[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Sulfonation of 1-Methyl-3-phenylindane, a Dimer of Styrene[1]

BY MILTON J. ROSEN[2] AND PAUL E. SPOERRI

A study has been made of the sulfonation of 1-methyl-3-phenylindane, a dimer of styrene. A method has been developed for isolating in pure form three of the isomeric monosulfonates. Various derivatives of these sulfonates are described. The potassium salts of these sulfonates do not enter into the usual high temperature replacement reactions with cyanides, potassium ferrocyanide, or potassium formate. Instead, in these cases, or in the absence of any reagent, pyrolysis yields a mixture of methyl phenylindenes.

Because of the ready availability and comparatively low cost of styrene, an investigation of the possible utilization of this material in the preparation of a new type of alkyl aryl sulfonate has been made. Since a hydrophobic group of about 12–18 carbon atoms is usually associated with surface activity, dimeric, rather than monomeric or trimeric, styrene was chosen for our investigation.

Two dimers have been prepared directly from monomeric styrene,[3,4] 1,3-diphenylbutene-1 and 1-methyl-3-phenylindane. Only the latter was chosen for sulfonation, since the former is unstable in the presence of sulfuric acid.[5] The 1-methyl-3-phenylindane used in the sulfonation experiments was prepared from monomeric styrene in 67% yield by a method described previously.[4]

Since there are, in the hydrocarbon, two independent aromatic nuclei, disulfonates are readily produced. Only the monosulfonates were of interest, however, since the disulfonates were too water-soluble to have surface activity.

Preliminary sulfonation experiments showed that concentrated sulfuric acid would not be suitable for our purpose. The hydrocarbon proved to be quite inert to a moderate excess of cold, concentrated sulfuric acid (2.4 moles per mole of hydrocarbon). Higher temperatures or larger excesses of reagent tended to produce mainly disulfonates. The only conditions under which any appreciable amount of *mono*-sulfonates was obtained was at 80–90°, using a 2.4:1 molar ratio of sulfuric acid to hydrocarbon. After 8 hours of stirring, a yield of monosulfonates totaling 18% of the theoretical amount was isolated from the reaction mixture.

Chlorosulfonic acid proved more suitable. Several runs, in which conditions of time, temperature, solvent, and excess of sulfonating agent were varied, resulted in the selection of operating conditions under which 90% of the hydrocarbon was sulfonated.

Since there are seven possible aromatic monosulfonic acids of 1-methyl-3-phenylindane, separation of the isomeric products was a major problem. A procedure was finally developed by means of which three of the isomeric sulfonates were separated in substantially pure form. Two of them were isolated as the crystalline, free sulfonic acids (sulfonic acids II and III), while the third, which did not form a crystalline sulfonic acid, was isolated as the water-insoluble copper salt (copper sulfonate I).

All attempts to determine the position of the sulfonic acid group in any of these sulfonates were unsuccessful. The sulfonic acid group in these compounds is not replaced upon pyrolytic treatment of the corresponding potassium salts with either potassium ferrocyanide, potassium cyanide, a mixture of potassium and cuprous cyanides, or sodium formate. In all cases, the only material isolated from the reaction mixture, either by distillation *in vacuo* or by benzene extraction, was a yellow, unsaturated hydrocarbon oil, which varied only slightly in its physical properties with changes in sulfonate, reagent, and reaction conditions. Ultraviolet absorption spectra on two samples of this oil, with different refractive indices, obtained from two isomeric potassium sulfonates, indicated that there was very little difference between these products (Fig. 1). Oxidation of this oil with chromic acid in acetic acid gave a major yield of *o*-benzoylbenzoic acid (44%), a minor yield of anthraquinone (11%) and benzoic acid (0.8%). Reduction with metallic sodium in ethanol yielded

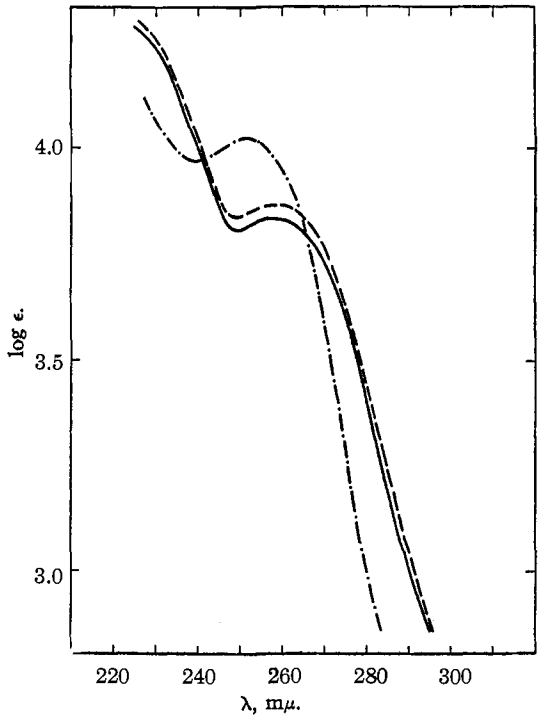

Fig. 1.—Ultraviolet absorption spectra: —, pyrolysis product, $n^{20}D$ 1.6112, from potassium sulfonate I (isopropyl alcohol); - - -, pyrolysis product, $n^{20}D$ 1.6142, from potassium sulfonate II (isopropyl alcohol); -·-·-, indene (hexane).[6]

(1) From a dissertation submitted by Milton J. Rosen to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1949.

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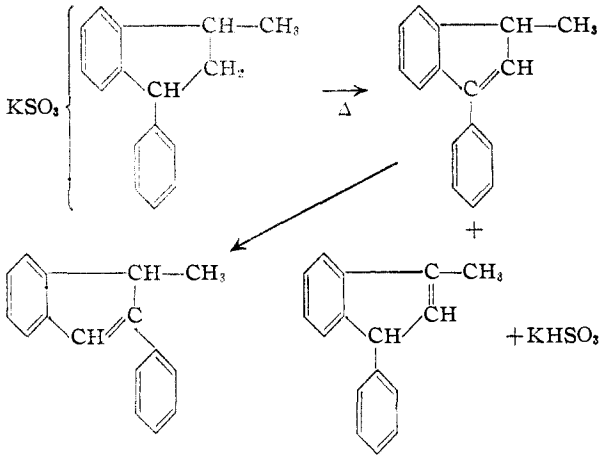
(3) J. Risi and D. Gauvin, *Can. J. Research*, **B14**, 255 (1936).

(4) P. E. Spoerri and M. J. Rosen, THIS JOURNAL, **72**, 4918 (1950).

(5) R. Stoermer and N. Kootz, *Ber.*, **61**, 2330 (1928).

a saturated, colorless, hydrocarbon oil, $n^{20}D$ 1.5883, which, upon oxidation with chromic acid, yielded benzoylbenzoic acid (33%), anthraquinone (3%) and benzoic acid (0.8%). Since carefully purified 1-methyl-3-phenylindane has a lower refractive index ($n^{20}D$ 1.5805), and yields no benzoic acid upon chromic acid oxidation,[4] but only *o*-benzoylbenzoic acid (40%) and anthraquinone (3.4%), it seemed probable that this saturated hydrocarbon was a mixture of 1-methyl-3-phenylindane and other isomeric hydrocarbons. The original hydrocarbon oil produced upon pyrolysis of the potassium salts of these sulfonates appeared, therefore, to be a mixture of methyl-phenylindenes. A comparison of the ultraviolet absorption spectrum of this oil and that of indene[6] (Fig. 1) confirmed this belief. The presence of benzoic acid among the oxidation products may be due to the presence of a small amount of 3-methyl-2-phenylindene. Its formation may be accounted for by a reaction analogous to the formation of 2-phenylindene from 1-phenylindene by distillation of the latter, under reduced pressure, over pumice at dark red heat.[7] Since this mixture of indenes was formed in all cases, regardless of the sulfonate used or the reagent added, we now submitted the dry potassium salt of one of the sulfonates to pyrolysis in the absence of any reagent. The products obtained were the same hydrocarbon oil, some carbonaceous material and sodium bisulfite.

On the basis of this evidence, therefore, it appears that the reaction occurring in all these pyrolyses may be described as



A somewhat similar reaction has been reported by Dziewonski and Stolyhwo.[8] In their work on two isomeric acenaphthene sulfonic acids, they found that both formed acenaphthylene upon being pyrolyzed with or without replacement reagents.

Experimental

Sulfonation of 1-Methyl-3-phenylindane with Chlorosulfonic Acid.—The 1-methyl-3-phenylindane (124.8 g., 0.6 mole) in a 3-necked flask provided with a sealed mechanical stirring device, a dropping funnel, a thermometer and a calcium chloride drying tube, was dissolved in four times its weight of dry chloroform. With constant agitation and cooling, 76.8 g. (0.66 mole) of freshly distilled chlorosulfonic acid was added dropwise, while the temperature was maintained at 30° by means of a water-bath. After addition of the chlorosulfonic acid was complete, the reaction mixture was stirred for an additional 4 hours at 30°.

The reaction mixture was well shaken with an equal volume (570 ml.) of water, and the layers were separated. The aqueous layer was extracted three times with carbon tetrachloride, and the extracts were combined with the chloroform layer. This solution, upon removal of the solvents, yielded 10.9 g. (8.7%) of unchanged 1-methyl-3-phenylindane.

Isolation of Crystalline Sulfonic Acid II.—The hydrocarbon-free, aqueous solution of sulfonates obtained above was shaken with two-thirds its volume (360 ml.) of concentrated hydrochloric acid and well chilled in the refrigerator for 3 days. The white, crystalline sulfonic acid which was precipitated was removed by filtration and washed twice with ice-cold 1:1 (volume) hydrochloric acid. The filtrate was replaced in the refrigerator for a few days, and any additional precipitated material was combined with the previous batch. This procedure was repeated until no additional yield was obtained.

The combined yield, upon being recrystallized once or twice from 1:2 hydrochloric acid, had a constant m.p. of 128–129° (cor. 130–131°), after drying *in vacuo* over phosphorus pentoxide. The yield of shining, white plates was 17.3 g. (10.3%, based on hydrocarbon sulfonated). This product is called **crystalline sulfonic acid II** in all subsequent work. It was rather unstable, and became gummy and yellowish after a few days. A neutralization equivalent on the freshly prepared material seemed to indicate one molecule of water in the compound. *Anal.* Calcd. for $C_{16}H_{15}SO_3H \cdot H_2O$: equiv. wt., 306.4. Found: equiv. wt., 307.0.

The methyl ester was prepared by suspending the acid in absolute ether and treating the suspension with an ethereal solution of diazomethane, according to the method of Bachmann and Struve.[9] The product, white prism clusters, after a few recrystallizations from petroleum ether (60–70°), had a constant m.p. of 92.7–93.0° (cor. 93.6–93.9°). *Anal.* Calcd. for $C_{16}H_{15}SO_3CH_3$: C, 67.5; H, 6.00; S, 10.60. Found: C, 67.5; H, 6.01; S, 10.33.

The *p*-toluidine salt of this sulfonic acid, prepared by the method of Fieser,[10] melted at 187.3–187.8° dec. (cor. 191.6–192.1°). *Anal.* Calcd. for $C_{16}H_{15}SO_3NH_3C_6H_4CH_3$: C, 69.9; H, 6.37; N, 3.54. Found: C, 70.4; H, 6.63; N, 3.99.

The *p*-chloraniline salt, prepared by essentially the same method, melted at 191–192° dec. (cor. 195.5–196.5°). *Anal.* Calcd. for $C_{16}H_{15}SO_3NH_3C_6H_4Cl \cdot H_2O$; C, 60.9; H, 5.57; N, 3.23. Found: C, 61.2; H, 5.38; N, 3.10.

Isolation of Copper Sulfonate I.—The filtrate, after removal of the crystalline sulfonic acid II, was allowed to separate into layers, and the upper layer, containing only a small quantity of disulfonic acids, was discarded. The yellow lower layer (365 ml.) was diluted with two and one-quarter times its volume of water, and neutralized by slowly adding 60 g. (0.27 mole) of copper basic carbonate, $Cu(OH)_2 \cdot CuCO_3$. The mixture was heated to boiling, made acid to congo red with hydrochloric acid, cooled in the refrigerator, and filtered. The residue was digested three times with 5% cupric chloride solution, and the washings were combined with the filtrate, labeled Solution A, and reserved for further use.

The residue was extracted several times with boiling water to remove any soluble copper sulfonates, and the extracts were combined and labeled solution B.

The water-insoluble residue, called copper sulfonate I, weighed 55 g. (28.3%, based on the hydrocarbon sulfonated). Upon recrystallization from 200–250 parts boiling water, it was obtained as pale green plates. Dehydration to constant weight at 100° and 15 mm. pressure in an Abderhalden pistol over phosphorus pentoxide indicated four molecules of water in the compound. *Anal.* Calcd. for $(C_{16}H_{15}SO_3)_2Cu \cdot 3H_2O$: C, 54.1; H, 5.39; Cu, 8.95; H_2O, 10.14. Found: C, 54.5; H, 5.88; Cu, 8.82; H_2O, 10.01.

Upon treatment of this salt with concentrated hydrochloric acid, no crystalline sulfonic acid was obtained. A

(6) C. S. Marvel and W. J. Peppel, THIS JOURNAL, **61**, 895 (1939).

(7) J. v. Braun and G. Manz, *Ber.*, **62**, 1059 (1929).

(8) K. Dziewonski and T. Stolyhwo, *ibid.*, **57B**, 1531 (1924).

(9) W. E. Bachmann and W. S. Struve in R. Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 50.

(10) L. Fieser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 482.

second liquid phase, containing the free sulfonic acid, was formed, but did not crystallize, even after several weeks in the refrigerator.

Since this copper salt has no definite melting point, the melting point of the *p*-chloroaniline salt made from it was used to indicate its purity. The *p*-chloraniline salt was prepared as follows: Five ml. of water was added to 0.1 g. of the copper sulfonate, the mixture was made alkaline with a few crystals of sodium carbonate and heated on a steam-bath until all the copper ion had been precipitated as brown copper oxide. A pinch of Norit was then added, and the hot solution filtered. The clear filtrate, containing the sulfonate as the soluble sodium salt, was cooled, acidified to congo red with dilute hydrochloric acid and added, with stirring, to 5 ml. of a cold solution of 0.1 g. of *p*-chloroaniline in dilute hydrochloric acid. The white **p-chloroaniline salt**, which was precipitated immediately, was removed by filtration, washed several times with water, and air-dried. It melted with decomposition at 183–184° (cor. 187.5–188.5°). *Anal.* Calcd. for $C_{16}H_{15}SO_3NH_3C_6H_4Cl\cdot H_2O$: C, 60.9; H, 5.57; N, 3.23. Found: C, 60.8; H, 5.34; N, 3.22.

Isolation of Additional Crystalline Sulfonic Acid II from Solution B.—Solution B was evaporated to one-half (900 ml.) of its original volume and allowed to cool in the refrigerator overnight. The silver-blue crystals of copper sulfonate which were precipitated were removed by filtration and converted to the free sulfonic acid by treatment with 300 ml. of 2:1 hydrochloric acid. The mixture was placed in the refrigerator overnight, and the precipitated crystalline sulfonic acid was removed by filtration, and washed well with cold 2:1 hydrochloric acid until free of copper ion (as evidenced by the disappearance of the greenish-yellow color due to the tetrachlorocuprate ion). The white residue, upon being recrystallized from 1:2 hydrochloric acid, and dried *in vacuo* over phosphorus pentoxide, melted at 126.5–129° (cor. 129.5–131°). The yield of this crude crystalline sulfonic acid II was 15.5 g. (9.2%, based on hydrocarbon sulfonated).

After a few more crystallizations from 1:2 hydrochloric acid, the product had a constant m.p. 128–129° (cor. 130–131°), showed no m.p. depression when mixed with a sample of the crystalline sulfonic acid II isolated previously, and yielded a methyl ester and a *p*-chloroaniline salt identical in m.p. with those of the latter.

Isolation of Crystalline Sulfonic Acid III.—Solution A was evaporated to 900 ml. (one-third its original volume), treated with 80 g. of cupric chloride dihydrate, chilled in the refrigerator, and filtered. The copper sulfonate residue was recrystallized a few times from 20% cupric chloride solution, and then leached with 300 g. of a 3% cupric chloride solution. The clear filtrate was evaporated to 100 ml., treated with 200 ml. of concentrated hydrochloric acid, and allowed to crystallize in the refrigerator. The precipitated sulfonic acid was removed by filtration, washed well with ice-cold 2:1 hydrochloric acid, and recrystallized twice from 2:1, then several times from 1:1, and finally from 2:3 hydrochloric acid, until a constant m.p. of 128–129° (cor. 130–131°) was obtained. The yield of **crystalline sulfonic acid III**, white prisms, was about 5 g. (about 3%, based on hydrocarbon sulfonated).

This product was quite unstable, and became discolored and gummy overnight, even when kept over phosphorus pentoxide in a vacuum desiccator. It was converted to the **methyl ester** by a method identical with that used for crystalline sulfonic acid II. The product, white prisms, had a constant m.p. of 110.5–111.5° (cor. 111.9–112.9°). *Anal.* Calcd. for $C_{16}H_{15}SO_3CH_3$: C, 67.5; H, 6.00; S, 10.60. Found: C, 67.3; H, 5.94; S, 10.79.

The *p*-chloroaniline salt, prepared by the same method as that used for crystalline sulfonic acid II, melted at 175.5–176.5° dec. (cor. 179–180°). *Anal.* Calcd. for $C_{16}H_{15}SO_3NH_3C_6H_4Cl\cdot H_2O$: C, 60.9; H, 5.57; N, 3.23. Found: C, 60.8; H, 5.27; N, 3.21.

Pyrolytic Reactions of Potassium Sulfonate I.—This sulfonate was prepared from copper sulfonate I by heating 8.7 g. of the latter with 4 g. of potassium carbonate and 200 ml. of water until the precipitation of brown copper oxide was complete. A small amount of Norit was added, and the hot mixture was filtered. The filtrate was made just alkaline to litmus with dilute hydrochloric acid, 10 g. of solid potassium chloride was added, and the solution was allowed to crystallize in the refrigerator. The precipitated potassium sulfonate was removed by filtration, dried at 110°, and kept over phosphorus pentoxide in a vacuum desiccator. The yield was quantitative.

The pyrolysis procedure was based on that of Fieser.[11] The potassium sulfonate (3.2 g.) and anhydrous potassium ferrocyanide (6.4 g.) were ground together in a mortar, then tumbled together in a closed jar, and finally placed in a 50-ml. distilling flask immersed in a Woods metal bath. The mixture was heated at a pressure of 1 mm. and when the bath temperature reached 350° a yellow oil distilled. The yield was 0.6 g. (34%). Upon redistillation, the product, $n^{20}D$ 1.6112, d^{20}_4 1.047, b.p. 155–157° (cor. 157–159°) (7 mm.), was still yellow. Elemental analysis of this product, by fusion with metallic sodium, according to the method of Shriner and Fuson,[12] revealed no nitrogen or sulfur present.

Treatment of 2.5 g. (0.012 mole) of the product in boiling 95% ethanol with 5 g. (0.22 mole) of metallic sodium, followed by steam distillation of the reaction mixture, yielded an oil, $n^{20}D$ 1.5883, with an odor similar to that of 1-methyl-3-phenylindane. The yield was 2.0 g. (79%). Treatment of 2 g. (0.0096 mole) of this oil with 10 g. (0.10 mole) of chromic acid in aqueous acetic acid, by the method previously described, yielded 0.7 g. of *o*-benzoylbenzoic acid (33%), 60 mg. of anthraquinone (3%) and 20 mg. of benzoic acid (0.8%).

A solution of this pyrolysis product, $n^{20}D$ 1.6112, in isopropyl alcohol, containing 0.1339 g. of hydrocarbon per 100 ml. of solution, was diluted 1:99 with isopropyl alcohol and the ultraviolet absorption of the resulting solution measured with a Beckman quartz spectrophotometer.

A repetition of this pyrolysis, using 3 g. of potassium sulfonate I and 6 g. of anhydrous potassium cyanide, yielded 0.7 g. (42%) of a similar oil.

A repetition of this pyrolysis, using 3 g. of potassium sulfonate I and a mixture of 5.1 g. of potassium cyanide and 4.9 g. of cuprous cyanide at a pressure of 19 mm., yielded 0.6 g. (34%) of a similar oil, $n^{23}D$ 1.6071 (upon redistillation).

Three grams of potassium sulfonate I and 4 g. of anhydrous sodium formate were heated together in a porcelain casserole at 200–250°, with frequent stirring. Samples taken at various times indicated that no water-insoluble acid was formed at any time. After 1 hour of heating, yellow fumes were evolved. The casserole was covered with a watch glass, and a few drops of this vapor were condensed upon it. The condensate was a yellow, unsaturated hydrocarbon oil, $n^{20}D$ 1.6117.

Pyrolytic Reactions of Potassium Sulfonate II.—This sulfonate was prepared from crystalline sulfonic acid II by dissolving 7.5 g. of the latter in 100 ml. of water, neutralizing the solution to litmus with potassium hydroxide, and allowing it to crystallize in the refrigerator overnight. The precipitated potassium sulfonate was removed by filtration, dried at 110°, and kept over phosphorus pentoxide in a vacuum desiccator. The yield was 7.7 g. (96%).

Three grams of this sulfonate was pyrolyzed in the presence of 6 g. of anhydrous potassium ferrocyanide at a pressure of 14 mm. by the usual procedure. The yellow oil distilled over when the bath temperature reached 350°. The yield was 0.9 g. (54%). Upon redistillation, the product, $n^{20}D$ 1.6142, d^{20}_4 1.047, boiled at 153–155° (cor. 155–157°) (6 mm.).

Oxidation of 2.3 g. (0.011 mole) of the product with 11.5 g. (0.115 mole) of chromic acid in aqueous acetic acid by the usual method yielded 1.1 g. (44%) of *o*-benzoylbenzoic acid, 263 mg. (11.3%) of anthraquinone and 23 mg. (0.8%) of benzoic acid.

A solution of the pyrolysis product, $n^{20}D$ 1.6142, in isopropyl alcohol, containing 0.1366 g. of hydrocarbon per 100 ml. of solution, was diluted 1:99 with isopropyl alcohol, and the ultraviolet absorption of the resulting solution measured with a Beckman quartz spectrophotometer.

The pyrolysis was repeated, using 2 g. of potassium sulfonate II, but omitting the potassium ferrocyanide. The yellow oil again distilled when the bath temperature reached 350°. The yield was 0.3 g. (24%). The residue in the flask was leached with water. The aqueous extract had a *p*H of 7–8 and, upon acidification, evolved sulfur dioxide.

(11) L. F. Fieser, THIS JOURNAL, **54**, 4110 (1932).

(12) R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 52.

The black, water-insoluble residue (0.6 g.) was almost completely acetone- and benzene-insoluble, and consisted mainly of carbonized material.

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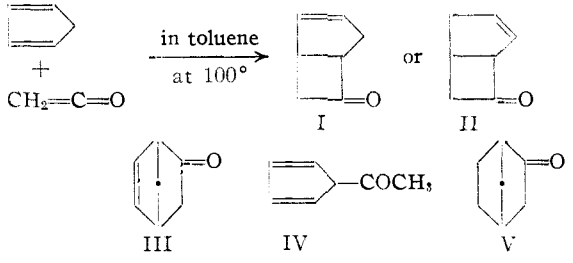
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Addition of Ketene to Cyclic Conjugated Dienes

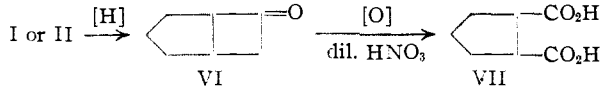
BY A. T. BLOMQUIST AND JACK KWIATEK[1]

The addition of ketene to cyclopentadiene and 1,3-cyclohexadiene has been found to afford unsaturated bicyclic ketones derived from bicyclo[3.2.0]heptane and bicyclo[4.2.0]octane, respectively. The saturated ketone derived from the ketene–cyclopentadiene adduct yields *cis*-cyclopentane-1,2-dicarboxylic acid on oxidation. Complete reduction of the ketene–cyclohexadiene adduct gave the previously described bicyclo[4.2.0]octane. A number of compounds containing the bicyclo-[3.2.0]heptane and bicyclo[4.2.0]octane ring structures are described.

Although several investigators have reported the addition of ketoketenes to conjugated dienes as affording cyclobutanone derivatives,[2,3,4,5] there are few recorded studies of the parent compound ketene to dienes. Hurd and co-workers[6] observed that liquid ketene did not add to isoprene while Smith, *et al.*, stated that ketene itself was inert toward cyclopentadiene under a variety of conditions. Subsequently Brooks and Wilbert[7] obtained an unsaturated ketone when a mixture of ketene and cyclopentadiene in toluene was heated at 100° under pressure. This ketone, presumably resulting from a 1,2-addition of ketene to the diene, was indicated as having either structure I or II, although structures III and IV are also possible. The evidence given in support of the cyclobutanone structure (I or II) for the adduct was the following. Hydrogenation of the adduct gave a saturated ketone which was not identical with norcamphor (V), and oxidation of this saturated ketone yielded glutaric acid.



If the saturated ketone obtained from the adduct were a cyclobutanone derivative (VI), it should yield cyclopentane-1,2-dicarboxylic acid (VII) upon oxidation. Accordingly we have repeated the



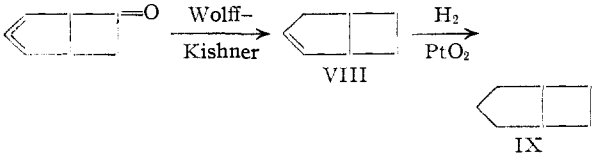
experiment of Brooks and Wilbert.[7] From the reaction of ketene with cyclopentadiene carried out at 100° for two hours in toluene under pressure there was obtained a liquid unsaturated ketone in 17–18% yield (as the semicarbazone based on ketene). The pure unsaturated ketone absorbed 0.996 molar equivalent of hydrogen to form a liquid ketone not identical with norcamphor. Oxidation of the saturated ketone with dilute nitric acid gave *cis*-cyclopentane-1,2-dicarboxylic acid, characterized by its anhydride and N-phenylimide. This confirms the bicyclo[3.2.0]-?-hepten-6-one structure (I or II) for the ketene–cyclopentadiene adduct as proposed by Brooks and Wilbert. Table I gives a comparison of the properties of the saturated and unsaturated ketones obtained in this investigation with those obtained by Brooks and Wilbert. The differences are possibly due to the different methods used in the purification of the unsaturated ketone. Brooks and Wilbert effected the purification of their adduct through the bisulfite addition product.

TABLE I

	Bicyclo[3.2.0]-?-hepten-6-one		Bicyclo[3.2.0]heptan-6-one	
Property	This study	Brooks and Wilbert[7]	This study	Brooks and Wilbert[7]
B.p., °C.	162–164	157.5–159	162–166	164–165
M.p., °C.[a]	219–220	222	198.5–201	216
d^{20}_4	1.0248	0.9813	0.9940	0.9958
$n^{20}D$	1.4819	.....	1.4679	1.5030
M_D	30.08	.....	30.80	32.72
M_D (calcd.)	30.18	.....	30.65	.....

[a] M.p. of semicarbazone.

Using the Huang-Minlon modification of the Wolff–Kishner reduction[8] hydrocarbons containing the bicyclo[3.2.0]heptane ring were prepared. Bicyclo[3.2.0]2-heptene (VIII) was obtained in 70% yield from bicyclo[3.2.0]-?-hepten-6-one and on hydrogenation over platinum oxide it gave bicyclo[3.2.0]heptane (IX). These hydrocarbons have not been previously reported.



The addition of ketene to 1,3-cyclohexadiene has also been studied under conditions similar to those

(1) Allied Chemical and Dye Predoctoral Fellow, 1949–1950.

(2) J. R. Lewis, G. R. Ramage, J. L. Simonsen and W. G. Wainwright, *J. Chem. Soc.*, 1837 (1937).

(3) E. H. Farmer and M. O. Farooq, *ibid.*, 1925 (1938).

(4) L. I. Smith, C. L. Agree, R. M. Leekley and W. W. Prichard, THIS JOURNAL, **61**, 7 (1939).

(5) J. M. Witzel, Thesis, Doctor of Philosophy, Cornell University, 1941.

(6) C. D. Hurd, A. D. Sweet and C. L. Thomas, THIS JOURNAL, **55**, 335 (1933).

(7) B. T. Brooks and G. Wilbert, *ibid.*, **63**, 870 (1941).

(8) Huang-Minlon, *ibid.*, **68**, 2487 (1946).