derivatives. The **bis-salicylidene derivative** formed yellow needles (from alcohol), m. p. 125–126°.

Anal. Calcd. for $C_{23}H_{22}N_2O_4$: N, 7.2. Found: N, 7.2.

The **bis-5-bromosalicylidene derivative** formed orange-yellow needles from alcohol; m. p. 198–199°.

Anal. Calcd. for $C_{23}H_{20}Br_2N_2O_4$: N, 5.1. Found: N, 5.1.

6,7-Dimethoxyquinazoline (XI).—A mixture of 2-amino-4,5-dimethoxybenzylamine hydrochloride (2 g.), anhydrous sodium formate (1.5 g.) and 100% formic acid (4 ml.) was refluxed for ninety minutes. The excess formic acid was then evaporated from a water-bath. The solid residue was dissolved in water, basified with sodium hydroxide and ether extracted. After drying over solid potash, then removal of the ether, a white solid was obtained which still melted over the range 126–136° after many recrystallizations from benzene suggesting a mixture of the quinazoline and dihydroquinazoline. Hence potash solution (2 ml. of 33%) was added to a solution of some of the solid (0.16 g.) in water (5 ml.) followed by an aqueous solution of potassium ferricyanide (0.72 g.). Potash solution (20 ml. of 33%) was then added and the base collected with ether, then recrystallized from petroleum ether; fluffy white needles, m. p. 146–147° (reported,[7] 143°).

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.1; H, 5.3; N, 14.7. Found: C, 62.9; H, 5.3; N, 13.7.

The **hydrochloride** melted at 225–227° (reported 227°).

2-(*m*-Nitrophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroquinazoline (XII).—A solution of the diamine II (0.5 g.) and *m*-nitrobenzaldehyde (0.42 g.) in a little alcohol was refluxed for fifteen minutes. An orange-red compound was induced to crystallize on cooling. Recrystallized from absolute ethanol it formed red needles, m. p. 119–120°.

Anal. Calcd. for $C_{16}H_{17}N_3O_4$: C, 61.0; H, 5.4; N, 13.3. Found: C, 60.5; H, 5.4; N, 13.5.

2-Nitro-4,5-dimethoxybenzylurea (XIII).—I (7.6 g.) was heated with water (80 ml.) and nitrourea (4 g.) at 100° for an hour. After cooling the product was collected and recrystallized from much alcohol; pale yellow needles, m. p. 227–231° dec.

Anal. Calcd. for $C_{10}H_{13}N_3O_5$: C, 47.1; H, 5.1; N, 16.5. Found: C, 46.9; H, 5.1; N, 16.5.

2-Amino-4,5-dimethoxybenzylurea (XIV).—The nitro compound XIII (2 g.) was reduced in hot alcohol (400 ml.) with hydrogen and Raney nickel. The product formed fine white needles from absolute ethanol, m. p. 190–191°; yield 1.3 g. (76%).

Anal. Calcd. for $C_{10}H_{15}N_3O_3$: C, 53.3; H, 6.7; N, 18.7. Found: C, 52.9; H, 6.7; N, 18.5.

Acknowledgments.—We are indebted to the Commonwealth Research Fund for a Studentship which enabled one of us (A. M. D.) to take part in this work; and to Miss Joyce Fildes for the microanalyses recorded in this paper.

Summary

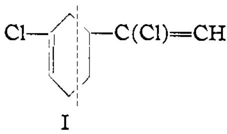
Application has been made of Einhorn's amidomethylation procedure to nitroveratrole and several acylated 2-nitro-4,5-dimethoxybenzylamines prepared. Some of these can be directly converted to quinazoline derivatives by reduction. Hydrolysis of them yields 2-nitro-4,5-dimethoxybenzylamine, which can be reduced to 2-amino-4,5-dimethoxybenzylamine, and this, in turn, can be converted to 6,7-dimethoxyquinazoline derivatives by standard procedures.

SYDNEY, AUSTRALIA RECEIVED JULY 5, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. VII. Structure of the Eight-membered Cyclic Dimer of Chloroprene[1]

BY ARTHUR C. COPE AND WILLIAM R. SCHMITZ



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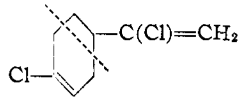

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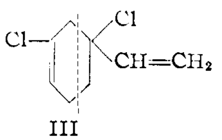

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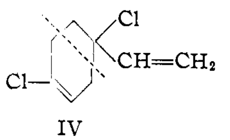

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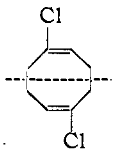

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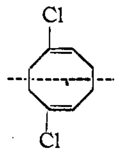

VI

Chloroprene (2-chloro-1,3-butadiene) has been observed to dimerize on standing or heating in the presence of polymerization inhibitors, yielding a mixture from which two six-membered cyclic dimers and one eight-membered cyclic dimer have been isolated.[2–6] Dimerization by a normal Diels–Alder diene addition reaction and a related process of self-addition in which both of the monomer units are united through the 1,4-positions theoretically could yield six structurally isomeric dimers (I–VI), depending on the orientation of the monomer units. In one of the six-membered cyclic dimers actually isolated both chlorine atoms are inert (vinyl) in character, as would be the case in I and II; in the other, one chlorine is vinyl and the other allylic as in III and IV. A monochlorotriene, presumably derived from the dimer containing reactive chlorine by elimination of hydrogen chloride, also has been isolated from the mixture of dimers. Brown,

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[1] Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

[2] Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4211 (1931).

[3] Brown, Rose and Simonsen, *J. Chem. Soc.*, 101 (1944).

[4] Foster and Schreiber, THIS JOURNAL, **70**, 2303 (1948).

[5] Cope and Bailey, *ibid.*, **70**, 2305 (1948).

[6] Klebanskii and Denisova, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 703 (1947); *C. A.*, **42**, 1215 (1948).

Rose and Simonsen[3] wrote structure I for the six-membered cyclic dimer containing unreactive chlorine atoms, but their structural evidence, which consisted in cleavage of the cyclic double bond by ozonization followed by conversion of the product to β-substituted derivatives of adipic acid, is equally in accord with formula II. Klebanskii and Denisova[6] found that the dimer gave p-chlorobenzoic acid on oxidation with potassium permanganate and concluded that II was the correct structure. The monochlorotriene which they isolated also yielded p-chlorobenzoic acid on oxidation, from which they concluded that the second six-membered cyclic dimer had structure IV.

Structural evidence concerning the eight-membered cyclic dimer consists in its hydrogenation to cyclooctane,[3,4,5] dehalogenation to 1,5-cyclooctadiene,[4,5] and ozonization followed by oxidation to succinic acid.[3] No evidence is available which permits a choice between the head-to-tail dimer structure V and the head-to-head structure VI, although Brown, Rose and Simonsen wrote formula V for the compound. We have obtained evidence that the eight-membered cyclic dimer actually has the head-to-head, tail-to-tail structure VI. It is of interest in this connection that the cyclic dimers (cyclobutane derivatives) of several substituted ethylenes have been found to have the structure of head-to-head, tail-to-tail dimers.[7]

Incidental to this investigation, data were obtained which are in accord with structures II and IV for the six-membered cyclic dimers.

A previously described procedure for the dimerization of chloroprene[5] was modified by use of picric acid rather than phenothiazine as a polymerization inhibitor, and treatment of the crude mixture of dimers with pyridine to remove the six-membered cyclic dimer containing a reactive chlorine atom (probably IV) as a quaternary salt. Fractional distillation separated the remaining six-membered cyclic dimer (II), formed in 40–46% yield, from the higher boiling eight-membered cyclic dimer VI (12.0–15.5%). VI solidified on cooling and had a freezing point of 6.8°, which was raised to a constant value of 13.8° by several recrystallizations from ether. After determination of the freezing point depression constant for VI it could be calculated that the isomeric impurity present before recrystallization which lowered the f. p. by 7° amounted to 11%. The other possible eight-membered cyclic dimer V was not isolated from the recrystallization mother liquors, and no positive evidence was obtained for its presence; if it was formed at all in the dimerization of chloroprene under the conditions investigated its yield was less than 1.5%.

Evidence establishing the structure of the eight-membered cyclic dimer as VI was obtained by ozonization, and by reaction with concentrated sulfuric acid. Ozonization of VI in ethyl acetate followed by decomposition of the ozonide by catalytic hydrogenation gave succinyl chloride and succinaldehyde, which were converted into derivatives immediately (without isolation) by treatment with aniline, phenylhydrazine and p-nitrophenylhydrazine. Succinanilide and succinphenylhydrazide were isolated as derivatives of succinyl chloride in 47 and 42% yields, respectively, while the bis-p-nitrophenylhydrazone of succinaldehyde was isolated in 10% yield. The best yield of a succinaldehyde derivative was obtained by hydrolyzing the ozonide of VI in the presence of 2,4-dinitrophenylhydrazine reagent, which gave succinaldehyde bis-2,4-dinitrophenylhydrazone in 25% yield. Formation of the succinaldehyde derivative under these circumstances precludes any possibility that the aldehyde was derived from succinyl chloride, which could conceivably form succinaldehyde subsequent to hydrogenation of the ozonide by further catalytic reduction.

The second line of evidence supporting structure VI for the dimer was obtained by utilizing a type of reaction reported by Wichterle,[8] who found that a number of compounds containing chlorocrotyl ($CH_3C(Cl){=}CHCH_2$—) groups were converted to compounds containing $CH_3COCH_2CH_2$— groups without rearrangement by reaction with concentrated sulfuric acid. In a number of cases the products isolated were the products of the intramolecular aldol condensation of the intermediate methyl ketones. Under optimum conditions, VI on treatment with sulfuric acid gave a 70–77% yield of a ketone which proved to be bicyclo[3.3.0]-1(5)-octen-2-one (VII), the product expected from an internal aldol condensation of cyclooctan-1,4-dione, which presumably is formed as an intermediate. Evidence for the skeletal structure of the bicyclic ketone VII was obtained by hydrogenation in the presence of a palladium catalyst, which gave the known saturated ketone, *cis*-bicyclo[3.3.0]octan-2-one (VIII).[9] Identity of the saturated ketone VIII was established by direct comparison with a known sample[10] and conversion of the ketone from the two sources into semicarbazone and 2,4-dinitrophenylhydrazone derivatives, which were proved to be identical by m. p. and mixed m. p. The double bond in the unsaturated ketone VII was shown to be in a position α,β- to the carbonyl group by its ultraviolet absorption spectrum (Fig. 1), which showed a maximum

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[7] Henne and Ruh, THIS JOURNAL, **69**, 279 (1947); Coyner and Hillman, *ibid.*, **71**, 324 (1949).

[8] Wichterle, *Chem. Listy*, **37**, 180 (1943); *C. A.*, **39**, 1841 (1945); Wichterle and Hudlicky, *Collection Czech. Chem. Commun.*, **12**, 101 (1947); *C. A.*, **41**, 4148 (1947); *ibid.*, **12**, 129 (1947); *C. A.*, **41**, 4793 (1947); Wichterle, Prochazka and Hofman, *ibid.*, **13**, 300 (1948); *C. A.*, **42**, 8162 (1948).

[9] Cooke and Linstead, *J. Chem. Soc.*, 955 (1934).

[10] We are indebted to Hugh C. Campbell for preparation of this sample by the procedure of ref. 9.

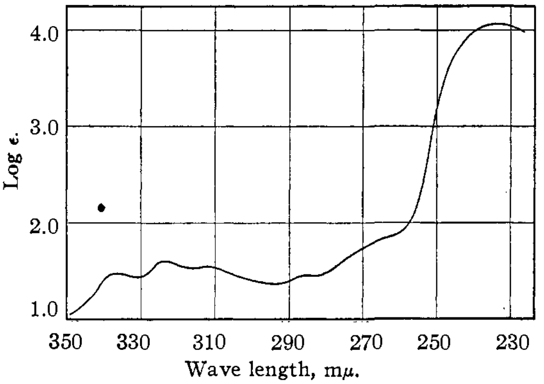
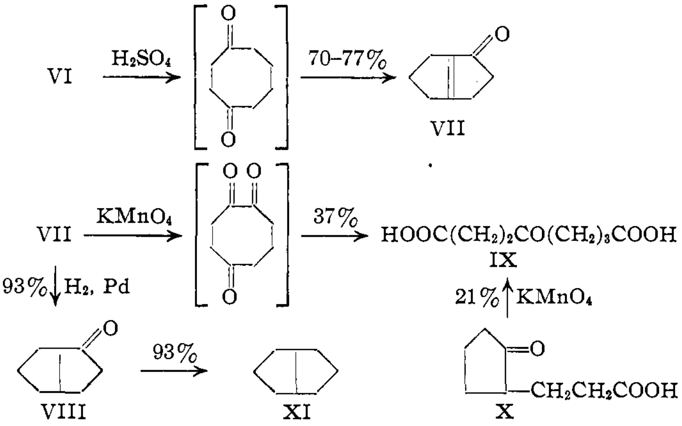


Fig. 1.—Ultraviolet absorption spectrum of bicyclo[3.3.0]-1(5)-octen-2-one (VII) in cyclohexane.

at 234 mμ (log ε = 4.05). The double bond should be in the 1,5-position (as shown in formula VII) initially because of the method of synthesis, but it was necessary to establish its position because rearrangement in the presence of concentrated sulfuric acid could result in formation of either of the other possible α,β-unsaturated structures. The ketone appeared to be a single isomer, for it crystallized on cooling to a solid, m. p. 17.2–19.0°, and formed a pure semicarbazone in high yield. The position of the double bond in VII was proved by oxidation with potassium permanganate, which gave a keto-suberic acid (reduced by the Wolff–Kishner method to suberic acid). Formation of such an oxidation product can be explained on the basis of structure VII by initial hydroxylation of the double bond, cleavage of the intermediate glycol to a triketone, and cleavage of the triketone between the adjacent carbonyl groups, as shown in the following equation. According to this interpretation the acid formed in the oxidation should be γ-ketosuberic acid, which has not been described previously. This structure (IX) for the acid was confirmed by preparation of a known sample by oxidation of cyclopentanone-2-β-propionic acid (X).



Reduction of the saturated ketone VIII by a modified Wolff–Kishner method[11] gave *cis*-bicyclo-[3.3.0]octane (XI) in 93% yield.[12] Reduction of the semicarbazone of the unsaturated ketone VII under similar conditions apparently formed a mixture of bicyclo[3.3.0]octenes; quantitative hydrogenation of the mixture gave *cis*-bicyclo-[3.3.0]octane (XI) which was identical (from comparison of the infrared spectra) with a sample prepared from VIII.

Oxidation of the six-membered cyclic dimer II with potassium permanganate gave *p*-chlorobenzoic acid, in agreement with the results reported by Klebanskii and Denisova,[6] but the yield was very low (2.3%). Much better yields (17.5%) were obtained by a route which began by treatment of II with two molar equivalents of N-bromosuccinimide in benzene in the presence of benzoyl peroxide. The mixture of bromo compounds which was formed was dehydrobrominated by warming with triethylamine; subsequent oxidation with potassium permanganate yielded *p*-chlorobenzoic acid.

The pyridinium salt which was formed when the crude mixture of chloroprene dimers was heated with pyridine was isolated in an impure form and could not be purified readily by crystallization. Oxidation of the crude salt with potassium permanganate gave *p*-chlorobenzoic acid in 2.3% yield; this result is in accord with structure IV for the dimer, but the yield is so small that it is not certain to be valid structural evidence. The pyridinium salt of IV (which might be formed by direct displacement of the reactive chlorine atom by pyridine, or be the product of an allylic rearrangement) reacted with mercuric chloride in ethanol to give a crystalline complex salt, m. p. 98.8–102.0°, in good yield. Analysis showed that the salt was derived from one molar equivalent each of IV, pyridine and mercuric chloride.

Experimental[13]

1,6-Dichloro-1,5-cycloöctadiene (VI).—The procedure for dimerization of chloroprene previously described[5] was modified as indicated by the following typical preparation. A stabilized 50% solution of chloroprene in xylene was fractionated through a Widmer column in a nitrogen atmosphere, and the chloroprene fraction (1494 g.) was collected in a 3-l. three-necked flask containing a small amount of picric acid. Additional picric acid was added to make the total concentration 0.1%, and the flask was equipped with a mercury-sealed stirrer, thermometer and reflux condenser attached to a source of nitrogen through a mercury pop-valve. The mixture was stirred[14] in a nitrogen atmosphere maintained at a positive pressure of 1 cm. of mercury and heated with an electric mantle so that the chloroprene

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[11] Huang-Minlon, THIS JOURNAL, **68**, 2488 (1946).

[12] Rytina, Schiessler and Whitmore, *ibid.*, **71**, 751 (1949), have prepared XI recently by a similar method.

[13] Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy and his associates for analyses.

[14] The results of subsequent preparations by F. A. Hochstein and Mark R. Kinter have shown that stirring is unnecessary.

refluxed slowly. After three to four days the liquid temperature increased to 80°, and was kept at that temperature for an additional three days. At that time the dimerization mixture (1458 g.) was transferred to a 2-l. round-bottomed flask and distilled rapidly through a simple still-head at 1 mm., separating 149 g. (10%) of a mixture of chloroprene and xylene which collected in Dry-Ice traps which protected the vacuum pump, 1094 g. (73%) of chloroprene dimers, and 150 g. (10%) of a residue of chloroprene polymers. The dimer fraction was heated with 500 g. of pyridine at 50–60° for sixteen hours to remove 1,4-dichloro-1-vinyl-3-cyclohexene (IV) as a pyridinium salt. The solution was decanted from the salt into 12 l. of water containing 500 ml. of concentrated hydrochloric acid. The mixture was stirred thoroughly and then extracted with several portions of ether. The combined ether extracts (about 4 l.) were washed with 1 l. of water, dried over magnesium sulfate, and concentrated. Rapid distillation of the residue at 1 mm. through a simple still head gave 974 g. of dimers, which were fractionated carefully through a total condensation, variable take-off type column with a 60 × 1.4 cm. section packed with glass helices. Two components were separated: 4-chloro-1-(α-chlorovinyl)-3-cyclohexene (II), 686 g. (46%), b. p. 54–58° (0.8 mm.), $n^{25}\text{D}$ 1.5135–1.5142, and 1,6-dichloro-1,5-cycloöctadiene (VI), 204 g. (13.7%), b. p. 75–77° (0.8 mm.), $n^{25}\text{D}$ 1.5332–1.5340.

On redistillation II was obtained with the following properties: b. p. 53° (0.9 mm.); $n^{25}\text{D}$ 1.5135; d^{25}_4 1.1653.

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.37; H, 5.61; Cl, 39.82.

After redistillation VI had b. p. 69° (0.8 mm.), $n^{25}\text{D}$ 1.5335, d^{25}_4 1.2138. The sample solidified on cooling and had a freezing point of 6.8°. Although this material was analytically pure, recrystallization from ether separated an isomeric impurity and three to six crystallizations gave pure VI with a constant freezing point of 13.8°, b. p. 64° (0.25 mm.), $n^{25}\text{D}$ 1.5339, d^{25}_4 1.2167, freezing point depression constant, 61 ± 3° per mole-fraction of solute.

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.22; H, 5.70; Cl, 39.85.

At least part of the isomeric impurity present in VI before recrystallization was a compound containing a more reactive chlorine atom, such as IV or an allylic isomer of IV. A 5.07-g. sample of VI, f. p. 5.7°, which was heated with 100 ml. of water in the presence of 10 g. of calcium carbonate for twenty-four hours liberated 3.7% of its chlorine as chloride ion, according to Volhard titration, and the recovered sample of I had f. p. 6.7°. A pure sample of I under the same conditions liberated 1.4% of chloride ion and the recovered sample had f. p. 13.8°.

Picric acid was chosen as the polymerization inhibitor for use in chloroprene dimerizations as the result of a series of experiments in which 150-g. samples of freshly distilled chloroprene and various inhibitors were placed in a 350-ml. pressure bottle and heated in a bath at 80° for six days with continuous shaking. The yield of total dimers, 1,6-dichloro-1,5-cycloöctadiene and polymer was determined in each case by the procedure described above for a large scale preparation. Data are summarized in Table I. In similar experiments in which 1,3,5-trinitrobenzene, 2,5-di-*t*-butylhydroquinone, iodine, silver chloride and cuprous chloride were used as inhibitors, each present to the extent of 1% by weight, practically complete polymerization resulted with the formation of solid reaction mixtures.

TABLE I

DIMERIZATION OF CHLOROPRENE IN THE PRESENCE OF VARIOUS POLYMERIZATION INHIBITORS

Inhibitor and concentration, %		Yield of dimers, %	Yield of VI, %	Yield of polymer, %
1	Phenothiazine	69	10	18
1	Pyrogallol	62	9	15
1	*p*-*t*-Butylcatechol	71	10	13
1	Chloranil	61	10	20
0.5	Picric acid	77	12	10
0.2	Picric acid	76	13	10
0.1	Picric acid	77	12	10
1	Benzoquinone	65	9	18

Ozonization of 1,6-Dichloro-1,5-cycloöctadiene (VI).—A solution of 0.935 g. of VI in 25 ml. of dry ethyl acetate was ozonized at −20° in a stream of oxygen delivering 28 mg. of ozone per minute for twenty-three minutes. The solution of the ozonide was cooled with Dry Ice and hydrogenated in the presence of 0.3 g. of 10% palladium-on-Norite catalyst for thirty minutes, and then for an additional thirty to sixty minutes after removing the Dry Ice. The catalyst was removed by filtration and the filtrate was divided into two equal portions, one of which was added to 1.5 g. of aniline in 60 ml. of benzene. A precipitate of succinanilide and aniline hydrochloride which formed immediately was collected on a funnel after one hour, washed with 100 ml. of hot water to remove aniline hydrochloride, and dried. Recrystallization of the crude succinanilide from 95% ethanol yielded 0.33 g. (47%), m. p. 229.5–231.5° Recrystallization from ethanol gave succinanilide with a constant m. p. of 230.8–231.5°, which was not depressed on mixture with a known sample. The other half of the filtrate was added to 2.2 g. of *p*-nitrophenylhydrazine in 300 ml. of 0.1 *N* hydrochloric acid. The mixture was warmed on a steam-bath for about ten minutes, allowed to cool, and filtered. The bis-*p*-nitrophenylhydrazone of succinaldehyde which was separated was recrystallized from absolute ethanol; yield 0.09 g. (10%), m. p. and mixed m. p. with a known sample 184–187°.

Repetition of the above procedure with substitution of 1.8 g. of phenylhydrazine for the aniline gave a 42% yield of succinphenylhydrazide, m. p. and mixed m. p. with a known sample 215.6–218.4°.

A solution of 0.935 g. of VI in 25 ml. of dry ethyl acetate was ozonized as described above for twenty minutes. One-half of the solution of the ozonide was added to a solution prepared from 1.2 g. of 2,4-dinitrophenylhydrazine, 6 ml. of concentrated sulfuric acid, 9 ml. of water and 30 ml. of 95% ethanol. The mixture was warmed on a steam-bath for ten minutes, and the succinaldehyde bis-2,4-dinitrophenylhydrazone which formed was collected on a filter. Recrystallization from pyridine yielded 0.29 g. (25%), m. p. 263–264.8°, and a second crystallization gave the derivative with a constant m. p. of 267–267.5°. A mixed m. p. with a known sample was not depressed.

Bicyclo[3.3.0]-1(5)-octen-2-one (VII).—Concentrated sulfuric acid (50 ml.) was placed in a 500-ml. three-necked flask fitted with gas inlet and outlet tubes, a mercury-sealed stirrer and a dropping funnel. The acid was cooled with an ice-bath, and 15.5 g. of VI was added dropwise with stirring during twenty-five minutes. After the addition was completed the mixture was stirred at room temperature for five minutes and at a bath temperature of 70° for thirty minutes. Hydrogen chloride was evolved during the reaction, and was swept from the flask with nitrogen and collected in a water trap. The reaction mixture was poured onto cracked ice and neutralized with sodium hydroxide. The product was extracted with one 300 ml. and three 100-ml. portions of ether, and the extracts were dried over magnesium sulfate. Distillation yielded VII, 7.7 g. (72%), b. p. 65–66° (0.5 mm.); $n^{25}\text{D}$ 1.5202, d^{25}_4 1.0540. VII purified in this way contained a small amount (less than 1%) of VI, which has a similar boiling point, according to analyses which were about 0.5% low in carbon and showed the presence of approximately 0.3% of chlorine. VII was readily purified through the semicarbazone. For example, a 27.4-g. sample of VI was treated with concentrated sulfuric acid by the procedure described above. After neutralization of the reaction mixture with sodium hydroxide, the ketone was separated by steam distillation. The steam distillate (600 ml.) was heated nearly to the boiling point and ethanol was added dropwise until a clear solution was obtained, followed by

12 g. of semicarbazide hydrochloride and 18 g. of sodium acetate trihydrate. The mixture was allowed to cool, and after it had stood for twenty hours at room temperature the semicarbazone of VII was separated by filtration; yield 18.5 g. (67% from VI), m. p. 226.5–227.5°. An analytical sample which was recrystallized from 50% aqueous ethanol had m. p. 230–232.2°.

Anal. Calcd. for $C_9H_{13}ON_3$: C, 60.32; H, 7.31; N, 23.45. Found: C, 60.49; H, 7.52; N, 23.65.

The ketone VII was regenerated from its semicarbazone by adding 4.3 g. to 20 g. of oxalic acid in 250 ml. of water. The mixture was distilled, water being added to keep the volume of the solution constant, and VII was collected with about 350 ml. of steam distillate. VII was separated by extraction with ether; the extracts were dried over magnesium sulfate and distilled, yielding 1.6 g. of VII, b. p. 62° (0.9 mm.), m. p. 17.2–19°, n^{25}_D 1.5202, d^{25}_4 1.0534.

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.51; H, 8.23.

The ultraviolet absorption spectrum of VII (Fig. 1) was determined in solution in purified cyclohexane with a Beckman model DU quartz ultraviolet spectrophotometer. The spectrum showed a maximum at 234 mμ (ϵ = 11,280).

***cis*-Bicyclo[3.3.0]octan-2-one (VIII).**—A solution of 4.75 g. of VII in 25 ml. of dry methanol was hydrogenated in the presence of 0.25 g. of 10% palladium-on-Norite; 98.2% of one molar equivalent of hydrogen was absorbed in a period of one and one-quarter hours. After separation of the catalyst and concentration, distillation yielded 4.5 g. (93%) of analytically pure VIII,[9] b. p. 50° (2.3 mm.)[6]; n^{25}_D 1.4766, d^{25}_4 1.0060, M_D calcd. 34.77, found 34.88. The semicarbazone of VIII was prepared as a derivative and recrystallized from absolute ethanol. Its m. p. was 178.8–180.2° (ref. 9 reports m. p. 180°), and a mixed m. p. with an authentic sample was not depressed.

The 2,4-dinitrophenylhydrazone of VIII was prepared by adding 0.37 g. of VIII in 12 ml. of ethanol to a solution containing 0.4 g. of 2,4-dinitrophenylhydrazine, 2 ml. of concentrated sulfuric acid, 3 ml. of water, and 10 ml. of ethanol. The yellow derivative which formed at once was separated after two days; yield 0.37 g. (63%), m. p. 110–113°. After recrystallization from absolute ethanol the 2,4-dinitrophenylhydrazone had m. p. 110–114.5° (ref. 9 reports m. p. 115–116°), and a mixed m. p. with a known sample was not depressed. This derivative was analytically pure, but further recrystallization from absolute ethanol raised the m. p. until a constant value of 140–140.2° was reached after six recrystallizations, at which point only 5–8% of the original derivative remained.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.00; H, 5.32; N, 18.52.

The 2,4-dinitrophenylhydrazone of VIII prepared by the procedure of Cooke and Linstead[9,10] behaved in the same manner on recrystallization, giving a small amount of a high melting form after several recrystallizations which did not depress the m. p. of the high melting form of the derivative of VIII described above. The high and low melting forms could not be interconverted by crystallization, and mixed melting points were intermediate, indicating that the forms are not dimorphous. The most probable explanation of the m. p. behavior is that the derivative as originally obtained is a mixture of *syn* and *anti* forms, from which one form was separated by recrystallization.

γ-Ketosuberic Acid (IX).—A 2.5% solution of potassium permanganate was added in 5–10-ml. portions with stirring at 5–10° to 5.65 g. of VII until a slight excess was present. A total of 600 ml. of the solution was added in a period of three hours, after which the mixture was stirred at room temperature for one hour. The reaction mixture was acidified with hydrochloric acid and sodium bisulfite solution was added until the manganese dioxide was reduced and a homogeneous solution was obtained. The aqueous solution was extracted with ether in a continuous extractor for twenty hours. Distillation of the ether and recrystallization of the residue from ethyl acetate yielded 3.18 g. (37%) of γ-ketosuberic acid (IX), m. p. 130–132°. Further recrystallization from ethyl acetate gave an analytical sample with a constant m. p. of 132.5–134.6°.

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 50.91; H, 6.38.

A 1.65-g. sample of γ-ketosuberic acid prepared by oxidation of VII was reduced by a modified Wolff–Kishner procedure similar to the one described below for reduction of VIII. Suberic acid was isolated in a yield of 0.30 g. (20%), m. p. 131–139°, and after recrystallization from ethyl acetate had m. p. and mixed m. p. with a known sample of 139–141.5°.

A sample of IX was prepared by the oxidation of cyclopentanone 2-β-propionic acid[15] (X) for comparison. A 2.5% solution of potassium permanganate was added in 5-ml. portions with stirring at 5–10° to a solution of 1.04 g. of X in 50 ml. of water until decolorization no longer occurred. After addition of 150 ml. in a period of four hours, an additional 50 ml. of 2.5% potassium permanganate solution was added and the mixture was stirred at room temperature for eighteen hours. The product was isolated by the procedure described above, and amounted to 0.26 g. (21%) of γ-ketosuberic acid, m. p. 127.5–130.6°. Recrystallization from ethyl acetate gave a sample which was identical (m. p. and mixed m. p.) with the sample of IX described above.

***cis*-Bicyclo[3.3.0]octane (XI).**—A solution of 10 g. of VIII in 50 ml. of butyl carbitol, 10 ml. of 85% hydrazine hydrate, and 13 g. of potassium hydroxide in 50 ml. of butyl carbitol were mixed and distilled slowly through a 20 × 0.8 cm. column during a period of six and one-half hours, with a final bath temperature of 180°, according to a procedure described by Huang-Minlon.[11] Water and XI collected in the distillate, and distillation of the hydrocarbon layer gave 8.3 g. (93%) of XI, b. p. 136–136.5°, n^{25}_D 1.4580–1.4586. An analytically pure sample was obtained by passing the hydrocarbon over silica gel until the refractive index was constant; n^{25}_D 1.4595, d^{25}_4 0.8638.

Bicyclo[3.3.0]octenes.—The semicarbazone of VII (18.5 g.) in 300 ml. of butyl carbitol and 32 g. of potassium hydroxide were distilled slowly under conditions similar to those described above for preparation of XI. The yield of a mixture of bicyclo[3.3.0]octenes was 4.5 g. (40%), b. p. 130–134°, n^{25}_D 1.4715. Redistillation from sodium gave a sample with constant index of refraction; n^{25}_D 1.4730, d^{25}_4 0.8813.

Anal. Calcd. for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.44; H, 11.09.

A solution of 1.0 g. of the mixture of bicyclo[3.3.0]octenes in 3 ml. of glacial acetic acid was hydrogenated in the presence of 0.1 g. of pre-reduced Adams platinum oxide catalyst; 94% of one molar equivalent of hydrogen was absorbed. The solution was made basic with sodium carbonate and extracted with ether. Distillation yielded 0.24 g. of XI, b. p. 61–62° (70 mm.), which after passage through silica gel had n^{25}_D 1.4594.

Conversion of 4-Chloro-1-(α-chlorovinyl)-3-cyclohexene (II) to *p*-Chlorobenzoic Acid.—A solution of 5.3 g. of II in 100 ml. of dry benzene was heated under reflux for four hours with 10.7 g. of recrystallized N-bromosuccinimide and 0.15 g. of benzoyl peroxide. The succinimide formed was removed by filtration, and the filtrate was washed with 10% sodium bicarbonate solution and water and concentrated. Distillation of the residue yielded 6.8 g. of a mixture, b. p. 80–135° (1.8 mm.), which was heated on a steam-bath with 30 ml. of triethylamine for sixty hours. Triethylamine hydrobromide (6.6 g.) was separated by filtration, and the filtrate was acidified with 100 ml. of dilute hydrochloric acid and extracted with three 70-ml. portions of ether. The combined extracts were washed with dilute hydrochloric acid and water and the ether was distilled. A 2% solution of potassium permanganate was added to a suspension of the residue in 30 ml. of water in 5-ml. portions at 5–10° with stirring until a slight excess was present, which required addition of 400 ml. in a period

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(15) King, *J. Chem. Soc.*, 983 (1935).

of four hours. The mixture was stirred at 50–60° for an additional two hours, after which it was acidified with dilute hydrochloric acid and sodium bisulfite was added until the manganese dioxide was reduced. The insoluble crystalline acid was collected on a filter and recrystallized from 4:1 benzene–ethyl acetate; the yield of *p*-chlorobenzoic acid, m. p. 238–241.5°, was 0.82 g. (17.5%). A second crystallization from 4:1 benzene–ethyl acetate gave *p*-chlorobenzoic acid with m. p. and mixed m. p. with a known sample of 239.5–242°.

Oxidation of a suspension of 5.0 g. of II in 180 ml. of water containing 4 g. of potassium hydroxide with 41 g. of potassium permanganate according to the procedure described by Klebanskii and Denisova[6] yielded 0.1 g. (2.3%) of *p*-chlorobenzoic acid, m. p. 239–240.5°.

Pyridinium Salt Derived from 1,4-Dichloro-1-vinyl-3-cyclohexene (IV).—Attempts to recrystallize the crude pyridinium salt obtained by heating the mixture of chloroprene dimers with pyridine were unsuccessful. A solution of 10 g. of the crude salt in 200 ml. of water containing 20 ml. of concentrated sulfuric acid was treated with 30 g. of potassium permanganate, added slowly during a period of three hours. The mixture was heated under reflux for three hours, cooled, and sodium bisulfite was added to reduce the manganese dioxide. The solution was extracted with ether, the extracts were distilled and the residue recrystallized from aqueous ethanol, yielding 0.14 g. (2.3%) of *p*-chlorobenzoic acid, m. p. and mixed m. p. with a known sample 238–239°.

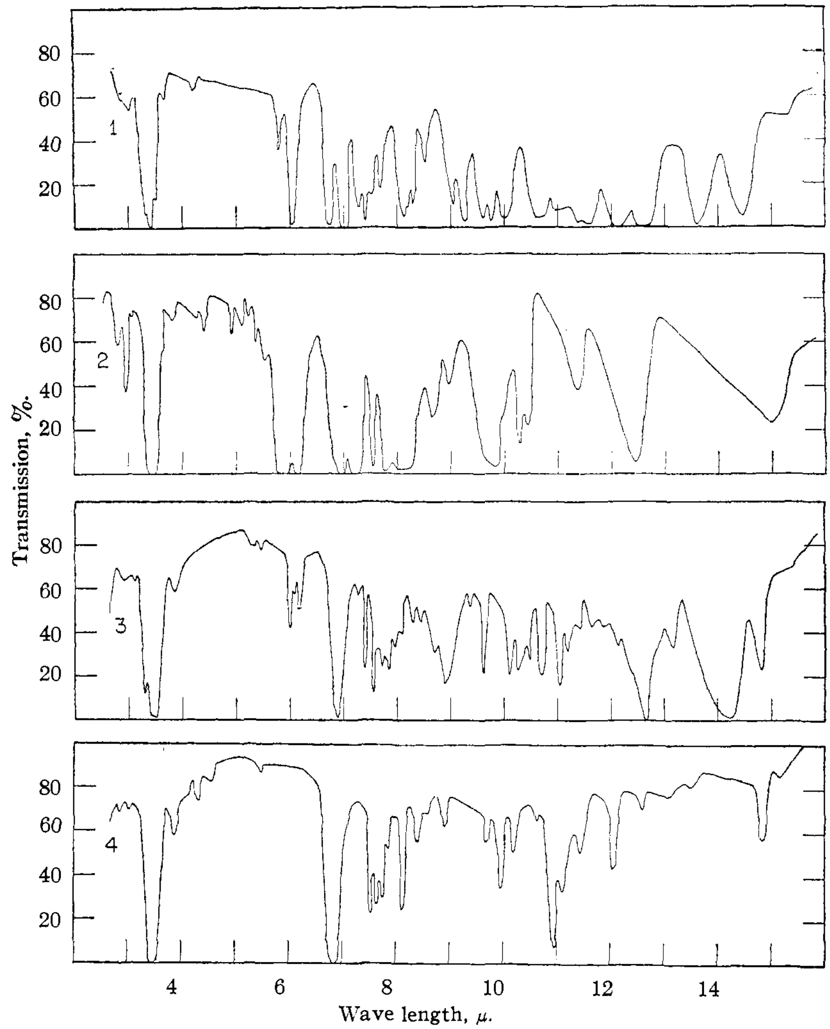

Fig. 2.—Infrared spectra: curve 1, 1,6-dichloro-1,5-cycloöctadiene (VI) purified by recrystallization, f. p. 13.8°; curve 2, bicyclo[3.3.0]-1(5)-octen-2-one (VII); curve 3, mixture of bicyclo[3.3.0]octene isomers; curve 4, *cis*-bicyclo[3.3.0]octane (XI).

A solution of 12 g. of mercuric chloride in 50 ml. of 95% ethanol was added to a hot solution of 10 g. of the crude pyridinium salt in 50 ml. of 95% ethanol. An oil precipitated immediately and crystallized on cooling. Recrystallization from 800 ml. of 95% ethanol yielded 20 g. (97%) of a white crystalline salt, m. p. 90–93°. Recrystallization from 95% ethanol raised the m. p. of the salt to a constant value of 98.8–102°.

Anal. Calcd. for $C_{13}H_{15}NCl_4Hg$: C, 29.59; H, 2.86; N, 2.65; Cl, 26.88. Found: C, 29.98; H, 3.12; N, 2.74; Cl, 26.87.

Hydrogen sulfide precipitated mercuric sulfide from a solution of the salt in hot water, and after separation of the mercuric sulfide concentration of the aqueous solution left a partially crystalline residue which could not be crystallized satisfactorily.

Infrared Spectra.—We are indebted to Dr. Richard C. Lord, Mr. R. S. McDonald and Miss B. J. Fax for the determination of infrared spectra (Fig. 2). The spectrum of VI purified by fractionation but not by crystallization showed the presence of an (isomeric) impurity which was not present in recrystallized samples (curve 1). Comparison of spectra indicated that the impurity was not II; other possibilities are IV or an allylic isomer of IV and the head-to-tail eight-membered cyclic dimer V. The spectrum of the unsaturated ketone VII (curve 2) is consistent with the structure assigned to it on the basis of chemical evidence, for it contained no C–H band at a wave length shorter than the strong band at 3.44 μ, which would be expected to be present if a —CH═C— grouping were present. The spectrum of the bicycloöctene sample prepared from VII semicarbazone (curve 3) contained C═C bands at 6.01 and 6.19 μ (and a weak C═C band at 6.1 μ), indicating that the sample probably was a mixture containing differently situated double bonds. Catalytic hydrogenation of the bicycloöctene sample gave *cis*-bicyclo[3.3.0]octane with an infrared spectrum identical within experimental error with a sample prepared from VIII by Wolff–Kishner reduction (curve 4), showing that no isomers other than those formed by migration of the double bond were present in the unsaturated hydrocarbon.

Summary

The structure of the eight-membered cyclic dimer of chloroprene has been established as 1,6-dichloro-1,5-cycloöctadiene (VI) through degradation by ozonization. The dimer VI on treat-

ment with concentrated sulfuric acid yields bicyclo[3.3.0]-1(5)-octen-2-one (VII) in 70–77% yield. The unsaturated ketone VII was identified by reduction to the known saturated ketone VIII and by oxidation with potassium permanganate, which yielded γ-ketosuberic acid.

CAMBRIDGE, MASSACHUSETTS
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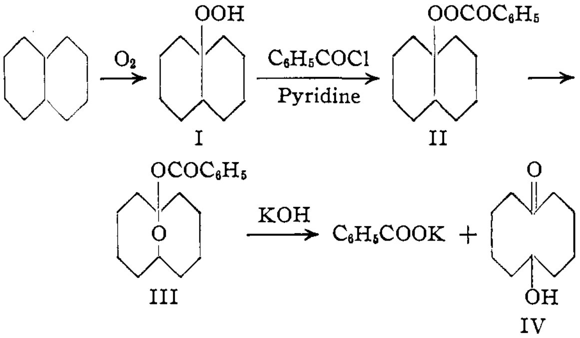
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. VIII. Reactions of 6-Hydroxycyclodecanone and Cyclodecan-1,6-diol *p*-Toluenesulfonates

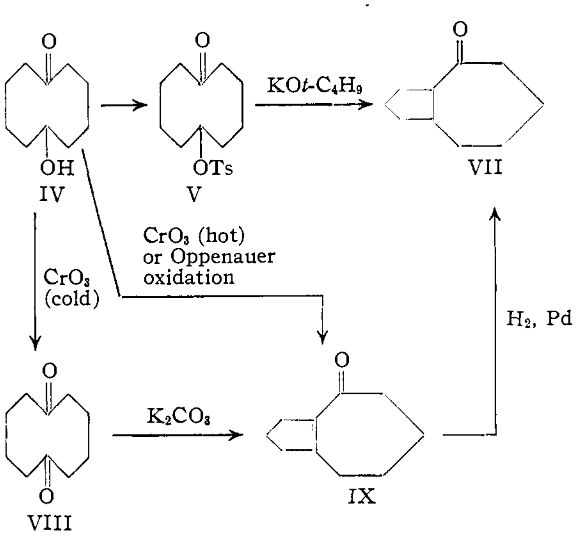
BY ARTHUR C. COPE AND GEORGE HOLZMAN[1]

This paper reports an investigation of the possible utility of 6-hydroxycyclodecanone (IV), prepared from decalin by the route discovered by Criegee,[2] as an intermediate in the synthesis of ten-membered cyclic polyolefins.



The oxidation of decalin to *trans*-9-decalylhydroperoxide (I) was shortened to one and one-half to two and one-half-hours and the conversion to I was improved to 2.5–3.0% by using a reaction temperature of 130° with periodic addition of benzoyl peroxide as a catalyst. Previously the oxidation had been conducted at 110° for twenty-four hours with no added catalyst[2a] (1.4% conversion) and at 70° for two hundred hours with irradiation by ultraviolet light[3] (1.0–1.5% conversion). *trans* - 9 - Decalylhydroperoxide was isolated conveniently from the dilute solution obtained by adsorption on silica gel in a large chromatographic column, removal of decalin by washing with hexane, and selective elution with methylene chloride. Removal of the solvent from the effluent left crystalline I in a form readily purified by recrystallization. Preparation of *trans*-9-decalylhydroperoxide benzoate (II), rearrangement of II to III, and saponification of III to 6-hydroxycylodecanone (IV) by modified procedures gave yields slightly higher than those reported previously[2b] for small-scale preparations.

6-Hydroxycyclodecanone was converted into its *p*-toluenesulfonate (V) in 82% yield by reaction with an excess of *p*-toluenesulfonyl chloride in pyridine at 5–10°. The ester V was only moderately stable, and decomposed after standing for several weeks at room temperature. Its reactions with bases were investigated as a possible means for preparing cyclodec-5-en-1-one (VI). The reaction of V with potassium *t*-butoxide in *t*-butanol proceeded very rapidly, but by an internal Haller–Bauer type of alkylation reaction, and yielded the saturated bicyclic ketone, bicyclo [5.3.0]decan-2-one (VII) (cyclopentanocycloheptanone). The empirical formula of VII was established as $C_{10}H_{16}O$ by analysis, and the absence of unsaturation by quantitative hydrogenation in the presence of Adams platinum catalyst in acetic acid, which required one molar equivalent of hydrogen and reduced the carbonyl group. VII gave two isomeric 2,4-dinitrophenylhydrazones, m. p. 162–163° and 219–220°, which were easily separated by crystallization; the higher melting isomer was obtained in larger amount. The structure of VII was definitely established by synthesis by a previously described method[4] from cyclodecan-1,6-dione (VIII). Oxidation of IV with chromium trioxide in cold acetic acid gave VIII, which on treatment with aqueous potassium carbonate yielded bicyclo[5.3.0]dec-1(7)en-2-one



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[1] Arthur D. Little Postdoctorate Fellow, 1947–1948.

[2] (a) Criegee, *Ber.*, **77B**, 22 (1944); (b) *Ber.*, **77B**, 722 (1944). See also Criegee and Dietrich, *Ann.*, **560**, 135 (1948); Criegee and Schnorrenberg, *ibid.*, **560**, 141 (1948).

[3] Ivanov and Savinova, *Compt. rend. acad. sci. U. R. S. S.*, **48**, 31 (1945); *C. A.*, **40**, 4706 (1946).

[4] Hückel and Schnitzspahn, *Ann.*, **505**, 274 (1933).