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.

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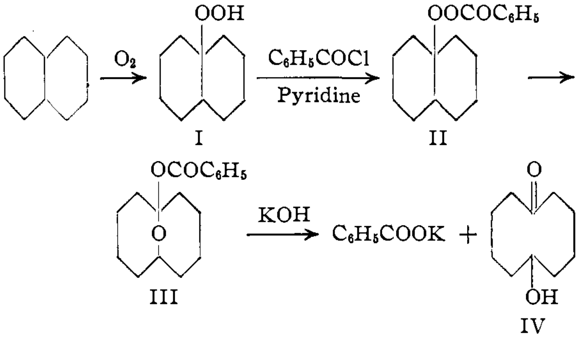
Cyclic Polyolefins. VIII. Reactions of 6-Hydroxycyclodecanone and Cyclodecan-1,6-diol *p*-Toluenesulfonates

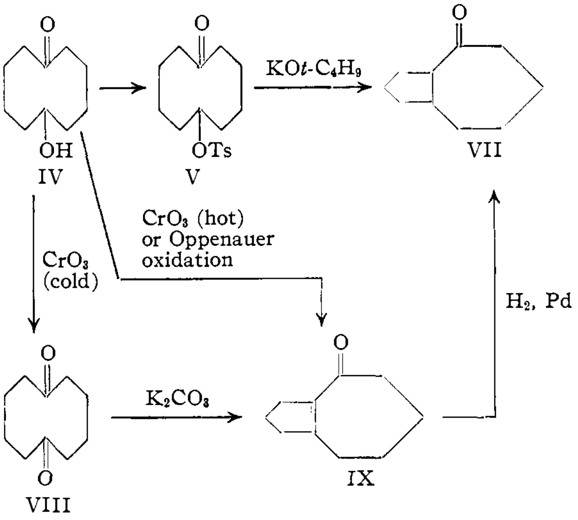
BY ARTHUR C. COPE AND GEORGE HOLZMAN[1]

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.

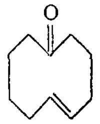
[2] (a) Criegee, *Ber.*, **77B**, 22 (1944); (b) *Ber.*, **77B**, 722 (1944). See also Criegee and Dietrich, *Ann.*, **560**, 135 (1948); Criegee and Schnorrenberg, *ibid.*, **560**, 141 (1948).

[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).

(cyclopentenocycloheptanone). Catalytic hydrogenation of IX yielded a known sample of VII, from which two 2,4-dinitrophenylhydrazones were obtained which were proved to be identical with derivatives of VII prepared from V by mixed m. p. VII prepared by this route gave predominantly the lower melting 2,4-dinitrophenylhydrazone. The two derivatives are presumably derived from *cis* and *trans* forms of VII; neither could have been derived from IX present as an impurity in VII, for IX gave a dark red 2,4-dinitrophenylhydrazone, m. p. 249–251°. IX also was obtained directly from IV by oxidation under conditions which resulted in an internal aldol condensation of the intermediate diketone VIII, either by treatment with chromium trioxide in hot acetic acid or by an Oppenauer oxidation in the presence of aluminum *t*-butoxide.

6-Hydroxycyclodecanone *p*-toluenesulfonate (V) reacted rapidly with diethylaniline at 160–170° to give a product which proved to contain approximately 90% of the unsaturated ketone VI, and about 10% of cyclopentanocycloheptanone (VII).



VI

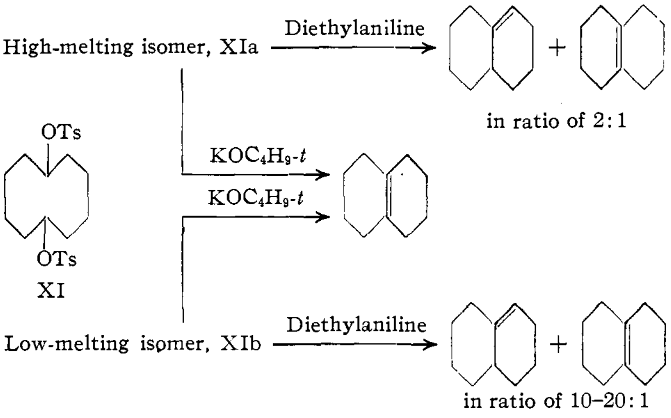
The ketone absorbed 92–94% of two molar equivalents of hydrogen in the presence of Adams platinum catalyst in acetic acid, and 90% of one molar equivalent of hydrogen in the presence of palladium on carbon in methanol. The product of the latter hydrogenation was identified as cyclodecanone by its m. p., 23.5–24.5° (lit. 24.7–25.0°),[5] and the m. p. of its semicarbazone, which did not depress the m. p. of a known sample.

The per cent. hydrogen absorption in quantitative hydrogenations of VI suggested the presence of about 10% of an isomeric bicyclic saturated ketone. Positive evidence for the presence of the bicyclic ketone VII as an impurity in VI was obtained by preparation of the 2,4-dinitrophenylhydrazone, which was separated by chromatography into the 2,4-dinitrophenylhydrazone of VI, m. p. 174–176°, and about 10% of the high melting form of the 2,4-dinitrophenylhydrazone of VII, identified by m. p. and mixed m. p.

Catalytic reduction of 6-hydroxycyclodecanone (IV) in the presence of Raney nickel gave 94% of a mixture of the stereoisomeric cyclodecan-1,6-diols (X), which Criegee[2b] obtained by reduction of IV with sodium amalgam, and Plattner and Hulstkamp[6] prepared by hydrogenation of VIII. The approximate ratio of the stereoisomers in X prepared in this way was indicated by conversion to the dibenzoates, which gave two isomers,[6] m. p. 165.5–167.5° and 73.5–75°, in a ratio of about 1:1.5. The reaction of X with *p*-toluenesulfonyl chloride in cold pyridine gave a 95% yield of a mixture of two isomeric *p*-toluenesulfonates (XI), m. p. 136–137° (dec.) and 111–112° (dec.), in a ratio of about 1:2. These esters were easily separated because the higher melting isomer was much less soluble in benzene. The high melting isomer (XIa) was quite stable, while the low melting form (XIb) decomposed on standing for a few weeks at room temperature.

The low melting isomer XIb reacted quantitatively with two molar equivalents of potassium *t*-butoxide in refluxing *t*-butanol to give an olefin, $C_{10}H_{16}$, which contained only one double bond and was identified as 9,10-octalin by preparation of the blue nitrosochloride derivative (identical with a known sample by mixed m. p.). Reaction of XIb with one molar equivalent of potassium *t*-butoxide in *t*-butanol, added slowly to XI in refluxing *t*-butanol so that no large excess of base was present at any time, gave partial conversion to 9,10-octalin and partial recovery of XI. The high melting isomer XIa also reacted with potassium *t*-butoxide in *t*-butanol to give 9,10-octalin, identified as the blue nitrosochloride. XIa reacted much more slowly than XIb, undoubtedly in part because of its lower solubility in *t*-butanol.

The low melting isomer XIb reacted with diethylaniline at 160–170° to give a 62–65% yield of $C_{10}H_{16}$ hydrocarbons containing one double bond. The product was characterized as a mixture of 1,9-octalin and 9,10-octalin in an approximate ratio of 10–20:1, based on the relative yields of the nitrosochlorides of these compounds. 1,9-Octalin was characterized by its white nitrosochloride, which was converted to the nitrolpiperidine derivative; both were identified by m. p. and mixed m. p. with known samples prepared from 1,9-octalin obtained from chlorodecalin.[7]



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(5) Prelog, Frenkiel, Kobelt and Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

(6) Plattner and Hulstkamp, *ibid.*, **27**, 211 (1944).

(7) Bartlett, Condon and Schneider, THIS JOURNAL, **66**, 1531 (1944).

The high melting isomer XIa reacted with diethylaniline at 160–170° to give a 59% yield of $C_{10}H_{16}$ hydrocarbons which proved to contain 1,9-octalin and 9,10-octalin in an approximate ratio of 2:1, based on the yields of the two nitrosochlorides. The difference in the products obtained by reaction of the high and low melting forms of XI with potassium-*t*-butoxide and diethylaniline cannot be ascribed to rearrangement of the octalins after formation, for interconversion of 1,9-octalin and 9,10-octalin did not occur on heating with potassium *t*-butoxide in *t*-butanol or diethylaniline under conditions used for the elimination reactions. Failure to isolate 1,9-octalin from the products obtained from XI and potassium *t*-butoxide cannot be explained by difficulties in isolation of the nitrosochloride, for 1,9-octalin nitrosochloride is less soluble and accordingly easier to isolate than 9,10-octalin nitrosochloride.

It is evident from these results that the spatial configuration of the cyclodecan-1,6-diol di-*p*-toluenesulfonates permits bridging to occur (with formation of the bicyclic ring system of octalin) more rapidly than formation of a double bond, through elimination of one of the two molecules of *p*-toluenesulfonic acid which are eliminated in the over-all reaction. If bridging is the first step, *cis* and *trans*-9-decalol *p*-toluenesulfonates might be the intermediates formed, and the rates of their formation and the subsequent elimination reaction forming octalin would govern the proportions of 1,9- and 9,10-octalins formed. This problem is being investigated at present.

Experimental[8]

***trans*-9-Decalyl Hydroperoxide (I)**.—Decalin suitable for use in preparing the hydroperoxide was obtained by passing technical decalin through silica gel[9] (1 kg. per gallon of decalin) in a 120 × 5.1 cm. chromatographic column with slight suction at a rate of 1 liter per hour. Decalin recovered from as many as three previous oxidations was equally satisfactory. Four liters of decalin were placed in a 5-liter three-necked flask fitted with a glass propeller stirrer driven by a motor rated at 5,000 r. p. m., a reflux condenser, a thermometer and a gas inlet tube reaching to the bottom of the flask. The liquid was heated to 130° with an electric mantle and maintained at that temperature ±10° during the slightly exothermic reaction by alternate cooling and heating. Oxygen was introduced at a rate of 1.5–2 l. per minute with vigorous stirring. Five grams of benzoyl peroxide was added initially and 5-g. portions were added every ten minutes until 40 g. had been added, followed by 5 g. every fifteen minutes until the total reached 60 g.[10] The mixture was heated at 130° for ten minutes after the final addition, making the total reaction time two and four-tenths hours, after which it was cooled rapidly in an ice-bath. Under these conditions a maximum peroxide concentration of 1.0–1.1 molar was reached after 45 g. of benzoyl peroxide had been added (in several preparations the addition was stopped at this point), and then decreased slowly. The peroxide concentration was determined periodically by removing 0.2–1.0 ml. aliquots containing 0.16–0.27 millimole of peroxide and adding them to 20 ml. of glacial acetic acid containing 1 ml. of 10% potassium iodide. The solutions were allowed to stand for twenty minutes shielded from light, diluted with 5 ml. of water, and titrated with 0.1 *N* sodium thiosulfate to the disappearance of the iodine color. The analyses were not strictly stoichiometric, but were accurate to approximately 10% under these conditions.

trans-9-Decalyl hydroperoxide was isolated by the following procedure. A 2.04-l. portion of the decalin solution was washed with three 200-ml. portions of 10% sodium hydroxide solution to remove tetralin hydroperoxide and other acidic by-products. A red pigment (yellow in acid solution) remained in the decalin solution, and was removed by extraction with 50-ml. portions of ethylene glycol. As many as seven extractions were required to remove the pigment from decalin which had not been oxidized previously, while fewer extractions were required when recovered decalin was used. The decalin solution was washed with 200 ml. of 10% sulfuric acid, then with water and dried over sodium sulfate. The dried solution (1.76 l.) was 0.7 molar in peroxide according to titration. Only about 30% of this amount of *trans*-9-decalyl hydroperoxide could be isolated from the solution, either because of losses in isolation or the presence of other peroxides which were separated in the purification. Silica gel[9] (1 kg.) was placed in a 120 × 5.1 cm. Pyrex tube sealed to a 4 mm. stopcock. The column was pre-washed with 500 ml. of purified decalin, and a 1.1-l. aliquot of the dried decalin solution containing the peroxide was filtered through the gel with slight suction at a rate of about 1 l. per hour. The amount of peroxide in 1.1 l. of the 0.7 molar solution was approximately the maximum adsorbed by 1 kg. of silica gel, as determined by preliminary experiments in which the decalin and hexane effluents were tested periodically for peroxide. The decalin was removed by passing 1.5 l. of hexane (b. p. 56–61°) through the column under gravity flow. The product then was eluted with 2 l. of methylene chloride at a flow rate of 10–15 ml. per minute. The solvent was removed from the effluent by distillation under reduced pressure, while the temperature of the liquid was kept below 25°. The residue crystallized, and *trans*-9-decalylhydroperoxide (30 g., m. p. 81–89°) was separated by filtration and washing with two 25-ml. portions of hexane. An additional 3 g. separated from the hexane solution on standing at 0–5°. The conversion to I was 2.4%, and 85–90% of the decalin was recovered. The yield of I was increased to 41.1 g. (3.0%) by rechromatographing the hexane mother liquor, diluted with 500 ml. of hexane. Two recrystallizations of I (m. p. 81–89°) from hexane gave pure I (m. p. 95–96°) with a recovery of 75–80%.

Smaller-scale preparations gave comparable results. For example, under conditions similar to those described above 1-g. portions of benzoyl peroxide were added every five minutes to 1 l. of decalin (stirred with oxygen) until 17 g. had been added in one and four-tenths hours. The volume of the decalin solution after washing and drying was 0.9 l. and the peroxide concentration was 0.58 molar. A single chromatographic adsorption of 890 ml. of the solution yielded 26.9 g. (2.5%) of I.

Oxidation of decalin purified by washing with concentrated sulfuric acid gave no detectable amount of peroxide under the conditions used by Criegee[2a] (in the absence of an added peroxide catalyst). Oxidation of technical decalin at 85–87° for twenty-four hours without an added catalyst gave only 0.2% of I compared to 1.4% reported by Criegee[2a] from a similar oxidation at 110°, and increasing the time to forty-eight hours did not improve the yield significantly. Such differences can be attributed to the presence in technical decalin of variable amounts of more easily oxidized impurities, such as tetralin, which yield peroxides that catalyze the oxidation of decalin.

Isolation of I by distillation of the decalin at 25–30° (0.2 mm.) followed by crystallization of the residue[2a] was

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

[9] Mesh size 28–200, obtained from The Davison Chemical Corporation, Baltimore, Md.

[10] This procedure may be unsafe because of the possibility of a benzoyl peroxide explosion as the portions are added. Rapid gas evolution with reduction of the peroxide content of the solution to zero occurred in one instance when the temperature of the mixture reached 150°.

less efficient under the conditions which were investigated than the procedure described. Aliquots from one oxidation of decalin gave an over-all conversion of 1.5% to I isolated by crystallization after distillation of recovered decalin, and a conversion of 2.4–3.0% to I isolated by adsorption on silica gel and elution.

***trans*-9-Decalylhydroperoxide Benzoate (II).**—The hydroperoxide I (9.95 g.) was dissolved in 25 ml. of pyridine. The solution was cooled below 10° and 9.85 g. of benzoyl chloride was added with stirring during five minutes. The solution was allowed to stand at 25° for one hour and poured into 200 ml. of cold 10% sulfuric acid. The crystalline precipitate was separated and washed with two 20 ml. portions of methanol. The yield of II was 14.75 g. (92%), m. p. 61–65°. After recrystallization by dissolving the crude product in methanol at room temperature and cooling, II had m. p. 67–68°, in agreement with the value reported.[2a] Crude I (30 g., m. p. 85–90°) and 37 g. of benzoyl chloride under similar conditions gave II as an oil which crystallized after extraction with ether and removal of the solvent; yield 29.4 g. (62%), m. p. 63.5–65.5°, plus 6.0 g. (13%) recovered from the methanol washings.

Preparation of the Benzoate of 6-Hydroxycyclodecanone Hemiacetal (III) from I.—*trans*-9-Decalyl hydroperoxide (15.35 g.) was dissolved in 35 ml. of pyridine. The solution was cooled in an ice-bath and 14.0 g. of benzoyl chloride was added during ten to fifteen minutes with stirring. The solution was allowed to stand at room temperature for one hour and added with stirring to a cold solution of 40 g. of concentrated sulfuric acid in 300 ml. of water. The solid was separated, washed well with water, and dried in air. The product (24.5 g.) was heated under reflux with 50 ml. of methanol for one hour. The hot solution was filtered and cooled, and the crystals were separated and washed with a small amount of methanol. The yield of III was 14.9 g. (60%), m. p. 95.5–97°. Concentration of the mother liquor yielded an additional 0.9 g. (4%), m. p. 85–94°. A sample recrystallized twice from methanol had m. p. 96.5–97.5°. This procedure consistently gave yields of 60–69% from pure I, while yields by the procedure of ref. 2b, in which both the benzoylation and rearrangement were conducted in pyridine, were 5–10% lower. Preparations of III from 30–100 g. quantities of crude I (m. p. in the range 75–90°, 75–80% purity) gave 47–56% yields of III by the procedure described.

Since this work was completed Criegee and Kaspar[11] have described the merits of stronger acids (*p*-nitrobenzoic and chloroacetic) in transforming I to esters analogous to III.

Rearrangement of II to III.—II (5 g.) was heated under reflux with 10 ml. of methanol on a steam-bath for one hour. On cooling, 3.5 g. (70%) of III separated, m. p. 93–95°, and 0.3 g. (6%), m. p. 80–90°, was isolated from the filtrate. Similar rearrangements of 5-g. samples of II in 10 ml. of pyridine, toluene and cyclohexane gave yields of III of 66, 60 and 66%, respectively.

6-Hydroxycyclodecanone (IV).—III (50.0 g., m. p. 95–97°) was heated under reflux for four hours with a solution of 11.2 g. of potassium hydroxide in 800 ml. of methanol and 20 ml. of water. The solution was cooled, exactly neutralized with hydrochloric acid, and concentrated under reduced pressure. The residue in 200 ml. of water was made alkaline with sodium hydroxide and extracted with three 100-ml. portions of methylene chloride. The extracts were dried over sodium sulfate and concentrated. The residue of IV amounted to 29.0 g. (94%), m. p. 66–69°. After two crystallizations from cyclohexane the m. p. was 69–70°. The hydrolysis was complete under the conditions described in two and one-half hours and by use of a 100% excess of potassium hydroxide under conditions otherwise similar the hydrolysis was completed in one-half hour (yields of IV by these procedures were 95–96%).

6-Hydroxycyclodecanone *p*-Toluenesulfonate (V).—A solution of 4.23 g. of IV (m. p. 65–67°) in 25 ml. of pyridine was cooled to 10° and 5.66 g. of *p*-toluenesulfonyl chloride was added slowly. The mixture was allowed to stand overnight at 5–6° and then was added to 200 ml. of cold 3 *N* hydrochloric acid. The oil which separated crystallized after a few minutes and was collected on a filter and washed with water. The crude product, which amounted to 7.35 g. (91%), m. p. 61–66°, was recrystallized by dissolving it in 100 ml. of ether and 150 ml. of 35–60° petroleum ether and cooling the solution with Dry-Ice. The yield of V with m. p. 69.5–71° was 6.57 g. (82%). An analytical sample recrystallized in the same way had m. p. 71–72°.

Anal. Calcd. for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.46. Found: C, 62.80; H, 7.45.

The yield of V was lower if the pyridine solution was allowed to stand overnight at 25–30°. The ester V decomposed to a dark oil after standing at room temperature for several weeks.

Preparation of Cyclopentanocycloheptanone (VII) from V.—A solution of 3.07 g. of V in 25 ml. of warm dry *t*-butanol was treated with 10 ml. of 0.924 *M* potassium *t*-butoxide in *t*-butanol (98% of the theoretical amount). A salt precipitated immediately, and after dilution with 10 ml. of *t*-butanol the solution was neutral. The mixture was diluted with water and extracted with ether. The extracts were dried over sodium sulfate, concentrated, and the residue was distilled through a 30 × 0.6 cm. semimicro column.[12] Two mid-fractions (0.945 g., 66%) of VII were collected, b. p. 104–105° (10 mm.), $n^{25}\text{D}$ 1.4862.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.84; H, 10.67.

Hydrogenation of 0.166 g. of VII prepared in this way in 5 ml. of acetic acid in the presence of 0.10 g. of prereduced Adams catalyst required 101% of one molar equivalent of hydrogen; the product did not react with 2,4-dinitrophenylhydrazine or semicarbazide. VII reacted with hydroxylamine to give a mixture of oximes[4] which could not be separated easily with the small quantities available, but gave 2,4-dinitrophenylhydrazones which were separated readily. VII (0.100 g.) was added to a hot solution of 0.200 g. of 2,4-dinitrophenylhydrazine in 10 ml. of glacial acetic acid. On cooling, 0.120 g. of an orange derivative separated, m. p. 210–214°. Dilution of the filtrate with 25 ml. of water gave 0.050 g. of another orange 2,4-dinitrophenylhydrazone, m. p. 150–157°. The high melting isomer was washed with acetic acid and recrystallized twice from absolute ethanol; m. p. 219–220° and mixed m. p. with a known sample of the high melting form of VII dinitrophenylhydrazone described below, 218–219°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07. Found: C, 57.61; H, 6.41.

The low melting 2,4-dinitrophenylhydrazone of VII was recrystallized from aqueous ethanol and then from absolute ethanol; m. p. 162–163° (mixed m. p. with a known sample 158–161°).

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07. Found: C, 57.56; H, 6.19.

Cyclodecan-1,6-dione (VIII).—A solution of 5 g. of IV in 10 ml. of glacial acetic acid was added to a cold solution of 2.0 g. of chromium trioxide in 40 ml. of 50% acetic acid. The solution was allowed to stand for one day at 5° and one day at room temperature. The solution was cooled in ice, diluted with 100 ml. of water, and neutralized to *p*H 6 with 16 g. of potassium carbonate. The product which separated during neutralization was collected on a funnel and washed with water; the yield of crude VIII, m. p. 93–97°, was 1.36 g. (27%). Optimum conditions for the oxidation were not determined. Recrystallization

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[11] Criegee and Kaspar, *Ann.*, **560**, 127 (1948).

[12] Gould, Holzman and Niemann, *Anal. Chem.*, **20**, 361 (1948). The receiver holder was modified to a 29/42 joint with four cups 65 × 8 mm. prepared from 8 mm. tubing as receivers, each with a capacity of 1.8 ml., in which the distillate was collected dropwise. The thermocouple well at the top of the column was replaced by a 15 cm. thermometer with a small mercury bulb.

from aqueous ethanol and absolute ethanol gave an analytically pure sample of VIII, m. p. 99–100° (lit. 100°).[6,13]

Cyclopentenocycloheptanone (IX).—A sample of IX was prepared by treating VIII with potassium carbonate in boiling aqueous methanol and characterized as the known oxime,[4] benzoyl oxime[4] and semicarbazone.[13] In addition, the dark red 2,4-dinitrophenylhydrazone was prepared and purified by recrystallization from nitrobenzene and from nitromethane; m. p. 250–252° (dec.).

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49. Found: C, 57.87; H, 5.48.

Another sample of IX was prepared from IV by heating a solution of 2.0 g. in 35 ml. of acetone and 50 ml. of benzene with 4 g. of aluminum *t*-butoxide in 30 ml. of benzene under reflux for eight hours. The crude product obtained by acidification, extraction and distillation gave the oxime of IX in 12% yield, m. p. after recrystallization from aqueous methanol 130–131°; optimum conditions for this conversion were not sought. Another sample of IX was obtained by heating a solution of 1.0 g. of IV in 75 ml. of 75% acetic acid with 0.40 g. of chromium trioxide on a steam-bath for thirty minutes, and was isolated as the oxime.

Preparation of Cyclopentanocycloheptanone (VII) from IX.—Hydrogenation of 0.243 g. of IX in 5 ml. of methanol in the presence of 0.1 g. of 10% palladium-on-Norite was complete in fifteen minutes; 101% of one molar equivalent of hydrogen was absorbed. Treatment of the product with 2,4-dinitrophenylhydrazine by the procedure described for VII prepared from V gave two isomeric 2,4-dinitrophenylhydrazones. One isomer was insoluble in glacial acetic acid and had m. p. 219–220.5° after recrystallization from absolute ethanol, while the lower melting isomer was precipitated from acetic acid by water and after recrystallization from aqueous ethanol had m. p. 158–159.5°.

Cyclodec-5-en-1-one (VI).—A mixture of 5.0 g. of V and 35 ml. of diethylaniline was heated at 160–170° for thirty minutes. The solution was cooled, diluted with 250 ml. of ether, washed with 10% sulfuric acid followed by water to remove diethylaniline, dried over magnesium sulfate and concentrated. Distillation of the residue through a semi-micro column[12] gave VI in three fractions totaling 1.97 g. (84%), b. p. 79–84.5° (4.3–5.5 mm.), $n^{25}D$ 1.4932–1.4970. The main fraction amounted to 1.35 g., b. p. 81.5–84° (4.4–5.0 mm.); $n^{25}D$ 1.4936; d^{25}_4 0.976.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.67; H, 10.52.

Hydrogenation of a 0.146-g. sample of VI in 5 ml. of glacial acetic acid in the presence of 0.15 g. of pre-reduced Adams platinum oxide catalyst proceeded rapidly for twenty minutes and then slowly to completion with the absorption of 92% of two molar equivalents of hydrogen in two hours. Hydrogenation of a 0.295-g. sample in 5 ml. of methanol in the presence of 0.15 g. of 10% palladium-on-Norite was complete in forty-five minutes and required 90% of one molar equivalent of hydrogen. After separation of the catalyst the solution was diluted to 40 ml. with methanol and one-third of the solution was treated with semicarbazide acetate. The semicarbazone of cyclodecanone was obtained in a yield of 0.057 g., m. p. 194–198° (dec.), and after three crystallizations from 95% ethanol had m. p. 203–205° (dec.) and mixed m. p. with a known sample[5] 202–204° (dec.) (samples introduced in the m. p. bath at 200°). The remaining two-thirds of the methanol solution was concentrated and the residue was cooled with Dry-Ice. The crystals which formed were separated by filtration and purified by two crystallizations from methanol, which yielded 0.055 g. of cyclodecanone, m. p. 23.5–24.5°.[5]

Cyclodecanone (VI) was characterized and the presence of cyclopentanocycloheptanone (VII) as an impurity was proved by preparation of the 2,4-dinitrophenylhydrazone. A 0.43-g. sample of VI was added to 0.8 g. of 2,4-dinitrophenylhydrazine in 40 ml. of hot glacial acetic acid, and after the solution cooled to room temperature the derivative was precipitated by addition of 100 ml. of water. The precipitate was extracted with 20 ml. of hot 1:1-benzene–ligroin, which left a residue of dinitrophenylhydrazine that was washed with 10 ml. of ligroin. A 2,4-dinitrophenylhydrazone (50 mg., m. p. 198–204°) separated from the benzene–ligroin filtrates on cooling. One crystallization from absolute ethanol gave 31 mg., m. p. 209–212.5°, and an additional crystallization from absolute ethanol followed by three crystallizations from ethyl acetate gave 4 mg. of the high melting form of the 2,4-dinitrophenylhydrazone of cyclopentanocycloheptanone, m. p. 217–219°, which gave no depression in a mixed m. p. with a known sample. Evaporation of the filtrate gave 0.32 g. of a crude dinitrophenylhydrazone, m. p. 145–160°, which on crystallization from 95% ethanol yielded 0.205 g., m. p. 155–165°. Purification of this derivative by fractional crystallization was very difficult. Purification was accomplished by placing the sample in 10 ml. of 1:1 benzene–ligroin on a 23 × 2.5 cm. chromatographic column of 2:1 silicic acid-Celite, prewashed with 75 ml. of ether followed by 150 ml. of ligroin. Development of the column with 75 ml. of 1:1 benzene–ligroin gave a 5-mm. top band of dinitrophenylhydrazine, a 2-cm. blank zone, and a 15-cm. diffuse orange zone. Extraction of the upper 10-cm. portion with ether gave 90 mg. of a dinitrophenylhydrazone, m. p. 168–174°, and the lower 5-cm. portion yielded 49 mg., m. p. 153–162°. (In a separate experiment in which the 2,4-dinitrophenylhydrazone of VII had not been partially separated by crystallization, it was found to be concentrated in the lower portion of the column.) One crystallization of the higher melting fraction from a mixture of 95% ethanol and ethyl acetate followed by two crystallizations from ethyl acetate gave 19 mg. of the 2,4-dinitrophenylhydrazone of cyclodec-5-en-1-one (VI), m. p. 174–176°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07. Found: C, 57.61; H, 6.18.

The presence of an olefinic linkage in the dinitrophenylhydrazone of VI was indicated by the fact that a solution of a sample in 1:1 ethanol–ethyl acetate reduced 2% aqueous potassium permanganate rapidly, while a sample of the dinitrophenylhydrazone of VII reacted slowly and incompletely under the same conditions.

Cyclodecan-1,6-diols (X).—A solution of 11.58 g. of IV in 140 ml. of methanol was hydrogenated in the presence of 2 ml. of W-7 Raney nickel catalyst[14] at atmospheric pressure and 25°. Hydrogenation was rapid initially and stopped after eleven hours and absorption of 94% of one molar equivalent of hydrogen. The catalyst was separated and the methanol distilled. Crystallization of the residue from 200 ml. of acetone yielded 9.63 g. (82.3%) of a mixture of stereoisomeric cyclodecan-1,6-diols, m. p. 145.5–146.5°, and an additional 1.34 g. (11.4%), m. p. 134–138°, was isolated from the mother liquor. A sample (2 g.) of the stereoisomers of X prepared by this method was treated with benzoyl chloride in pyridine. The dibenzoates were separated by the procedure described by Plattner and Hulstkamp[6] into 1.41 g. (32%) of the high melting α-dibenzoate and 2.0 g. (45%) of the low melting β-dibenzoate.

Cyclodecan-1,6-diol Di-*p*-toluenesulfonates (XIa and XIb).—A solution of X (6.0 g., m. p. 145.5–146.5°) in 40 ml. of pyridine was cooled to 10° and 16 g. of *p*-toluenesulfonyl chloride was added during ten minutes with stirring. The solution was allowed to stand overnight at room temperature and then added to 300 ml. of cold 3 *N* hydrochloric acid. The solid was collected on a filter, washed with water and air-dried; yield 15.88 g. (95%), m. p. 110–112° (dec.). A 10.43-g. sample of this solid was extracted with two 50-ml. portions of benzene. The benzene-insoluble high melting isomer XIa (3.20 g., 31%) remained undissolved, and addition of 250 ml. of 35–60° petroleum ether to the filtrate precipitated 6.55 g. (63%) of the benzene-soluble low melting isomer, XIb. The solubilities of the two isomers in benzene at 27° were ap-

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[13] Hückel, Danneel, Schwartz and Gercke, *Ann.*, **474**, 121 (1929).

[14] Adkins and Billica, THIS JOURNAL, **70**, 3121 (1948).

proximately 0.04 and 8.0 g. per 100 ml., respectively. Both isomers decomposed at their melting points at temperatures which depended markedly on the rate and total time of heating. Fairly reproducible decomposition points could be determined by introducing samples in m. p. capillaries into a bath rising at 1 to 2° per minute and noting the minimum temperature at which decomposition occurred within a definite time interval. Mixed melting points of the two isomers determined in this way were intermediate between their separate decomposition points.

In several preparations the m. p. of XIa varied from 136 to 139° (dec.).[15] The high melting isomer XIa (unlike XIb, described below) did not decompose on standing for several months at room temperature. A 0.3-g. sample of XIa, m. p. 136–137° (dec.)[15] which was recrystallized twice from 20 ml. of nitrobenzene and washed with ether had m. p. 114–115° (dec.)[15] and a mixed m. p. with part of the same sample which was not recrystallized of 125–126° (dec.).[15] The recrystallized material had the same solubility characteristics as samples which were not recrystallized, and the reason for the change in decomposition point is not known.

Anal. Calcd. for $C_{24}H_{32}O_6S_2$: C, 59.98; H, 6.71. Found (sample with m. p. 136–137° dec.[15]): C, 60.02; H, 6.91. Found (recrystallized sample with m. p. 114–115° dec.[15]): C, 60.01; H, 6.87.

The low melting isomer XIb decomposed into a dark oil on standing for a few weeks at room temperature. A sample decomposed on standing overnight over phosphorus pentoxide, and the compound was best handled by air drying after recrystallization from a mixture of benzene and petroleum ether and storing in a refrigerator, under which conditions it was stable for a month or more. In several preparations XIb melted within the range of 98 to 112° (dec.),[15] and the crude samples always melted several degrees higher than samples recrystallized from benzene–petroleum ether.

Anal. Calcd. for $C_{24}H_{32}O_6S_2$: C, 59.98; H, 6.71. Found (sample with m. p. 111–112° dec.[15]): C, 59.80; H, 6.76.

Reaction of XIb with Diethylaniline.—The low melting isomer XIb (14.0 g.) and 125 ml. of diethylaniline were heated at 160–170° for forty-five minutes. Ether (400 ml.) was added and the diethylaniline was extracted with 10% sulfuric acid. The ether solution was washed with water, dried over magnesium sulfate, and concentrated. Distillation of the residue through a semi-micro column[12] gave 2.59 g. (65%) of a hydrocarbon, b. p. 72–76° (14 mm.), $n^{25}\mathrm{D}$ 1.4883–1.4932. The product from a similar preparation, b. p. 81–82° (18 mm.), $n^{25}\mathrm{D}$ 1.4905 was analyzed.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.31; H, 11.89.

Hydrogenation of a 149-mg. sample in 5 ml. of glacial acetic acid in the presence of 50 mg. of pre-reduced Adams platinum oxide catalyst required 99% of one molar equivalent of hydrogen.

A 330-mg. sample of the main fraction of the hydrocarbon from the preparation described, $n^{25}\mathrm{D}$ 1.4919, was converted into nitrosochloride derivatives by the procedure described below for preparing nitrosochlorides from the isomeric octalins. The white nitrosochloride of 1,9-octalin was obtained in a crude yield of 131 mg., m. p. 125–126° (dec.)[15]; after recrystallization from acetone the m. p. and mixed m. p. with a known sample was 139–140° (dec.).[15] A sample of this nitrosochloride was converted to the nitrolpiperidine derivative; m. p. and mixed m. p. with the nitrolpiperidine derivative of 1,9-octalin, 174–175° (dec.).[15] A small yield (12 mg.) of the blue nitrosochloride of 9,10-octalin, m. p. 85–89°, was also obtained from this hydrocarbon sample. From these data and approximate analysis of similar preparations by conversion to nitrosochloride derivatives, the product obtained from XIb and diethylaniline was concluded to be a mixture of 1,9-octalin and 9,10-octalin in the ratio of 10–20:1.

Reaction of XIa with Diethylaniline.—A 12.0-g. sample of the high-melting isomer XIa, m. p. 138–139° (dec.)[15] and 100 ml. of diethylaniline were heated at 160–170° for fifty minutes. The hydrocarbon formed (2.0 g., 59%) was isolated in the manner described for the corresponding preparation from XIb. The main fraction, b. p. 76–77° (14 mm.), $n^{25}\mathrm{D}$ 1.4917, was proved to be a mixture of 1,9- and 9,10-octalins by analysis, quantitative hydrogenation, and preparation of the nitrosochlorides. Samples (200 mg.) gave 58 and 54 mg. of the white nitrosochloride of 1,9-octalin and 20 and 33 mg. of the blue nitrosochloride of 9,10-octalin, identified by m. p. and mixed m. p. with known samples, in duplicate experiments.

Reaction of XIa and XIb with Potassium *t*-Butoxide.—A 3.15-g. sample of XIb was heated under reflux for one hour with 0.028 mole of potassium *t*-butoxide in 90 ml. of *t*-butanol. Titration showed that 98% of two equivalents of the base had been neutralized. The hydrocarbon formed was isolated by adding the reaction mixture to water, extraction with ether and distillation; yield 0.48 g. (54%). It was identified as 9,10-octalin by the m. p. of the blue nitrosochloride, which did not depress the m. p. of a known sample.

A 4.0 g. sample of the high-melting ester XIa was heated under reflux with 0.033 mole of potassium *t*-butoxide in 50 ml. of *t*-butanol for twenty hours. (In a similar experiment titration showed that the reaction was 77% complete after eight hours.) The hydrocarbon isolated weighed 0.405 g. (36%), and was identified as 9,10-octalin by the m. p. of its blue nitrosochloride, which did not depress the m. p. of a known sample.

Dropwise addition of 10 ml. of a 0.924 *M* solution of potassium *t*-butoxide to 4.45 g. (0.0093 mole) of XIb in 150 ml. of refluxing *t*-butanol during a period of one hour followed by cooling gave a precipitate containing potassium *p*-toluenesulfonate and unchanged XIb. Dilution of the filtrate with petroleum ether gave an additional quantity of XIb, making the total recovery 2.01 g. (45%), identified by m. p. and mixed m. p. Distillation of the filtrate gave 0.34 g. (27%) of 9,10-octalin, identified by the m. p. of its blue nitrosochloride, which did not depress the m. p. of a known sample.

A sample of octalins composed principally of the 1,9-isomer (prepared from XIb and diethylaniline) was unchanged in composition, according to approximate analysis by preparation of the nitrosochlorides, after heating under reflux with one molar equivalent of potassium *t*-butoxide in *t*-butanol for one hour. Likewise a sample of octalins composed principally of the 9,10-isomer prepared from chlorodecalin and potassium hydroxide[7] was essentially unchanged in composition, according to approximate analysis by preparation of the nitrosochlorides, after heating with diethylaniline at 160–170° for forty-five minutes.

1,9-Octalin and 9,10-Octalin.—A mixture of 1,9- and 9,10-octalins (ratio 1:4–5 based on yields of the nitrosochlorides) was prepared from chlorodecalin by the procedure of Bartlett, Condon and Schneider.[7] The nitrosochlorides were prepared by adding 1.0 g. of the octalin mixture to 2 g. of butyl nitrite and 3 ml. of acetic acid, cooling the solution, and adding 2 ml. of concentrated hydrochloric acid dropwise with stirring. The precipitate was separated by filtration and washed with a few ml. of acetone. The residual white nitrosochloride of 1,9-octalin (0.10 g.) had m. p. 136–137° (dec.).[15] The blue nitrosochloride of 9,10-octalin (0.40 g., m. p. 79–88°) was obtained by cooling the acetone filtrate. Two crystallizations of 1,9-octalin nitrosochloride from acetone gave an analytically pure sample, m. p. 142–143° (dec.).[15] Melting points determined in the usual way were lower. This derivative has been reported to melt at 121°,[7] 127°,[16] 129°,[17] and 135°[13] and it has been noted previously that its melting point depends on the method of heating.[16] 1,9-Octalin nitrosochloride was converted to the nitrol-

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(15) Minimum temperature at which a sample introduced in a capillary decomposed within thirty seconds.

(16) Hückel and Naab, *Ann.*, **502**, 136 (1933).

(17) Hückel and Blohm, *ibid.*, **502**, 134 (1933).

piperidine derivative by dissolving 50 mg. in 5 ml. of acetone, adding 0.2 ml. of piperidine and heating the mixture on a steam-bath for about five minutes, until the volume was reduced to 2 ml. Addition of water precipitated the nitrolpiperidine derivative, m. p. 173–174° (dec.).[15] Two crystallizations from acetone raised the m. p. to 178–179° (dec.)[15]; melting points taken in the ordinary way were lower. This derivative has been reported to melt at 173°,[17] 179°[16] and 181°,[13] the m. p. depending on the rate of heating.[16]

Recrystallization of 9,10-octalin nitrosochloride from acetone raised the m. p. to 89.5–90.5°. A sample derived from 9,10-octalin prepared from β-decalol[18] melted at 91–92°.

Summary

trans-9-Decalylhydroperoxide (I) has been prepared by the reaction of decalin and oxygen, catalyzed by benzoyl peroxide, and isolated by chromatography on silica gel. 6-Hydroxycyclodecanone has been prepared from I by the route discovered by Criegee, and converted to the *p*-toluenesulfonate (V). The reaction of V with potassium *t*-butoxide resulted in an internal Haller–Bauer type of alkylation and yielded cyclopentanocycloheptanone (VII), while reaction of V with diethylaniline yielded cyclodec-5-en-1-one (VI) containing about 10% of the bridged isomer VII.

Hydrogenation of 6-hydroxycyclodecanone yielded a mixture of two stereoisomers of cyclodecan-1,6-diol, from which two isomeric di-*p*-toluenesulfonates (XI) were prepared. Reaction of these isomeric esters with diethylaniline gave mixtures of 1,9- and 9,10-octalin in quite different ratios, while the reaction of both isomers with potassium *t*-butoxide yielded 9,10-octalin.

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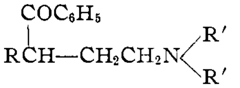
[18] Campbell and Harris, THIS JOURNAL, **63**, 2725 (1941).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION OF SCHERING CORPORATION]

Anomalous Alkylation of Desoxybenzoin and Phenacylpyridine with Dialkylaminoalkyl Halides[1]

BY NATHAN SPERBER, ROSEMARIE FRICANO AND DOMENICK PAPA

In the course of the synthesis of several series of compounds in which alkaline condensing agents were employed, we have had an opportunity to investigate the reaction of desoxybenzoin and phenacylpyridine with β-dialkylaminoalkyl halides. Eisleb[2] reported that desoxybenzoin and β-diethylaminoethyl chloride with sodamide yields γ-phenyl-γ-benzoyl-N,N-diethylpropylamine (Ib), a product comparable in structure to the C-alkylated compounds secured from desoxybenzoin and alkyl halides.[3] For the preparation of γ-phenyl-γ-benzoyl-N,N-dimethylpropylamine (I) and γ-(2-pyridyl)-γ-benzoyl-N,N-dimethylpropylamine (II), we employed the reaction conditions described by Eisleb for the synthesis of Ib.



$$\mathrm{R}\overset{\mathrm{COC_6H_5}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CH_2CH_2N}\begin{smallmatrix}\diagup \mathrm{R'}\\ \diagdown \mathrm{R'}\end{smallmatrix}$$

I, R = phenyl, R′ = methyl
Ib, R = phenyl, R′ = ethyl
II, R = 2-pyridyl, R′ = methyl

Our results with this synthesis are at variance with those reported by Eisleb in that the products obtained from desoxybenzoin and β-dimethylaminoethyl chloride (mixture A) or β-diethylaminoethyl chloride (Ib plus IVb) were not homogeneous. The reaction products mixture A and Ib plus IVb, underwent decomposition upon heating in 25% sulfuric acid. The oily product which separated was identified as desoxybenzoin. The ease of regenerating desoxybenzoin from these mixtures indicates that O-alkylation had occurred in the condensation reaction to yield the enol ethers IV and IVb.[4] The remaining acid solutions, after being freed of desoxybenzoin, gave upon neutralization the basic ketones I and Ib, the products of C-alkylation.

Eisleb[2] reported that the amino ketone Ib yielded a hydrochloride melting at 148°. In repeating this experiment, we obtained two hydrochlorides; one melting at 152° and the other at 183°. The former decomposed in warm sulfuric acid solution to give desoxybenzoin, while the latter was stable under these conditions. It is apparent therefore that the hydrochloride, m. p. 148°, obtained by Eisleb was that of the enol ether IVb and not that of the basic ketone Ib as reported.

Only one hydrochloride was obtained from mixture A and this was shown subsequently to be identical with the hydrochloride of an authentic sample of I. Similarly, only one picrate was obtained from mixture A and it was identical with the picrate of an authentic sample of I. Apparently, the hydrochloride and the picrate of the enol ether IV are not isolable under our experimental conditions.

Since the enol ether IV could not be separated from the amino ketone I by distillation or by suitable derivatives, its presence in mixture A was further established by catalytic reduction with Raney nickel in alcohol solution. The reduction products of mixture A were obtained as a low boiling, colorless oil and a high boiling, viscous

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[1] Presented in abstract before the Division of Organic Chemistry of the American Chemical Society at Atlantic City, September 20, 1949.

[2] Eisleb, *Ber.*, **74**, 1437 (1941).

[3] Meyer and Oelkers, *ibid.*, **21**, 1295 (1888).

[4] The susceptibility of enol ethers to acidic reagents has been demonstrated; compare Friedrich, *Ann.*, **219**, 316 (1883), and Schwenk, Fleischer and Whitman, THIS JOURNAL, **60**, 1702 (1938).