of residue, m.p. 164–167°, with rapid dehydration on melting. This dicarboxylic acid XIII showed infrared abs., $\lambda_{\max}$ 6.05 μ (broad). This acid XIII was not analyzed as such because of its tendency to dehydrate on heating. On recrystallization from methanol it was transformed completely into its monomethyl ester XIV, m.p. 103–105°, infrared abs. $\lambda_{\max}$ 5.75, 5.90 and 6.10 μ.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.95; H, 6.55.

A small amount of the diacid XIII was sublimed *in vacuo* at 140-150° to give a sublimate, m.p. 139–140°, which after recrystallization from ether–pentane had m.p. 144–145° and did not depress the m.p. of XII obtained earlier.

Reaction of I with Sulfur Dioxide.—A mixture of 5 g. of sulfur dioxide, 0.5 g. of I and 0.1 g. of N-phenyl-β-naphthylamine was kept in a sealed Pyrex bomb at room temperature for 2 days. After removal of the excess sulfur dioxide, the brown solid residue was triturated with several portions of boiling methanol. From the methanol solution 0.5 g. (60%) of the sulfone XVII crystallized as long needles. This XVII dissociates rapidly at 145–150°.

Anal. Calcd. for $C_7H_{10}SO_2$: C, 53.14; H, 6.37. Found: C, 53.13; H, 6.52.

2,3-Hydrindene from XIX.—A thorough mixture of 1 g. of XIX, 4 g. of barium oxide and 1 g. of 10% palladium–charcoal contained in a 10-ml. distillation flask was heated with the free flame of a micro burner. About 0.5 ml. of cloudy distillate was collected, dried with a few pieces of Drierite and redistilled at 183–185° (atm.) to give a clear liquid showing $n^{20}\mathrm{D}$ 1.5348 (reported in the literature for XX,[15] $n^{20}\mathrm{D}$ 1.5351). This sample of XX showed ultraviolet abs. $\lambda_{\max}$ 273, log ϵ 3.17; $\lambda_{\max}$ 267, log ϵ 3.10; $\lambda_{\max}$ 260, log ϵ 2.92 and a shoulder at 253 mμ.

Tetraethyl 2-Methyl-1,1,5,5-pentanetetracarboxylate (IIIa).—To a solution prepared by the addition of 92 g. (4 gram atoms) of sodium to 1 l. of absolute ethanol, there was added with stirring 1000 g. (6.2 moles) of diethyl malonate. After stirring a few moments, 432 g. (2 moles) of 1,3-dibromobutane was added over a 6-hr. period. After refluxing 2 hr. the mixture was stirred overnight, most of the ethanol removed and 1 l. of water added. The organic layer was separated and the aqueous layer extracted several times with benzene. The combined organic layer and benzene extracts, after distillation of the benzene, was distilled rapidly *in vacuo* to give 473.5 g. of diethyl malonate, b.p. 64–77° (0.2 mm.), $n^{20}\mathrm{D}$ 1.4157–1.4194; 138.8 g. of a mixture of diethyl malonate and diethyl 2-methyl-1,1-cyclobutanedicarboxylate, b.p. 76–79° (0.2-0.5 mm.), $n^{20}\mathrm{D}$ 1.4258–1.4349; 68.5 g. of a crude bromoester, b.p. 77–168° (0.5–2.0 mm.), $n^{20}\mathrm{D}$ 1.4420–1.4518; and 312 g. (41.5%) of the desired tetraester IIIa, b.p. 171–185° (1–2 mm.), $n^{20}\mathrm{D}$ 1.4440–1.4490. A still residue of *ca.* 100 g. remained. The yield of IIIa varied from 31–41% and dropped to *ca.* 15% when less diethyl malonate was used. A redistilled sample of IIIa showed b.p. 160° (0.5 mm.), $n^{20}\mathrm{D}$ 1.4441.

Anal. Calcd. for $C_{18}H_{30}O_8$: C, 57.73; H, 8.08. Found: C, 57.53, 57.58; H, 7.94, 8.01.

Tetraethyl 3-Methyl-1,1,2,2-cyclopentanetetracarboxylate (IVA).—After the addition of 200 ml. of dry ether to a solution resulting from the addition of 12.5 g. (0.54 gram atom) of sodium to 200 ml. of absolute ethanol, there was added a solution of 100 g. (0.27 mole) of IIIa in 200 ml. of dry ether. Following the slow addition of 43.0 g. (0.54 mole) of bromine to this cooled and stirred mixture, stirring was continued overnight. The resulting mixture was washed with 250 ml. of water and the water layer extracted twice with ether.

The residue resulting from removal of ether from the combined ether layer and extracts was dried by distilling with a small amount of benzene. The dried residue, which sometimes solidified on cooling, was distilled *in vacuo* to give 86.7 g. (86.7% of the cyclized ester IVa, b.p. 166–170° (2.6 mm.), n^{20}_D 1.4562 (supercooled). The ester IVa rapidly solidified to show m.p. 51–53° which was unaltered after recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 58.05; H, 7.58. Found: C, 57.78; H, 7.44.

The tetraester IVa was recovered unchanged after refluxing with concentrated hydrochloric acid for two weeks.

Diethyl 3-Methyl-1,2-cyclopentanedicarboxylate (VIa).—A solution of the crude IVa obtained from 245 g. of IIIa in 1 l. of methanol containing 230 g. of potassium hydroxide was refluxed for three days with occasional removal of methanol and addition of water. After removal of the alcohol, the solution was made strongly acidic with concentrated hydrochloric acid. The acidic mixture was refluxed three days, concentrated and extracted thoroughly with ether. After removal of the ether 106 g. (94%) of crude 3-methyl-1,2-cyclopentanedicarboxylic acid (Va) was obtained.[27] A portion of this, after recrystallization from concentrated hydrochloric acid, was obtained as a brownish solid, m.p. 114–117°, which after two sublimations *in vacuo* was colorless and had m.p. 115–117°[28] (Perkin[29] reported m.p. 104°).

Esterification of 106 g. of the crude Va by the azeotropic method described for diethyl adipate[30] gave 117.6 g. (78.8% based on IIIa) of the diester VIa, b.p. 128–134° (8–12 mm.), n^{25}_D 1.4430.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.44; H, 8.81, 8.71.

1,2-Bis-(hydroxymethyl)-3-methylcyclopentane (VIIa).—Lithium aluminum hydride reduction of 101 g. (0.44 mole) of VIa gave 51.1 g. of the glycol VIIa as a viscous liquid, b.p. 137–141° (5 mm.), n^{19}_D 1.4740.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.19. Found: C, 66.49, 66.59; H, 11.14, 11.14.

The bis-phenylurethan derivative of VIIa as first obtained showed m.p. 105–114°. After three recrystallizations from chloroform–hexane, it had m.p. 113–115.5°.

Anal. Calcd. for $C_{22}H_{26}O_4N_2$: C, 69.02; H, 6.85. Found: C, 69.02; H, 6.50.

The glycol VIIa was acetylated with acetic anhydride–pyridine. From 51 g. of VIIa there was obtained 80 g. (98%) of the diacetate VIIIa, b.p. 126–130° (4 mm.), n^{20}_D 1.4481.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.04, 63.16; H, 8.80, 8.87.

1,2-Bis-(bromomethyl)-3-methylcyclopentane (IXa).—Following the same procedure used for the preparation of 1,2-bis-(bromomethyl)-cyclobutane,[2] from 55 g. of VIIa there was obtained 84 g. (81%) of the dibromide IXa, b.p. 87–90° (1.5 mm.), n^{25}_D 1.5271.

Anal. Calcd. for $C_8H_{14}Br_2$: C, 35.58; H, 5.23; Br, 59.19. Found: C, 35.71; H, 5.21; Br, 59.00.

1,2-Bis-(dimethylaminomethyl)-3-methylcyclopentane Dimethobromide (Xa).—This bis-quaternary ammonium bromide, prepared in the manner previously described for its lower homolog, was obtained as a glassy solid. It was characterized as the bis-quaternary ammonium picrate, m.p. 158–178° from ethanol.

Anal. Calcd. for $C_{26}H_{36}O_{14}N_8$: C, 45.61; H, 5.30. Found: C, 45.90; H, 5.47.

1,2-Dimethylene-3-methylcyclopentane (II). (A) From XIa.—The glassy, solid bis-quaternary ammonium bromide Xa obtained from 42 g. of the dibromide IXa was dissolved in 50 ml. of water and washed with methylene chloride to remove traces of unreacted IXa. This aqueous solution was then treated with freshly prepared silver oxide as described in the preparation of I. There was obtained 6 g. of crude diene II, n^{25}_D 1.4731, which on redistillation showed b.p. 50° (60 mm.), n^{25}_D 1.4692, d^{25}_4 0.8163.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18; M_D, 36.21. Found: C, 88.73; H, 11.20; M_D, 36.91.

(B) From VIIIa.—Using the same pyrolysis procedure described for I from 30 g. of VIIIa, there was obtained 1.3 g. of II showing b.p. 75–78° (120 mm.), n^{20}_D 1.4690.

Reduction of II.—Quantitative hydrogenation of 81.4 mg. (0.752 mmole) of II in ethyl acetate using Adams catalyst required 37.6 ml. of hydrogen at 25° and 734 mm. (0.998 molar equivalent for two double bonds). After 23 ml. of hydrogen had been absorbed, it was necessary to add 1 drop of concd. hydrochloric acid to speed up the reaction.

Diels–Alder Adducts of II. (A) With Maleic Anhydride.—This adduct of II was prepared as described for XVIII. This anhydride adduct (XIIIa) had m.p. 74–75°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.37; H, 7.10.

In a quantitative experiment the adduct was isolated as the dicarboxylic acid XIVa, m.p. 180–182° from 25% aq. ethanol, in quantitative yield from II.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.33; H, 7.42.

In the above the same results were obtained using II prepared by either of the two methods described.

(B) With *p*-Benzoquinone.—As described previously for preparation of the adduct VIII from I, an equimolar mixture of the diene II and *p*-benzoquinone afforded the mono-adduct XIIa in 88% yield. After recrystallization from hexane, XIIa showed m.p. 114.5–116°.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.78; H, 7.49.

1-Methyl-2,3-hydrindene from XIVa.—Degradation of 1 g. of XIVa, carried out as described previously for XIX, gave 0.4 g. of a cloudy distillate. After drying and distilling this gave a product having b.p. 180° (micro), n^{25}_D 1.5230 (lit. value, b.p. 182–183°, n^{20}_D 1.5260).[15] The ultraviolet absorption spectrum of this XVa was identical with the ultraviolet spectrum of a sample of XVa prepared by hydrogenation of 1-methylindene[31] and showed λ_{max} 273 mμ, log ϵ 3.13; λ_{max} 267 mμ, log ϵ 3.11; λ_{max} 260, log ϵ 2.98 and a shoulder at 253 mμ.

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[27] This crude acid probably comprised a mixture of the four possible racemates, and succeeding derivatives of it would be expected to be mixtures of stereoisomers and perhaps show broad melting point ranges.

[28] This sublimed acid probably consisted of one or both of the two possible racemates having *trans* configuration of the carboxyl groups.

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