The infrared spectrum of fraction (1) was unlike that of any known cyclodecane derivative; that of fraction 3 showed it to be a mixture of *cis*- and *trans*-cyclodecene and that of fraction 2 was a mixture of (1) and (3).

Analysis of the quantitative infrared spectrum of fraction (3), the cyclodecene fraction, indicated the following concentrations of isomers: *cis*, 19%; *trans*, 69%.

Cyclodecyl-S-methyl Xanthate.—The procedure of O'-Connor and Nace[20] was adapted for the preparation. To a solution of 20.1 g. (0.13 mole) of cyclodecanol in 450 ml. of reagent grade benzene was added 31 g. of sodium hydride. The mixture was stirred and refluxed for 20 hr. To the cooled solution was then added 254 g. of carbon disulfide, followed by another 20 hr. refluxing. After cooling to room temperature, 455 g. of methyl iodide was added to the mixture. The mixture again was refluxed for 24 hr.

Excess sodium hydride was hydrolyzed by the careful addition of 20 ml. of water after which the reaction mixture was poured into 200 ml. of water. The benzene solution was washed with water, dried and evaporated under reduced pressure to yield 34 g. of crude xanthate.

A small amount of the crude material was chromatographed on alumina (Merck) and eluted with 30–60° petroleum ether. The initial fraction, after removal of the solvent, was a clear, slightly yellow oil, n^{20}_{D} 1.5577.

Anal. Calcd. for $C_{12}H_{22}S_2O$: C, 58.54; H, 8.94; S, 26.02. Found: C, 58.79; H, 8.77; S, 25.87.

The xanthate decomposed when attempts were made to distil it *in vacuo*.

Thermal Decomposition of Cyclodecyl-S-methyl Xanthate.—The decomposition of the xanthate was carried out by the procedure of Alexander and Mudrak.[10] A sample of crude xanthate (12 g.) was placed in a 100-ml. flask, equipped with a Friedrich condenser and a bubbler, and heated until vigorous bubbling indicated the onset of decomposition (about 130°). The temperature was maintained at 135–140° for 45 min., then raised to 195–205° for 10 min.

The mixture was cooled, transferred to a Claisen flask and distilled under water-pump vacuum, yielding 4.6 g. of a crude yellow mixture of cyclodecenes, b.p. 80–86° (17 mm.).

A 30–60° petroleum ether solution of the distillate was chromatographed on silica gel, removing the yellow contaminant. After removal of the solvent the residue was distilled to yield 1.2 g. (44%) of a mixture of cyclodecenes, b.p. 192–193° (744 mm.), n^{20}_{D} 1.4820. Analysis of the quantitative infrared spectrum of this mixture showed the presence of the following concentrations of isomeric cyclodecenes: *cis*, 14%; *trans*, 86%.

Isomerization of *cis*- and *trans*-Cyclodecene. (A) By β-Naphthalenesulfonic Acid.—A mixture of cyclodecenes (1.1 g.), which analyzed for 14% *cis* and 77% *trans* was mixed with 50 mg. of β-naphthalenesulfonic acid and 50 mg. of hydroquinone. The flask was flushed with dry nitrogen, tightly stoppered and heated on a steam-bath for 22 hr. After filtration the mixture was distilled from a microdistilling flask to give a colorless liquid, b.p. 180–190° (740 mm.), n^{20}_{D} 1.4848.

Analysis of the quantitative infrared spectrum indicated the following concentrations of isomers of cyclodecene: *cis*, 82%; *trans*, 16%.

(B) By Silver Nitrate.—A sample of a mixture of cyclodecenes (2.1 g.), which analyzed for 14% *cis* and 77% *trans*, was dissolved in a solution of 95% ethanol which contained 0.5 g. of silver nitrate. The solution was allowed to stand in the dark for 22 hr.

Dilution with water permitted the recovery of the cyclodecene fraction which was then washed with water, dried and distilled; b.p. 191° (740 mm.), n^{20}_{D} 1.4818.

Analysis of the quantitative infrared spectrum of the distillate indicated the following concentrations of isomeric cyclodecenes: *cis*, 13%; *trans*, 78%.

(C) By Ultraviolet Radiation.—A sample of pure *cis*-cyclodecene, n^{20}_{D} 1.4851, a sample of pure *trans*-cyclodecene, n^{20}_{D} 1.4820, and a sample of a mixture of the isomeric cyclodecenes, n^{20}_{D} 1.4836, which analyzed for 71% *cis* and 36% *trans*, were each placed in small quartz test-tubes. The tubes were flushed with dry nitrogen, tightly stoppered and exposed to ultraviolet light, from four 15-watt General Electric 360 BL fluorescent bulbs arranged in a semi-circular reflector, for 95 hr.

The refractive indices of the resulting samples were: *cis*-cyclodecene, n^{20}_{D} 1.4851; *trans*-cyclodecene, n^{20}_{D} 1.4822; mixture of *cis* and *trans*, n^{20}_{D} 1.4839.

The infrared spectrum of the irradiated sample of the *cis* isomer did not show any absorption characteristic of the *trans* form; that of *trans*-cyclodecene did not show any absorption of the *cis* isomer.

Analysis of the quantitative infrared spectrum of the irradiated sample of the mixture of *cis*- and *trans*-olefins showed the following concentrations of cyclodecene isomers: *cis*, 64%; *trans*, 33%.

ITHACA, N. Y.

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[20] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5457 (1952).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

The Synthesis of *dl*-Cryptone

BY MILTON D. SOFFER AND MARGARET A. JEVNIK[1]

RECEIVED SEPTEMBER 13, 1954

The racemic form of the naturally occurring ketone, cryptone, 4-isopropyl-2-cyclohexenone, has been synthesized *via* Wilds–Nelson–Birch reduction of *p*-isopropylanisole and also by bromination of 4-isopropylcyclohexanone followed by dehydrobromination with collidine. The latter reaction produced a mixture of cryptone and the isomeric β,γ-unsaturated ketone, which were separated by fractionation. The β,γ-isomer also is convertible to cryptone through the α,β-unsaturated semicarbazone.

This paper is a report on two different syntheses of *dl*-cryptone (4-isopropyl-2-cyclohexenone). The first synthesis proceeds through the Birch reduction of *p*-isopropylanisole, which yields the enol ether, 2,5-dihydro-4-isopropylanisole.[2] In initial experiments the crude reduction[3] product was converted[4] directly to cryptone 2,4-dinitrophenylhydrazone in only 27% over-all yield. When, however, the reduction step was carried out with lithium by the new procedure of Wilds and Nelson,[4] similar treatment afforded the same derivative in 84% yield from *p*-isopropylanisole. Similarly, the Wilds–Nelson reduction product gave the pure α,β-unsaturated semicarbazone in good yield on boiling with methanolic semicarbazide hydrochloride. With somewhat

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[1] From the M.A. thesis of Margaret A. Jevnik, Research Fellow, 1952–1954.

[2] This derivative is apparently one of the products obtained recently by similar reduction of *p*-isopropenylanisole. In that case, however, further elaboration of the reduced material through the unsaturated ketone gave as the final product cryptone semicarbazone of somewhat low melting point in only about 7% over-all yield [A. Bhati, *Current Sci. India*, **21**, 314 (1952); *C. A.*, **48**, 1975 (1954)].

[3] A. J. Birch, *J. Chem. Soc.*, 593 (1946).

[4] A. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5361 (1953).

milder treatment the semicarbazone obtained was a mixture of the α,β- and β,γ-isomers. The regeneration of cryptone from its semicarbazone, which has already been carried out,[5] completes the synthesis.

The more direct route to the α,β-unsaturated ketone through hydrolysis of the enol ether and isomerization of the β,γ-unsaturated ketone[3] has the disadvantage that the product is sensitive to acid and base treatment[6] and that the isomerization of certain 4-alkyl-3-cyclohexenones is inhibited by an adverse equilibrium.[3,7,8] The corresponding β,γ-unsaturated dinitrophenylhydrazones are isomerized much more readily[3] than the ketones themselves, in accordance with the greater electron-withdrawing effect of the dinitrophenylhydrazimino group, and the same effect would operate with the semicarbazones in a reduced degree.

The second route involved the hydrogenation of *p*-isopropylphenol, and the oxidation of the saturated alcohol, with N-bromoacetamide in superior yields, to 4-isopropylcyclohexanone. The unsaturated ketone obtained by subsequent bromination with N-bromosuccinimide and collidine dehydrobromination showed the characteristic absorption maximum for α,β-unsaturation ($\lambda_{\text{max.}}$ 227 mμ), but the extinction coefficient (ϵ 6670) was considerably lower than that of natural cryptone ($\lambda_{\text{max.}}$ 226.3 mμ, ϵ 12,600[5]) and corresponded to that of an approximately equal mixture of the α,β- and β,γ-isomers. The two isomers were separated by fractionation in relatively pure condition and individually identified. Since both isomers are convertible to the α,β-unsaturated semicarbazone, *dl*-cryptone is made available by this route also.

The formation of the β,γ-unsaturated ketone in the collidine reaction is of special interest since the dehydrohalogenation of α-haloketones is in general use for the preparation of α,β-unsaturated ketones. Several further reactions of the α-bromoketone are described in the Experimental Part.

For purposes of comparison in the present work, the pure β,γ-unsaturated ketone and its semicarbazone, which have not been fully characterized previously, were prepared by known methods from the enol ether.

We are indebted to the National Science Foundation for a grant in support of this work.

Experimental Part[9]

p-Isopropylanisole was prepared from *p*-isopropylphenol by the usual procedure[10] in 77% yield, b.p. 81–82° (10 mm.), $n^{20}\text{D}$ 1.5038.

Reduction of p-Isopropylanisole.—The reactions were carried out in an unsilvered Dewar flask closed with a wooden lid which was fitted with an inlet tube, Hershberg stirrer, and an outlet tube protected with soda lime. A solution of 12.2 g. of *p*-isopropylanisole in 800 ml. of dry ether was treated as described[4] with 1 l. of liquid ammonia and 16.8 g. of lithium. During the reaction an additional 500 ml. of liquid ammonia was added in order to prevent the separation of the bronze lithium–ammonia layer. The crude enol ether, 2,5-dihydro-4-isopropylanisole,[2] was obtained as an almost colorless oil, 11.9 g. (96%), on removal of solvent from the washed and dried ether extract and was used directly in the next step. A sample of the product, boiled for two minutes with dinitrophenylhydrazine in 95% ethanol containing hydrochloric acid[4] gave crude **4-isopropyl-2-cyclohexenone 2,4-dinitrophenylhydrazone**, m.p. 118–128°, which was recrystallized from absolute ethanol in deep orange-red needles, m.p. 135–136°; $\lambda_{\text{max.}}$ 376 mμ, ϵ 28,100 (reported for the racemic product m.p. 130–131°,[11] 135–136°,[3] 136°[12]; $\lambda_{\text{max.}}$ 376 mμ, ϵ 29,300[12]). The derivative is very sensitive to extended heating in the acid–ethanol medium.

In initial experiments[13] the reduction was carried out by the method of Birch[3] using 7 g. of *p*-isopropylanisole, 18 g. of absolute ethanol, 350 ml. of liquid ammonia and 7 g. of sodium. The crude enol ether (6.7 g., 96%) was converted in 28% yield to the same dinitrophenylhydrazone, m.p. 123–125°, which on recrystallization from ethanol melted at 132–133° and did not depress the melting point of the derivative from the lithium reduction.

4-Isopropyl-2-cyclohexenone Semicarbazone.—The enol ether from the lithium reduction (152 mg.) was refluxed for 20 minutes with 1.1 g. of semicarbazide hydrochloride in 10 ml. of methanol. Water was added until the cooled solution became turbid and the mixture was refluxed 10 minutes longer. Further dilution with water precipitated the semicarbazone in fine white needles, 120 mg. (65%), m.p. 186–188°, which was recrystallized from aqueous methanol, m.p. 187–188°; $\lambda_{\text{max.}}$ 262 mμ, ϵ 21,200 (reported for the racemic product, m.p. 183–185°,[2] 188°,[11] 192°[12]).

When the reaction was carried out by heating for only three minutes in 95% ethanol, the semicarbazone obtained (170 mg., m.p. 162–168°) appeared to be a mixture of the α,β- and β,γ-unsaturated isomers.

4-Isopropyl-3-cyclohexenone.—The enol ether (3.95 g.) was converted[3] in aqueous ethanol[14] to the bisulfite derivative and washed thoroughly with ethanol and ether. The ketone regenerated with sodium carbonate and distilled (1.23 g., 34%) showed no absorption for α,β-unsaturation in the infrared or ultraviolet; b.p. 77–78° (7 mm.), $n^{20}\text{D}$ 1.4710; $\lambda_{\text{max.}}$ 5.85 μ; no maximum at 215–280 mμ (reported $n^{22}\text{D}$ 1.4817).[15]

4-Isopropyl-3-cyclohexenone Semicarbazone.—To a solution of 138 mg. of the foregoing ketone in 5 ml. of methanol at 0° was added a solution of 220 mg. of semicarbazide hydrochloride and 240 mg. of sodium acetate in 2 ml. of water containing two drops of pyridine. The product which crystallized immediately, 130 mg., m.p. 159–160°, was removed and an additional 50 mg., m.p. 157–159° (92% total), was obtained by adding water. Recrystallization from ether gave the pure derivative in delicate needles, m.p. 162–163°, $\lambda_{\text{max.}}$ 226 mμ, ϵ 13,800. The product reported in earlier work, m.p. 169–170°,[15] probably contained some of the higher melting α,β-unsaturated derivative.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.8. Found: C, 61.5; H, 8.9.

A sample of the compound, refluxed with excess semicarbazide hydrochloride in methanol as described for the formation of the α,β-unsaturated isomer, was converted to the

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[5] R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1408 (1938).

[6] O. Wallach, *Ann.*, **359**, 265 (1908).

[7] W. C. Wildman, R. B. Wildman, W. T. Norton and J. B. Fine, THIS JOURNAL, **75**, 1912 (1953).

[8] A contrary case reported recently [S. M. Mukherji and N. K. Bhattacharyya, *ibid.*, **75**, 4698 (1953)], *i.e.*, a facile rearrangement of 6-(4′-keto-1′-cyclohexenyl)-2-methyl-2-heptene to the conjugated ketone, is open to question. It is stated that no solid derivative could be prepared from the isomerized ketone, despite several attempts, and no evidence of the isomeric homogeneity of the product is presented. The low value reported for the extinction coefficient (λ_{max} 225 mμ, ϵ 5670) compared to that of cryptone, which has the same relevant functionality (λ_{max} 226.3 mμ, ϵ 12,600[5]), would indicate that less than half of the product obtained has the α,β-unsaturated structure assigned for it.

[9] Melting points are corrected and boiling points uncorrected. Ultraviolet absorption spectra were determined in 95% ethanol, except where another solvent is indicated. Infrared spectra were determined on liquids in the free state.

[10] G. S. Hiers and F. D. Hager, "Organic Syntheses," Coll. Vol. I, second edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 58.

[11] D. T. C. Gillespie and A. K. Macbeth, *J. Chem. Soc.*, 1531 (1939).

[12] K. G. Lewis, *ibid.*, 2765 (1951).

[13] We are indebted to Janice Joyce, B. A., 1952, for some preliminary experiments.

[14] M. D. Soffer, M. P. Bellis, H. E. Gellerson and R. A. Stewart, *Org. Syntheses*, **32**, 98 (1952).

[15] O. Wallach and R. Heyer, *Ann.*, **362**, 280 (1908).

4-isopropyl-2-cyclohexenone derivative m.p. and mixed m.p. 187–188°.

4-Isopropylcyclohexanone.—4-Isopropylcyclohexanol was obtained in 93% yield by hydrogenation[16] of *p*-isopropylphenol; b.p. 93–94° (10 mm.), $n^{20}\text{D}$ 1.4662 (reported $n^{20}\text{D}$ 1.4660).[16] Four 33-g. portions of 4-isopropylcyclohexanol were treated[17] separately with 66 g. of N-bromoacetamide in 900 ml. of acetone and 238 g. of ice, and were kept for 3 hours at 0–5°. The formation of the lachrymatory bromoacetone which was apparent when the reaction was carried out at higher temperatures was not noticed under these conditions. The red solution was decolorized with excess aqueous sodium sulfite and extracted with methylene chloride and the combined extracts were washed and dried, and thoroughly freed from solvent at reduced pressure. The residual oil was treated with 850 ml. of aqueous ethanolic sodium bisulfite[14] and the precipitated addition product was filtered and washed with 95% ethanol and ether. A small amount of unreacted ketone in the filtrate was recovered with ether after the addition of base, and was treated again with sodium bisulfite to give a second crop of the addition product. The combined snow-white solid (226 g., 90%) was treated with 10% potassium hydroxide solution and the ketone was extracted with ether and was washed, dried and distilled; yield 113 g. (87%), b.p. 87–88° (12 mm.), $n^{20}\text{D}$ 1.4572 (reported $n^{20}\text{D}$ 1.4560).[16] The semicarbazone was prepared in methanol, m.p. 186–187° (reported 187–188°).[16] The 2,4-dinitrophenylhydrazone crystallized from ethanol in yellow-orange plates, m.p. 118–119° (reported 119–121°),[18] $\lambda_{\max.}$ 363 mμ, ϵ 23,100.

2-Bromo-4-isopropylcyclohexanone.—A mixture of 28 g. of the foregoing ketone in 700 ml. of dry carbon tetrachloride and 36 g. of N-bromosuccinimide was refluxed with stirring for 12 hours in an atmosphere of nitrogen. The initially colorless suspension took on an amber color which disappeared at the end of the reaction. The succinimide was filtered and the filtrate was washed with small portions of cold water, dried over sodium sulfate, and the solvent removed at reduced pressure in a nitrogen atmosphere. The pale yellow oily residue was rapidly distilled through a Claisen flask under nitrogen at 0.05 mm. and the whole distillate was fractionated carefully through a 10-inch Vigreux column to give the pure bromo-ketone as a water-white oil, 30.2 g. (69%), b.p. 83–85° at 0.04 mm., $n^{20}\text{D}$ 1.5018. The crude product is unstable, and when the preliminary distillation was omitted considerable decomposition occurred during the fractionation. The pure compound slowly darkens on exposure to the atmosphere but is stable in the cold under dry nitrogen.

Anal. Calcd. for $C_9H_{15}OBr$: C, 49.3; H, 6.9; Br, 36.5. Found: C, 50.0; H, 7.1; Br, 36.5.

Collidine Dehydrobromination of 2-Bromo-4-isopropylcyclohexanone.—A solution of 21.9 g. of pure bromoketone in 70 ml. of freshly distilled collidine was refluxed in a nitrogen atmosphere for 20 minutes. At the end of this period the initial precipitate of collidine hydrobromide appeared as well defined colorless crystals. Water and ether were added and the ether extract was washed in the cold with excess dilute hydrochloric acid, 5% sodium hydroxide, thoroughly with water, and dried over sodium sulfate. Distillation through a Claisen flask gave 6.9 g. (50%) of colorless fragrant oil, b.p. 33–45° (0.1 mm.), $n^{20}\text{D}$ 1.4801, which from the absorption spectrum ($\lambda_{\max.}$ 227 mμ, ϵ 6670) appeared to be an approximately equal mixture of the α,β- and β,γ-unsaturated ketones. Fractionation of 6.6 g. of the distillate at 0.4 mm. through a Podbielniak Miniature Hypercal column (theoretical maximum sixty plates at atmospheric pressure), gave three fractions as follows: (I) 1.9 g., consisting mainly of **4-isopropyl-3-cyclohexanone,** b.p. 44–47°, $n^{20}\text{D}$ 1.4738; $\lambda_{\max.}$ 227 mμ, ϵ 2,100; (II) 1.9 g. of an intermediate fraction, b.p. 47–53°, $n^{20}\text{D}$ 1.4773; $\lambda_{\max.}$ 227 mμ, ϵ 6,150; and (III) 2.3 g. of relatively pure **4-isopropyl-2-cyclohexenone,** b.p. 53–56°, $n^{20}\text{D}$ 1.4818; $\lambda_{\max.}$ 227 mμ, ϵ 10,400 (reported $n^{20}\text{D}$ 1.4810[11]; $\lambda_{\max.}$ 226.3 mμ, ϵ 12,600[5]).

A sample of fraction I (110 mg.), treated at 0° for 30 minutes with the dinitrophenylhydrazine reagent of Wilds and Nelson,[4] prepared in 95% ethanol, gave 210 mg. (83%) of the 4-isopropyl-3-cyclohexenone 2,4-dinitrophenylhydrazone (m.p. 103–106°) which recrystallized from absolute ethanol in bright orange-yellow needles, m.p. 107–108° (reported[3] 107–108°), $\lambda_{\max.}$ 263 mμ, ϵ 22,400. The melting point was depressed (102–103°) by admixture with the 2,4-dinitrophenylhydrazone of the saturated ketone (m.p. 118–119°).

When 138 mg. of fraction I was refluxed for three minutes with 198 mg. of 2,4-dinitrophenylhydrazine in 14 ml. of 95% ethanol containing 0.4 ml. of concentrated hydrochloric acid, 280 mg. (88%) of the deep orange-red 2,4-dinitrophenylhydrazone of 4-isopropyl-2-cyclohexenone was obtained, m.p. 125.5–128°, which on recrystallization from absolute ethanol melted at 133–134° and was not depressed by admixture with the α,β-unsaturated dinitrophenylhydrazone obtained from the enol ether.

When 30 mg. of the β,γ-unsaturated dinitrophenylhydrazone was refluxed for two minutes in 95% ethanol containing 5% concentrated hydrochloric acid, 20 mg. of the orange-red derivative was obtained, which on recrystallization from ethanol had the same m.p. and mixed m.p. as the foregoing α,β-unsaturated derivative.

When 0.55 g. of fraction I was treated[8] for ten minutes at room temperature with a solution of sodium methoxide (from 130 mg. of sodium and 8 ml. of methanol) under nitrogen, the absorption spectra of the distilled neutral fraction, 0.29 g. (53%), b.p. 80–95° (7 mm.), $\lambda_{\max.}$ 227 mμ, ϵ 6570, indicated a distinct but incomplete isomerization to the conjugated compound (*cf.* ref. 8).

When the reaction was carried out by refluxing for 15 minutes in ethanolic sodium ethoxide, almost the entire material was converted to non-volatile material (*cf.* ref. 6 for base-catalyzed polymerization of cryptone).

Fraction II and III, by the hot acid–ethanol method, gave similarly the α,β-unsaturated dinitrophenylhydrazone in 83% and 86% yield, m.p. and mixed m.p. 134–135°.

The α,β-unsaturated semicarbazone was obtained in 77% yield from fraction III by the sodium acetate method, m.p. and mixed m.p. 187–188°.

2-Bromo-4-isopropylcyclohexanone 2,4-dinitrophenylhydrazone was prepared by refluxing equal weights (1.10 g.) of the bromo-ketone and 2,4-dinitrophenylhydrazine in 150 ml. of chloroform for 20 minutes in a nitrogen atmosphere. The suspended dinitrophenylhydrazine dissolved in about ten minutes. The clear orange solution was concentrated with vacuum to a small volume and upon addition of petroleum ether (b.p. 90–100°) the product crystallized in bright yellow-orange needles, 1.82 g. (91%), m.p. 133–135°, which on recrystallization from chloroform–petroleum ether melted sharply at 136° dec.; $\lambda_{\max.}^{CHCl_3}$ 361 mμ, ϵ 23,900.

Anal. Calcd. for $C_{15}H_{19}N_4O_4Br$: C, 45.1; H, 4.8; N, 14.0; Br, 20.0. Found: C, 45.6; H, 4.8; N, 14.2; Br, 19.3.

When 440 g. of the bromo-ketone was refluxed for three minutes with an equivalent amount of dinitrophenylhydrazine (400 mg.) in 24 ml. of 95% ethanol containing 1 ml. of acetic acid, the crude **2,4-dinitrophenylhydrazone of 2-ethoxy-4-isopropylcyclohexanone** was obtained in orange-yellow needles (420 mg., 58%), m.p. 133–138°, which gave the pure product upon three recrystallizations from absolute ethanol, m.p. 151.5–152°; $\lambda_{\max.}$ 358 mμ, ϵ 23,900.

Anal. Calcd. for $C_{17}H_{24}N_4O_5$: C, 56.0; H, 6.6; N, 15.4; C_2H_5O, 12.4. Found: C, 56.3; H, 6.6; N, 15.5; C_2H_5O, 12.2.

When 600 mg. of the bromodinitrophenylhydrazone was refluxed for three minutes in 4 ml. of acetic acid[19] the color of the solution progressively deepened. Addition of water in the cold precipitated the orange-red **dinitrophenylhydrazone of 4-isopropyl-2-cyclohexenone,** which upon one recrystallization from ethanol had m.p. 125–128° (100 mg., 21%) and on further recrystallization had the same m.p. and mixed m.p. as the authentic cryptone derivative.

In a separate experiment the above dehydrobromination reaction was repeated using 9.26 g. of the bromodinitrophenylhydrazone and 70 ml. of acetic acid. After refluxing for five minutes, 4.08 g. of 65% pyruvic acid[20] and 10 ml. of water were added and the refluxing was continued for 20 minutes. Only a small amount of the unsaturated ketone

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(16) R. L. Frank, R. E. Berry and O. L. Shotwell, THIS JOURNAL, **71**, 3889 (1949).

(17) H. L. Herzog, M. A. Jevnik, P. L. Pearlman, A. Nobile and E. B. Hershberg, *ibid.*, **75**, 266 (1953).

(18) A. K. Macbeth and J. R. Price, *J. Chem. Soc.*, 151 (1935).

(19) F. Ramirez and A. F. Kirby, THIS JOURNAL, **74**, 4331 (1952); **75**, 6026 (1953).

(20) E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948).

was obtained from the petroleum ether soluble portion of the neutral fraction; 0.20 g. (4%), b.p. about 80° (5 mm.), $n^{20}D$ 1.4818; $\lambda_{max.}$ 227 mμ, ϵ 7960. The absorption spectra correspond to a mixture of the α,β- and the β,γ-unsaturated isomer in a ratio of about 2 to 1. Treatment by the hot acid–ethanol method as described before gave the α,β-unsaturated dinitrophenylhydrazone.

4-Isopropyl-1,2-cyclohexanedione 2,4-dinitrophenylosazone was prepared according to Ramirez and Kirby by refluxing 200 mg. of the bromodinitrophenylhydrazone for three hours in 17 ml. of the reagent described.[19] The scarlet crystals, 240 mg. (93%), m.p. 183–185°, were recrystallized from chloroform–ethanol and from chloroform; m.p. 191.5–192° dec., $\lambda_{max.}$ 352 mμ, ϵ 30,600.

Anal. Calcd. for $C_{21}H_{22}N_8O_8$: C, 49.0; H, 4.3; N, 21.8. Found: C, 49.4; H, 4.2; N, 22.4.

NORTHAMPTON, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

Azabenzazulenes. I. 1-Azadibenz[b,f]azulene

BY CHESTER W. MUTH, DAN O. STEINIGER[1] AND ZINON B. PAPANASTASSIOU[1]

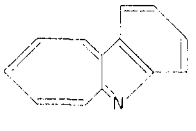
RECEIVED JUNE 23, 1954

The syntheses of the above-mentioned azabenzazulene as well as that of 1-azabenz[b]azulene and 1-azadibenz[b,h]azulene have been accomplished by preparing the appropriate ketones, followed by their conversion to hydroazaazulenes (indoles) and subsequent dehydrogenation.

Discussion

In 1950 when an unsuccessful attempt to prepare 1,4-diazatribenz[b,f,h]azulene[2] was started in this Laboratory there were no reported azaazulenes. Since then the preparation of 1-azabenz[b]azulene[3-5] (I), 1-azadibenz[b,h]azulene[5] (II) and 4-azabenz[b]azulene[6] have been reported.

In the meantime our program had been modified to include a study of the syntheses of azabenzazulenes I-III as well as 1-azatribenz[b,e,g]azulene and 1-azatribenz[b,f,h]azulene, the latter two of which will be the subject of a later communication.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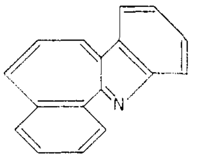
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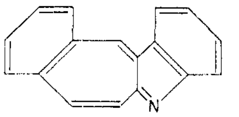
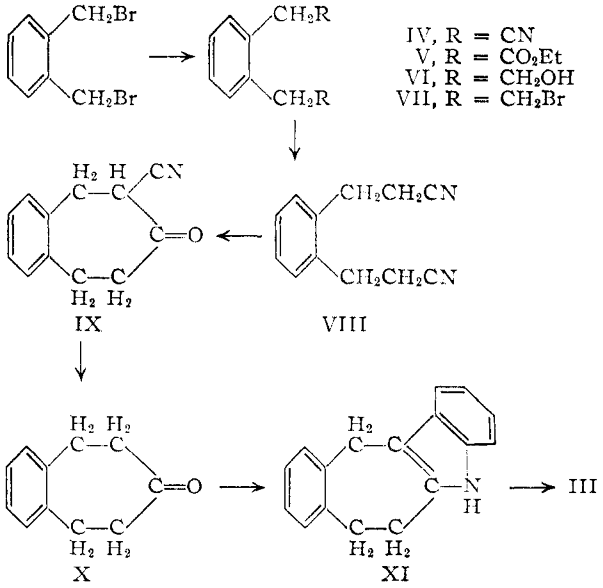

III

The synthetic routes for all the azabenzazulenes of this report may be divided into three phases: (a) synthesis of an appropriate ketone; (b) conversion of the ketone to a hydroazaazulene (indole); (c) dehydrogenation of the hydroazaazulene.

The study for the preparation of 1-azabenz[b]azulene (I) was included because at the time this work was begun there were conflicting reports[3,4] concerning the properties of this compound. The properties observed for I in this work agree with those reported by Anderson and Tazuma[3] as do those later reported by Treibs.[5]

The synthesis of 1-azadibenz[b,h]azulene (II) was completed and its characterization was in the final stages before this compound was reported by Treibs, *et al.*[5] Compound II was obtained by two dehydrogenation procedures including the one used by Treibs. The melting point and color observed for II agree with those reported by Treibs.

The preparation of 7H-5,6,8,9-tetrahydrocycloheptabenzen-7-one (X) was accomplished as outlined in the following diagram by standard paths. All of the compounds of this sequence following V except X are new compounds.



The synthesis of ketone X, in 64% over-all yield by the Ziegler cyclization[7] of VIII to IX followed by its hydrolysis is much superior to the previously used methods for the attempted preparation of X which involved either the Dieckmann reaction[8] or the thorium salt method.[9] It is of interest to note that the Ziegler cyclization product was ketocyano

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(1) From the M.S. thesis of D. O. Steiniger and the Ph.D. Dissertation of Z. B. Papanastassiou, both from West Virginia University, 1954

(2) W. L. Sung, "Attempted Syntheses of Some Derivatives of 4,5,6,7-Dibenzazepin-3-one," Unpublished M.S. thesis, West Virginia University, 1952.

(3) A. G. Anderson and J. Tazuma, THIS JOURNAL, **74**, 3455 (1952).

(4) W. Treibs, *Ann.*, **576**, 110 (1952).

(5) W. Treibs, R. Steinert and W. Kirchoff, *ibid.*, **581**, 54 (1953).

(6) W. Treibs, H. M. Barchet, G. Bach and W. Kirchoff, *ibid.*, **574**, 54 (1951).

(7) K. Ziegler, H. Eberle and H. Ohlinger, *ibid.*, **504**, 94 (1933).

(8) A. F. Titley, *J. Chem. Soc.*, 2571 (1928).

(9) B. Kubota and T. Isemura, *Bull. Chem. Soc. Japan*, **6**, 103 (1931).