[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conjugative Effects of Cyclopropane Rings. II. The Preparation and Properties of α-Hydroxyumbellulone

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α-Hydroxyumbellulone, an analog of the 2-hydroxycyclopentadienone system with a cyclopropane ring replacing one of the double bonds, has been prepared. The acidity of the substance is not significantly different from that reported for 2-hydroxy-2-cyclopentenones, demonstrating that the cyclopropane ring does not function as an electron-acceptor in the ground state.

The ultraviolet absorption spectrum of the terpene ketone umbellulone (I) demonstrates that the cyclopropane ring effectively conjugates with the contiguous α,β-unsaturated carbonyl system.[2] To gain additional information regarding the nature of the conjugative effect of the cyclopropane ring we have prepared α-hydroxyumbellulone (IV) and determined its acidity and infrared absorption characteristics.

Umbellulone (I) reacted smoothly with hydrogen peroxide in methanolic sodium hydroxide solution to give a nearly quantitative yield of epoxyumbellulone (II), a crystalline solid of m.p. 25–26°.[3] Hydrolysis of epoxyumbellulone with dilute aqueous sulfuric acid produced 1,2-dihydroxydihydroumbellulone (III), a water-soluble, hygroscopic solid of m.p. 65.9–66.7°, in 75% yield. Boiling a solution of the keto-glycol in 1% aqueous sodium hydroxide for a few minutes followed by acidification produced α-hydroxyumbellulone (IV) in 60% yield.

α-Hydroxyumbellulone is a white, crystalline solid of m.p. 75–78° which on exposure to air is irreversibly converted into a yellow oil of unknown constitution. α-Hydroxyumbellulone gives a deep-purple ferric reaction, dissolves in 10% sodium carbonate solution from which it is regenerated on acidification, shows an approximate pK of 9.8 in 50% alcohol, reduces Fehling solution as well as permanganate, and reacts with bromine in carbon tetrachloride solution to yield crystalline, bright-yellow, 1-bromo-2-ketodihydroumbellulone (V). The ultraviolet absorption spectrum of the α-hydroxy compound is very similar to that of umbellulone (Table I), and the infrared absorption of a mull[4] showed bands at 2.98, 5.92 and 6.07 μ indicative of the OH, C=O and C=C groups.

Exclusive of its ultraviolet absorption spectrum the properties of α-hydroxyumbellulone are very similar to those reported[5] for 2-hydroxy-2-cyclopentenones. Hence, the cyclopropane ring in α-hydroxyumbellulone is largely without effect on the ground state properties of the molecule as determined by acidic strength and the band positions in the infrared for the OH and C=O groups. This conclusion adds to the growing body of evidence that while the cyclopropane ring functions well as an unsaturated group in donating electrons to contiguous unsaturated groups,[6] it does not have the property of olefinic unsaturation of accepting electrons, a function which would be required of the cyclopropane ring in α-hydroxyumbellulone were the acidic strength and band positions for the OH and C=O groups anomalous.[7]

While other methods for the synthesis of α-diketones applied to umbellulone did not produce α-hydroxyumbellulone, the results obtained are not without interest. Selenium dioxide oxidation of β-dihydroumbellulone (VI) or of thujone (VII) provided 2-hydroxythymoquinone (VIII) in small yield, identity being established by comparison with an authentic sample.[8] The reaction of α-bromoumbellulone (IX) with piperidine in ether proceeded very slowly but yielded a substantial quantity of 2-piperidinothymol (X). 2-Piperidinothymol is, not unexpectedly, cryptophenolic and has the ultraviolet absorption spectrum of thymol, not that of an aminophenol, (Table I) as a consequence of hindrance that prevents the benzene and piperidine rings from becoming planar as required if the aniline-type of resonance interaction is to be operative.[9] In accord with this interpretation, 2-piperidinothymol, its conjugate acid and thymol have nearly identical ultraviolet absorption spectra (Table I).

(1) This material is taken from the Dissertation of James C. Selover offered in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Stanford University, where he was a du Pont Fellow, 1952–1953. Part of this material was reported at the American Chemical Society Meeting in Los Angeles, Calif., March 16, 1953.

(2) For a discussion of the spectrum see R. H. Eastman, THIS JOURNAL, **76**, 4115 (1954).

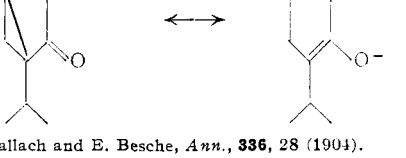
(3) A recent report of the chromatographic analysis of a sample of umbellulone into umbellulone and ψ-umbellulone raises some question as to the homogeneity of the substance [A. E. Gillam and D. G. Moss, *Nature*, **172**, 585 (1953)]. We have found no evidence of inhomogeneity in freshly fractionated samples of umbellulone and the excellent yield of the crystalline epoxy compound provides further evidence that our samples have been composed of a single substance. On the other hand, we have observed that on storage umbellulone undergoes a slow isomerization to thymol.

(4) Infrared absorptions were determined with a Perkin–Elmer model 21 instrument using rock-salt optics; band positions are accurate to ±0.02μ. The band assignments and sample preparations are given in Table I.

(5) G. Schwarzenbach and C. Wittwer [*Helv. Chim. Acta*, **30**, 659 (1947)] have determined the pK of 2-hydroxy-3-methyl-2-cyclopentenone accurately as 9.60, and that of the analogous cyclohexenolone as 11.23.

(6) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509, 3543, 3176 (1951); C. F. Bergstrom and S. Siegel, *ibid.*, **74**, 145, 254 (1952); ref. 2.

(7) In terms of structures, the following hybridization is unimportant in the ground state of the conjugate base of α-hydroxyumbellulone



(8) O. Wallach and E. Besche, *Ann.*, **336**, 28 (1904).

(9) L. N. Ferguson, *Chem. Revs.*, **43**, 385 (1948).

TABLE I

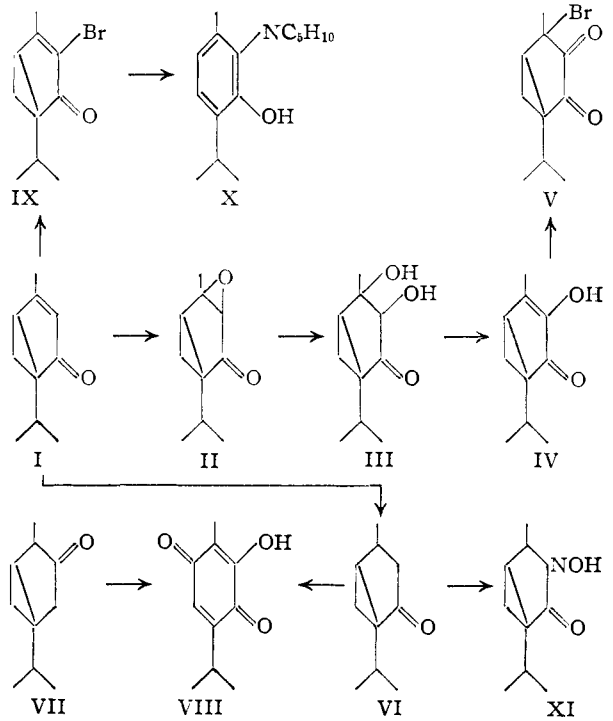
SPECTROSCOPIC PROPERTIES OF UMBELLULONE DERIVATIVES AND MODEL COMPOUNDS

Compound	Ultraviolet[a]	Infrared[a]	
Umbellulone (I)	220 (5900), 265 (3290), sh. 330 (210)	5.88 (C=O), 6.19 (C=C)	(f)[e]
α-Bromoumbellulone (IX)	220 (5800), 277 (3400), sh. 330 (310)	5.84 (C=O), 6.19 (C=C)	(f)
α-Hydroxyumbellulone (IV)	215 (6000), 290 (3500), sh. 335 (500)	2.98(OH), 5.92 (C=O), 6.07 (C=C)	(m)
α-Ethoxyumbellulone	220 (5400), 280 (3100), sh. 330 (600)	5.86 (C=O), 6.05 (C=C)	(f)
β-Dihydroumbellulone (VI)	210 (2470), 280 (35)	5.81 (C=O)	(f)
Epoxyumbellulone (II)	208 (4410), 301 (39)	5.77 (C=O)	(f)
1,2-Dihydroxydihydroumbellulone (III)	208 (2470), 285 (42)	3.00(OH), 5.79 (C=O)	(m)
1-Bromo-2-ketodihydroumbellulone (V)	No band, 220–350	5.63 (C=O), 5.71 (C=O)	(s)
Camphorquinone	No band, 220–350[b]	5.61 (C=O), 5.67 (C=O)	(s)
2-Isonitrosodihydroumbellulone (XI)	239 (12000)	3.07(OH), 5.85 (C=O), 6.16 (C=N)	(m)
Isonitroso camphor	241 (7600)	2.94(OH), 5.74 (C=O), 6.06 (C=N)	(m)
2-Piperidinothymol (X)	280 (3100)[c]	3.14(OH) 6.16, 6.34 (benzene nucleus)	(m)
Thymol	278 (2500)	3.15(OH) 6.14, 6.30 (benzene nucleus)	(m)
2-Hydroxythymoquinone (VIII)	264 (16000),[d]390 (1000)[d]		

[a] Determined with a Beckman model DU Instrument on alcohol solutions unless otherwise noted. The photomultiplier attachment was used below 220 mμ and optical density was determined at a maximum of 5 mμ intervals. Extinction coefficients are molar (ε) and are reliable to ±5%. [b] N. J. Leonard and R. M. Mader, THIS JOURNAL, 72, 5388 (1950). [c] The spectrum was the same in 1 *N* alcoholic hydrogen chloride. [d] In isoöctane solution. [e] Sample preparations are in parentheses: f = liquid film, m = mineral oil mull, s = 10% solution in CCl_4 (0.10 mm.).

Nitrosation of β-dihydroumbellulone using sodium ethoxide and ethyl or butyl nitrite produced the oximino ketone XI in small yield, identity being established by comparison of the ultraviolet and infrared spectra with those of isonitrosocamphor (*cf.* Table I). Attempts to hydrolyze the oximino ketone XI led to intractable materials. The major product of the nitrosation reaction was a neutral oil, hydrolyzable with alkali to a crystalline, amphoteric substance of the anomalous composition $C_{10}H_{19}NO_3$.

Boiling ethanolic alkali converted epoxyumbellulone (II) to α-ethoxyumbellulone and when epoxyumbellulone was refluxed briefly over alumina it was converted smoothly to 2-hydroxythymol. This last reaction, the results of the selenium dioxide oxidations and the formation of 2-piperidinothymol represent facile aromatizations of the type shown by umbellulone in its transformation by heat to thymol.[10]



Acknowledgment.—We express our appreciation to Mr. Gene Heckathorn of Heckathorn and Co., Richmond, Calif., for a generous gift of the oil of the California Bay tree, and to the E. I. du Pont de Nemours Co. for their fellowship which made the early completion of this work possible.

Experimental[11]

Umbellulone (I).—The isolation and properties of umbellulone have been previously described.[2] A freshly distilled sample of umbellulone had $n^{20}D$ 1.4835. After standing for two years it showed $n^{20}D$ 1.4885. A 5-ml. sample of the aged material was steam-distilled from 10 ml. of 3 *N* sodium hydroxide solution to yield 4.5 ml. of umbellulone of $n^{20}D$ 1.4828. Acidification of the alkaline residue produced 0.3 g. of thymol, identified by mixed melting point.

β-Dihydroumbellulone (VI).—β-Dihydroumbellulone of b.p. 131.8–131.9° at 90 mm. in a 1.5 foot Fenske column, $n^{20}D$ 1.4600, $[\alpha]^{25}D$ −55.1° (pure liquid, 1 dm.) was prepared in nearly quantitative yield by Raney nickel reduction, at room temperature and 900 p.s.i. hydrogen pressure, of umbellulone of b.p. 99–100° at 15 mm., $n^{20}D$ 1.4841, $\alpha^{25}D$ −39.4° (pure liquid, 1 dm.) following the method of Wienhaus.[12]

α-Bromoumbellulone (IX).—To 15 g. of umbellulone in 100 ml. of carbon tetrachloride cooled to −5° was slowly added 16 g. of bromine. After the addition was complete the excess bromine was destroyed by shaking the mixture with 100 ml. of ice-cold 10% sodium bisulfite solution. The organic layer was separated, dried over anhydrous sodium sulfate and then combined at −10° with 20 ml. of chilled piperidine. The mixture was allowed to come to room temperature and then to stand for one hour, whereupon dilute hydrochloric acid was added until the aqueous layer was acidic to litmus. The organic layer was separated, washed repeatedly with water after dilution with ether, dried and freed of solvent under reduced pressure. Distillation of the oil residue through a short Vigreux column yielded 16 g. of an oil of b.p. 145–150° at 22 mm. On being chilled the oil crystallized and recrystallization from light petroleum ether gave a good return of a white solid of m.p. 31–32°.

(10) F. W. Semmler, *Ber.*, **40**, 5019 (1907); **41**, 3992 (1908).

(11) Analyses are by Microchemical Specialties Co., Berkeley, Calif. Melting and boiling points are corrected. Ultraviolet and infrared spectra are reported in Table I.

(12) H. Wienhaus and K. Todenhöfer, *Schimmel's Report*, 285 (1929).

Anal. Calcd. for $C_{10}H_{13}BrO$: C, 52.40; H, 5.72. Found: C, 52.18; H, 5.82.

This substance is assigned the structure of α-bromoumbellulone (IX) on the basis of its spectroscopic properties (*cf.* Table I). The substance also results from treatment of umbellulone dibromide with potassium acetate in alcohol.[13] Attempts to hydrolyze α-bromoumbellulone with potassium acetate returned starting material; sodium methylate converted it into an intractable tar; hydrogen bromide in boiling acetic acid solution gave a small yield of umbellulone dibromide,[13] identified by mixed melting point determination.

2-Piperidinothymol (X).—A mixture of 5 g. of α-bromoumbellulone and 5 ml. of piperidine in 50 ml. of absolute ether was refluxed in the absence of oxygen for seven days after which time the piperidine hydrobromide which had separated was removed by filtration. The ethereal filtrate was washed several times with water and then extracted with 50 ml. of 10% sulfuric acid. Addition of sodium carbonate caused the separation of an oil which was taken up in hexane. Evaporation of the hexane left an oil (2.1 g.) which crystallized. Recrystallization from 85% alcohol gave 0.5 g. of white needles of m.p. 67.8–68.4°. The product was soluble in dilute acid and reprecipitated by base. It was insoluble in 10% sodium hydroxide solution but gave a deep-green color with ferric chloride solution in aqueous alcohol. The substance is assigned the structure of 2-piperidinothymol (X). Spectroscopic data are reported in Table I.

Anal. Calcd. for $C_{15}H_{22}NO$: C, 77.25; H, 9.87. Found: C, 77.29; H, 9.99.

Epoxyumbellulone (II).—To a cold solution of 10 g. of umbellulone and 20 ml. of 30% hydrogen peroxide in 60 ml. of methanol was slowly added 8 ml. of 4 *N* sodium hydroxide solution. After ten minutes the reaction mixture was diluted with water and the aqueous solution was repeatedly extracted with ether. Distillation of the residual oil after solvent removal gave 9.4 g. of colorless oil of b.p. 96.5–99.0° at 7–8 mm., $\alpha^{25}D$ −20.4° (pure liquid, 1-dm. tube) and $n^{20}D$ 1.4662. When chilled, the oil crystallized, and recrystallization from aqueous alcohol returned a white solid of m.p. 25–26° in good yield.[14]

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.44. Found: C, 72.40; H, 8.40.

Boiling epoxyumbellulone (10 g.) in 125 ml. of 5% alcoholic potassium hydroxide for 2 hours followed by dilution, extraction with ether and distillation as for the epoxy compound gave 7.6 g. of colorless oil, b.p. 80–83.5° at 3–4 mm., and $n^{20}D$ 1.4771 identified as **α-ethoxyumbellulone** through its spectroscopic properties (*cf.* Table I).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.23; H, 9.27. Found: C, 74.45; H, 9.54.

One gram of epoxyumbellulone was boiled with a pinch of alumina and a few grains of sodium bisulfite for five minutes. On being cooled, slow crystallization followed. Recrystallization from hexane gave 0.2 g. of a white crystalline substance, m.p. 90.1–90.8°, which dissolved in alkali gave a green color with ferric chloride solution, and to which is assigned the structure of **2-hydroxythymol**, on the basis of spectroscopic analysis (*cf.* Table I).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.44. Found: C, 72.21; H, 8.66.

1,2-Dihydroxydihydroumbellulone (III).—A mixture of 19 g. of epoxyumbellulone (II), 50 ml. of water and 15 drops of 20% sulfuric acid was heated with stirring on the steam-bath for 5 minutes whereupon a homogeneous solution resulted. Multiple ether extraction followed by drying and evaporation of the extract left an oily residue which was distilled through a short, helices-packed column to yield a colorless distillate of b.p. 135–140° at 4 mm., the majority of which solidified. Crystallization from light petroleum ether gave 8.0 g. of white crystalline material of m.p. 65.9–66.7°.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.20; H, 8.13.

The infrared and ultraviolet absorption characteristics showed that this material was 1,2-dihydroxydihydroumbellulone (III) (Table I).

α-Hydroxyumbellulone (IV).—To a solution of 1 g. of 1,2-dihydroxydihydroumbellulone (III) in 10 ml. of water was added 1 ml. of 10% sodium hydroxide solution. The mixture was heated under reflux for 5 minutes, cooled, acidified and chilled. The crystalline solid which formed was separated and dried and crystallized from hexane to yield 0.5 g. of a white, crystalline solid of m.p. 75–78°. This material was irreversibly converted to a yellow, viscous material on exposure to air and hence was analyzed only in the form of a derivative (*cf.* below). It dissolved in 10% sodium carbonate solution and was regenerated on acidification. With ferric chloride in alcohol it gave a purple color, and it reduced Fehling solution, alkaline hydrogen peroxide solution and dilute potassium permanganate solution. Titration of the compound in 50% alcohol solution using an equilibrated glass electrode showed an approximate *pK* of 9.8 and a neutralization equivalent of 167 to be compared with the calculated value of 166 for $C_{10}H_{14}O_2$. The infrared and ultraviolet absorption agreed with the structural assignment α-hydroxyumbellulone (IV) (*cf.* Table I).

Treatment of 0.5 g. of α-hydroxyumbellulone with 0.5 g. of bromine in 30 ml. of carbon tetrachloride solution followed by removal of excess bromine and solvent by distillation gave a crystalline residue which was recrystallized from aqueous alcohol to yield 0.15 g. of a bright-yellow material of m.p. 85.0–85.8°, identified as **1-bromo-2-ketodihydroumbellulone (V)** by comparison of its ultraviolet and infrared absorption spectra with those of camphorquinone[15] (*cf.* Table I).

Anal. Calcd. for $C_{10}H_{13}BrO_2$: C, 48.91; H, 5.17. Found: C, 48.48; H, 4.79.

Selenium Dioxide Oxidations. A. Of β-Dihydroumbellulone (VI).—A solution of 15 g. of β-dihydroumbellulone and 11.5 g. of selenium dioxide in 20 ml. of alcohol was boiled under reflux for 12 hours. Steam distillation of the resulting brown solution gave 0.8 g. of 2-hydroxythymoquinone of m.p. 165–166.5° after crystallization from alcohol. The substance was identified by comparison in mixed melting-point and spectroscopic properties with an authentic sample prepared from 2,6-dinitrothymol following the method of Carstanjen.[16]

B. Of Thujone.—Thujone (55 g. of b.p. 125.5–128.6° at 90 mm. in a 50 theoretical plate Lecky–Ewell column, and $\alpha^{25}D$ −9.0° (pure liquid, 1 dm. tube)) was boiled with 40 g. of selenium dioxide in 5.0 ml. of alcohol for 20 hours. Steam distillation followed by crystallization of the crude product from alcohol gave 1.7 g. of 2-hydroxythymoquinone of m.p. 165.3–167°, identified as described above.

Nitrosation of β-Dihydroumbellulone (VI).—To a solution of 5 g. of β-dihydroumbellulone in 75 ml. of dry ether was added a molar equivalent of sodium. The sodium dissolved slowly with evolution of hydrogen and formation of the sodium enolate of the ketone as evidenced by nearly quantitative recovery of β-dihydroumbellulone on addition of acid in one experiment. To a solution of the enolate thus prepared and cooled to 0° was added a two-fold excess of ethyl nitrite. After allowing the reaction mixture to come to room temperature during 2 hours, water and ether were added and the layers were separated. Acidification of the water layer with 10% sulfuric acid produced a heavy, red oil (2 g.) from which slowly crystallized **2-isonitrosodihydroumbellulone (XI)**, which was obtained as white crystals (0.06 g.) of m.p. 81.5–83° after multiple crystallizations from ligroin. The structure assignment is based upon the spectroscopic properties in comparison with those of isonitrosocamphor[17] reported in Table I.

Anal. Calcd. for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34. Found: C, 66.49; H, 8.33.

The ether layer (see above) was concentrated and the residual oil was distilled giving an ill-defined fraction (0.5 g.) of b.p. 130–145° at 4 mm. which gave a purple color with ferric chloride solution and dissolved on boiling for 45 minutes with 10% sodium hydroxide solution. Careful acidification of the saponification mixture to *p*H 6 produced an oil which crystallized on standing to yield 0.3 g. of a white solid of m.p. 154.1–154.6° after crystallization from alcohol.

(13) R. H. Eastman and A. Oken, THIS JOURNAL, **75**, 1029 (1953).

(14) For a discussion of the mechanism of epoxyketone formation see C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

(15) W. C. Evans, J. M. Ridgion and J. L. Simonsen, *J. Chem. Soc.*, 137 (1934).

(16) E. Carstanjen, *J. prakt. Chem.*, [2] **3**, 58 (1871).

(17) O. Forster, *J. Chem. Soc.*, 2670 (1926).

Anal. Calcd. for $C_{10}H_{19}NO_3$: C, 59.70; H, 9.45; N, 6.96; neut. equiv., 201. Found: C, 59.97; H, 9.46; N, 6.70; neut. equiv., 195.

The ultraviolet absorption spectrum of an alcohol solution of the substance showed no appreciable absorption down to 220 mμ. The infrared absorption showed strong similarities to that of the oxime of 3,7-dimethyl-6-ketoöctanoic acid[18] in the OH, carbonyl and double bond regions and the substance was found to be amphoteric, being soluble in 5% hydrochloric acid and dilute sodium bicarbonate solutions. Interest in this compound hinges on the fact that its molecular formula and properties are those of an acyclic, saturated oximino acid indicating that a reduction took place in its formation and suggesting that the cyclopropane ring participated in the nitrosation reaction.

(18) A. Baeyer and O. Manasse, *Ber.*, **27**, 1914 (1894).

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Stereochemistry of the Addition of Hydrogen Bromide to 1,2-Dimethylcyclohexene

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It has been found that 1,2-dimethylcyclohexene adds hydrogen bromide to give *trans*-1,2-dimethylcyclohexyl bromide in acetic acid and in pentane. If the reaction in pentane is carried out by condensing an excess of hydrogen bromide in the reaction cell at −195° and then warming the heterogeneous mixture to −78°, some 20% *cis* bromide is produced. Addition to the isomeric olefins, 2,3-dimethylcyclohexene and 2-methylmethylenecyclohexane give, respectively, 13 and 35% *cis* bromide. From these results it is inferred that the addition of hydrogen bromide is not the microscopic reverse of the first-order elimination reactions of the bromides which are observed under different conditions. This conclusion is further strengthened by the fact that the solvolysis rates of the *cis* and *trans* bromides are virtually identical indicating that there is no participation of the *trans* hydrogen during the ionization of the *trans* bromide.

The relative antiquity of the reaction of hydrogen halides with olefins is indicated by the fact that Markownikoff formulated his famous rule concerning the structural specificity of the reaction in 1875.[1] Many years later Kharasch, Mayo and their co-workers elucidated in considerable detail the free radical mechanism of the abnormal addition of hydrogen bromide to unsymmetrical olefins.[2] Very recently Goering, Abell and Aycock have reported data which indicate a surprising stereospecificity for the radical reaction.[3]

It is surprising in a way that no careful study has been made of the mechanism of the more usual "ionic" reaction. The gross aspects are indicated by the mechanistic equivalent of Markownikoff's rule. However, questions of timing and stereochemistry have not been investigated with any care. Two cases are known in which the steric course of hydrogen bromide addition to an olefin has been determined. It is reported that both bromomaleic and bromofumaric acids give *meso*-dibromosuccinic acid[4] and that dibenzo[2,2,2]-bicycloöctatriene-2,3-dicarboxylic acid gives the *trans* adduct.[5] These examples are of limited general value because of the possibility of isomerization of the initial products and because the role of the neighboring carboxyl groups has not been clarified.

Because of the importance of the general reaction we have studied the steric course of the addition of hydrogen bromide to 1,2-dimethylcyclohexene and its isomers. This olefin is particularly appropriate for the study for several reasons. First, it is symmetrical so only two diastereomeric products can be formed unless unexpected skeletal rearrangements occur. Second, the bromides may be distinguished by the differences in their reactivity in the second-order elimination reaction. Third, the reaction is so rapid at low temperatures that it is highly improbable that the radical reaction can compete with polar processes. Lastly, the addition of hydrogen bromide to two isomeric olefins, 2,3-dimethylcyclohexene and 2-methylmethylenecyclohexane, gives mixtures of the same bromides as products.

(1) S. Markownikoff, *Compt. rend.*, **81**, 670 (1875).

(2) For reviews see M. S. Kharasch, *J. Chem. Ed.*, **8**, 1703 (1931); F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

(3) H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

(4) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 302, cites unpublished results by Mansfield, Kharasch and Mayo. Details are not available but it is implied that the reaction is ionic.

(5) W. R. Vaughan and K. Milton, THIS JOURNAL, **74**, 5623 (1952).

Experimental

Preparation of 1,2-Dimethylcyclohexene and 2,3-Dimethylcyclohexene.—A mixture of the isomeric 1,2-dimethylcyclohexanols[6] was heated with a catalytic amount of iodine and the olefinic products were distilled from the reaction mixture as formed. The crude product was fractionated through a center-rod column operating at an efficiency of about 50 plates. In a typical run, 50 g. of crude product gave a trace of 2-methylmethylenecyclohexane, 7–8 g. of a product boiling at 129–131° from which about 5 g. of 2,3-dimethylcyclohexene could be isolated by refractionation, and about 40 g. of pure 1,2-dimethylcyclohexene. Physical constants are reported in Table I.

Oxidation of 2,3-Dimethylcyclohexene.—Since this olefin has apparently not been reported previously it was degraded to establish structure. Four grams of the olefin was stirred with 12 g. of potassium permanganate in 400 ml. of water. The reaction was allowed to proceed at ambient temperatures until the permanganate disappeared and the solution was boiled to coagulate the manganese dioxide and was then filtered. The filtrate was acidified with sulfuric acid and extracted with chloroform. The brown oil which remained after the removal of chloroform was not characterized but was stirred with an excess of aqueous sodium hypochlorite for 12 hours. At the end of this time the solution was brought to a boil, cooled, acidified and extracted with chloroform. The chloroform was removed by distillation and the residue was recrystallized from hexane giving 1.3 g. of pure α-methyladipic acid, m.p. 64°, and 1.2 g., m.p. 62–64°, over-all yield 53%, no melting point depression on admixture with authentic material.

2-Methylmethylenecyclohexane was prepared by Wallach[7] by decarboxylation of 2-methylcyclohexylideneacetic

(6) Prepared by the method of G. Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 241 (1938).

(7) O. Wallach and E. Beschke, *Ann.*, **347**, 337 (1906).