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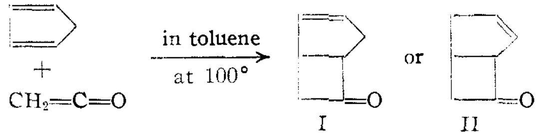
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Addition of Ketene to Cyclic Conjugated Dienes

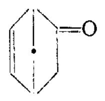
BY A. T. BLOMQUIST AND JACK KWIATEK[1]

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.



I II



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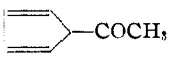
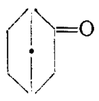
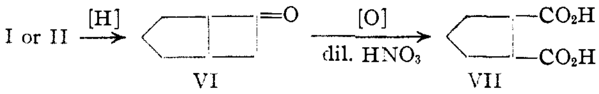


IV



V

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.



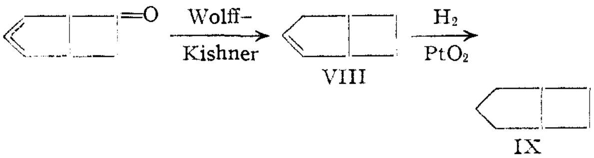
VI VII

TABLE I

Property	Bicyclo[3.2.0]-?-hepten-6-one This study	Bicyclo[3.2.0]-?-hepten-6-one Brooks and Wilbert[7]	Bicyclo[3.2.0]heptan-6-one This study	Bicyclo[3.2.0]heptan-6-one 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
MD (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.



VIII IX

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

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(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).

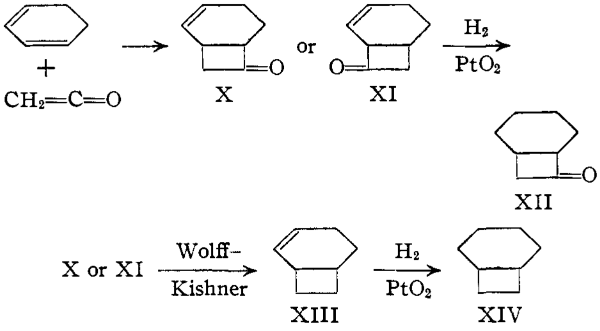
(5) J. M. Witzel, Thesis, Doctor of Philosophy, Cornell University, 1941.

(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).

described for cyclopentadiene. Bicyclo[4.2.0]-?-octene-7-one (X or XI), b.p. 190.5–192°, was obtained in *ca.* 5% yield (as semicarbazone from cyclohexadiene) and it added 99.6% of one molar equivalent of hydrogen on quantitative reduction.



Bicyclo[4.2.0]octan-7-one (XII) was obtained as its semicarbazone, m.p. 164–166°, in 43% yield from the bicyclooctenone (X or XI). Bicyclo-[4.2.0]2-octene (XIII), b.p. 137–139°, was obtained in 41.5% yield by a modified Wolff–Kishner reduction of X or XI. Hydrogenation of XIII over platinum oxide gave bicyclo[4.2.0]octane (XIV), b.p. 136–137.5°, in 59% yield. The latter hydrocarbon has been previously reported as having been prepared by passing cyclohexylethanol over thoria[9] and by reduction of cyclooctatetraene dichloride,[10] while recently it was obtained by Cope and Hochstein[11] from 1,3,5-cyclooctatriene as a 10–20% solution in cyclooctane. The infrared absorption spectrum of our bicyclooctane corresponded to that reported by Cope and Hochstein.

The position of the double bond in the two unsaturated ketones, bicyclo[3.2.0]-?-hepten-6-one and bicyclo[4.2.0]-?-octen-7-one has not been established. If their structure is analogous to the keto-ketene–diene adducts[2,3,4] the double bond would be in the 2-position. This point is being studied in connection with further work on the addition of ketene to cyclic dienes.

Acknowledgment.—We wish to thank Mr. J. J. Shipman of the Research Center of the B. F. Goodrich Company for his measurement and interpretation of the infrared absorption spectrum.

Experimental Part[12]

Ketene.—This was prepared by the pyrogenic decomposition of reagent grade acetone in a generator similar to that described by Williams and Hurd.[13] The generator was calibrated by passing the ketene through an excess of aniline in toluene and weighing the acetanilide formed.

Cyclopentadiene.—Dicyclopentadiene was heated in a modified Claisen flask[14] so that it refluxed about one-third of the distance up the column, cyclopentadiene being slowly collected in an ice-cooled receiver. The cyclopentadiene was kept in a refrigerator and freshly distilled before using. A fraction boiling at 39.5–42.5° was used.

1,3-Cyclohexadiene.—This was prepared according to the method of Ziegler, *et al.*,[15] but on a larger scale. From four runs each using 304 cc. of cyclohexene, 109.8 g. of N-bromosuccinimide and 450 cc. of carbon tetrachloride the following quantities of 3-bromocyclohexene, b.p. 70–85° (35 mm.) were obtained: 83.1 g., 84.0 g., 86.0 g., and 84.5 g. (*ca.* 85% average yield). Redistillation of the combined crude product from the four runs gave 307.6 g. of 3-bromocyclohexene, b.p. 68–70.5° (26 mm.). From a mixture of 117.6 g. (0.73 mole) of the bromocyclohexene and 350 cc. of quinoline 48.7 g. of crude cyclohexadiene was obtained. The impure diene was washed once with 3 *N* hydrochloric acid, dried over anhydrous magnesium sulfate, and redistilled to yield 42.1 g. (72.6%) of 1,3-cyclohexadiene, b.p. 79–81°.

Bicyclo[3.2.0]-?-hepten-6-one (I or II).—This was prepared according to the method described by Brooks and Wilbert.[7] Approximately 0.65 mole of ketene was absorbed in a mixture of 50 cc. of toluene and 0.65–0.70 mole of cyclopentadiene contained in a steel lecture bottle cooled by a Dry Ice–isopropyl alcohol mixture. The sealed bomb was heated at 100° for two hours and then cooled to room temperature. The reaction mixture from three such runs were combined and on distillation (in the hood) 105 g. of crude ketone, b.p. 145–185°, was obtained. The impure ketone was purified through its semicarbazone. From 105 g. of the crude ketone there was obtained 56 g. (17.4% based on ketene) of semicarbazone, m.p. 216–219.5°. After two recrystallizations from methanol–water (3:1) it melted at 219–220°.

Anal. Calcd. for $C_8H_{11}N_3O$: C, 58.16; H, 6.71; N, 25.44. Found: C, 58.36; H, 6.63; N, 25.62.

A mixture of 15.2 g. (0.092 mole) of recrystallized semicarbazone, 26.9 g. of phthalic anhydride and 50 cc. of water was steam distilled and the distillate extracted with 150 cc. of ether. The aqueous layer after being saturated with sodium chloride was further extracted with three 75-cc. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. Ether was then removed on the steam-bath and the residual ketone distilled *in vacuo* affording 8.4 g. (84.9%) of bicyclo[3.2.0]-?-hepten-6-one; b.p. 62–63.5° (20 mm.), 97–99° (99 mm.) 162–164° (atm.); $n^{20}{}_D$ 1.4819; $d^{20}{}_4$ 1.0248; M_D 30.08 (calcd. M_D 30.18).

Anal. Calcd. for C_7H_8O: C, 77.75; H, 7.46. Found: C, 76.88; H, 7.64.

On microhydrogenation of a 301-mg. sample over 30 mg. of pre-reduced platinum oxide catalyst in 10 cc. of 95% ethanol, 99.6% of one molar equivalent of hydrogen was absorbed.

Bicyclo[3.2.0]heptan-6-one (VI).—Reduction of 12.47 g. (0.115 mole) of the unsaturated ketone in 150 cc. of 95% ethanol over 0.12 g. of platinum oxide catalyst was carried out in a Parr hydrogenation apparatus. After removing the catalyst by filtration the alcohol was removed by distilling under reduced pressure and the residue upon distillation at atmospheric pressure gave 5.9 g.[16] of VI; b.p. 162–166°; $n^{20}{}_D$ 1.4679; $d^{20}{}_4$ 0.9940; M_D 30.80 (calcd. M_D 30.65).

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.20; H, 9.61.

The saturated ketone was converted to its semicarbazone which after two recrystallizations from methanol–water (3:1) had a melting point of 198.5–201°.

Anal. Calcd. for $C_8H_{13}N_3O$: C, 57.46; H, 7.84; N, 25.13. Found: C, 58.00; H, 7.86; N, 25.39.

cis-**Cyclopentane-1,2-dicarboxylic Acid** (VII).—In a 10-cc. round-bottomed flask fitted with a reflux condenser were placed 0.5 cc. of the bicycloheptanone and 2.6 cc. of dilute nitric acid (equal volumes of concd. nitric acid and water). The mixture was heated until reaction ensued when it was allowed to proceed without heating. After the initial evolution of heat had subsided the mixture was refluxed for three hours. The solution was then concentrated on a hot-plate and absolute ethanol was added to the clear liquid

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[9] N. A. Rozanov, Tyazhelov and Nikiforov, *J. Russ. Phys.-Chem. Soc.*, **61**, 2309 (1929); *C. A.*, **24**, 3766 (1930).

[10] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[11] A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

[12] All melting points and boiling points are uncorrected.

[13] J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

[14] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 18.

[15] K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 110 (1942).

[16] The alcoholic distillate contained some of the saturated ketone which was isolated as its semicarbazone, 5 g., m.p. 197–199°. The total yield of ketone and semicarbazone was 77%.

residue. After adding ether to the alcoholic solution a small amount of a colorless solid separated. This air-dried solid began to melt at 130°, resolidified, softened again at 154° with the formation of gas bubbles. The ether–alcohol mother liquor was evaporated to a clear liquid which solidified on standing for one day at room temperature. Ether was added, the solid filtered, and recrystallized from water; m.p. 131–134° (Fuson and Cole reported a melting point of 139° for *cis*-cyclopentane-1,2-dicarboxylic acid[17]); neut. equiv., calcd. 79.1; found neut. equiv., 81.9.

The acid was converted to its N-phenylimide by the method of Tingle and Cram.[18] After two recrystallizations from water–ethanol (1:1) it melted at 87.5–88.5° (m.p. 89° reported by Fuson and Cole[17]). The acid was converted to its anhydride by heating in a test-tube with a free flame until it distilled on the side of the tube. After cooling the solid residue was recrystallized twice from petroleum ether (b.p. 40–50°); m.p. 68–71° (Fuson and Cole reported a melting point of 73.5–74°[17]).

Bicyclo[3.2.0]2-heptene (VIII).—This olefin was formed from I or II by a modification of the Wolff–Kishner reduction.[8] From 8.4 g. (0.078 mole) of I or II, 4.9 g. (70%) of VIII, b.p. 101.5–103°, was obtained. On redistillation this gave 3.4 g.; b.p. 102.5–103°; n^{20}_{D} 1.4646; d^{20}_4 0.8703; M_{D} 29.88 (calcd. M_{D} 30.17).

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.10; H, 10.71.

On microhydrogenation of a 253-mg. sample over 25 mg. of pre-reduced platinum oxide catalyst in 10 cc. of 95% ethanol, 98.1% of one molar equivalent of hydrogen was absorbed.

Bicyclo[3.2.0]heptane (IX).—To the above hydrogenation mixture was added an additional 2.97 g. of VIII and this also was reduced. After removal of the platinum, 20 cc. of water was added to the alcoholic solution. The hydrocarbon layer was dried over anhydrous magnesium sulfate and distilled over sodium to give 2.5 g. (76%) of IX, b.p. 105–110°. The main fraction (2.1 g.) boiled at 109–109.5°; n^{20}_{D} 1.4532; d^{20}_4 0.8522; M_{D} 30.52 (calcd. M_{D} 30.64).

Bicyclo[4.2.0]-?-octen-7-one (X or XI).—This was prepared by a method similar to that used for I or II. A mixture of 80 cc. of toluene, 22 g. (0.27 mole) of 1,3-cyclohexadiene, and 0.34 mole of ketene was heated in a bomb at 100° for four hours and yielded 2.2 g. of crude ketone, b.p. 97–137° (92 mm.). This crude ketone gave 2.3 g. of its semicarbazone, m.p. 194.5–198.5° which was recrystallized from methanol–water (3:1), m.p. 200.5–201°.

Anal. Calcd. for $C_9H_{13}N_3O$: C, 60.31; H, 7.31; N, 23.45. Found: C, 60.36; H, 7.06; N, 23.56.

On hydrolysis, 2.22 g. of the semicarbazone afforded 1.00 g. (66%) of bicyclo[4.2.0]-?-octen-7-one; b.p: 190.5–192°; n^{20}_{D} 1.4950; d^{20}_4 1.024; M_{D} 34.79 (calcd. M_{D} 34.80).

On microhydrogenation of a 310-mg. sample over 30 mg. of pre-reduced platinum oxide catalyst in 10 cc. of 95% ethanol, 99.6% of one molar equivalent of hydrogen was absorbed.

Bicyclo[4.2.0]octan-7-one Semicarbazone.—To the above hydrogenation mixture was added an additional 0.624 g. of X or XI (total 0.934 g.) which was also reduced. After filtering the platinum the alcohol was removed by distillation under diminished pressure. The residue could not be distilled because of foaming and it was converted directly to its semicarbazone. After two recrystallizations from methanol–water (2:1), 0.6 g. (43.3%) of XII semicarbazone was obtained, m.p. 164–166°.

Anal. Calcd. for $C_9H_{13}N_3O$: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.47; H, 8.31; N, 23.14.

Bicyclo[4.2.0]-2-octene (XIII).—This was obtained from X or XI semicarbazone, m.p. 185–191°, without purification of the intermediate ketone. From 6.2 g. (0.0346 mole) of the semicarbazone 4.1 g. (97%) of crude ketone was obtained. This was reduced by the modified Wolff–Kishner method[8] to give 1.5 g. (41.5%) of XIII; b.p. 137–139°; n^{20}_{D} 1.4810; d^{20}_4 0.8948; M_{D} 34.40 (calcd. M_{D} 34.79). On microhydrogenation it absorbed 94.6% of one molar equivalent of hydrogen.

Bicyclo[4.2.0]octane (XIV).—To the above mixture obtained in microhydrogenation was added an additional 0.93 g. of XIII which was also reduced. After isolating the hydrocarbon in the usual way there was obtained 0.72 g. (59.4%) of XIV; b.p. 136–137.5°; n^{20}_{D} 1.436; d^{20}_4 0.866; M_{D} 35.08 (calcd. M_{D} 35.26). For this compound Reppe[10] has reported b.p. 136°, n^{20}_{D} 1.4613; d^{20}_4 0.8573.

Anal. Calcd. for C_6H_{14}: C, 87.19; H, 12.81. Found: C, 87.20; H, 12.71.

ITHACA, N. Y. RECEIVED OCTOBER 21, 1950

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

(18) J. B. Tingle and M. P. Cram, *ibid.*, **37**, 598 (1907).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, QUEEN'S UNIVERSITY]

2-Octadecenoic Acid. I. Preparation and Some Reactions of the *cis* and *trans* Isomers

BY GORDON S. MYERS[1]

The *trans* configuration for the 2-octadenoic acid melting at 58.5°, which has been proposed previously by other workers, is now further substantiated by the preparation of the *cis*-2-octadecenoic acid isomer (m.p. 50.5–51°). The configuration assigned to each isomer is based on the comparison of some of their physical and chemical properties. A comparison is made of some of the reactions and properties of the isomeric 2-octadecenoic acids with those of oleic and elaidic acid (*cis*- and *trans*-9-octadecenoic acid, respectively). It has been found that hydroxylation of *trans*-2-octadecenoic acid with peracetic acid and with alkaline potassium permanganate, gives the low-melting and high-melting dihydroxy acid, respectively. *trans*-9-Octadecenoic acid, on the other hand, gives the high-melting 9,10-dihydroxystearic acid on treatment with peracetic acid, and the low-melting isomer on hydroxylation with alkaline permanganate. An improved preparation of *trans*-2-octadecenoic acid, by dehydrohalogenation of 2-iodostearic acid with alcoholic alkali, is reported; and the following new compounds are described: 2,3-dibromostearic acid (m.p. 57°), 2,3-dihydroxystearic acid (m.p. 106–107°) and three 2,3(3,2)-bromoacetoxystearic acids.

Some 2-octadecenoic acid was required as an intermediate in the duplication of some naturally occurring lipids. Le Sueur[2] prepared one of the two possible geometric isomers, along with a by-product of 2-hydroxystearic acid, by dehydrohalogenation of 2-bromostearic acid. Ponzio[3] increased the yield somewhat by using 2-iodostearic acid and alkali. As far as the author is aware, the other isomeric 2-octadecenoic acid has not been described.

The known 2-octadecenoic acid (m.p. 58.5°) is reported to have the *trans* configuration. This is based on its similarity to elaidic acid (*trans*-9-octadecenoic acid) in (1) the melting point depression on mixing with stearic acid[4]; (2) parachor[5];

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(1) Research Laboratories, Ayerst, McKenna and Harrison Ltd., Montreal.

(2) Le Sueur, *J. Chem. Soc.*, **85**, 1708 (1904).

(3) Ponzio, *Gazz. chim. ital.*, **34**, II, 77 (1904).

(4) Semeria, *ibid.*, **55**, 79 (1925).

(5) Semeria and Ribotti-Lissone, *ibid.*, **60**, 862 (1930).