filtered dry air. The configurational composition of the alcohol mixture was determined from the infrared spectrum by the previously described method.[18,23] Except for slight carbonyl absorption (presumably due to traces of acetone), the spectra were composites of those for I and II.

To determine whether or not the isolation procedure results in fractionation, three synthetic mixtures of I and II containing 86, 55 and 31% I were dissolved in 35% aqueous acetone and isolated by the above procedure. The infrared spectra of the final solution corresponded to 86, 53 and 31% I, respectively. These experiments demonstrate that the isolation procedure is reproducible and does not result in fractionation. Moreover, the traces of acetone in the final solutions do not interfere with the analysis.

(23) H. L. Goering, T. D. Nevitt and E. F. Silversmith, This Journal, 77, 4042 (1955).

For one run on each of the isomeric alcohols (the third and seventh experiments in Table II) the compositions of the alcohol mixtures were determined from the infrared spectra of the pure liquid alcohols (no solvent). In these runs, all of the carbon disulfide was removed from the extracts at reduced pressure (ca. 25 mm.). While the carbon disulfide was being removed, the temperature of the residue did not exceed 28°. Bands at 11.86 μ (present only in the spectrum of I) and 12.38 μ (present only in the spectrum of II) were used for the analyses. A plot of composition against the ratio of the absorption at these two wave lengths for a series of synthetic mixtures of I and II was used to determine the compositions of the unknown mixtures. The infrared spectra of the isolated mixtures were composites of those of I and II.

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Reactions of the Cycloheptatrienylium (Tropylium) Ion

By W. von E. Doering[1] and L. H. Knox

The tropylium ion, whose preparation has been made more convenient, reacts as an electrophilic reagent with the bases water, hydrogen sulfide and ammonia to give ditropyl ether, sulfide and amine, respectively, with the bases acetamide, benzamide and succinimide to form the N-tropyl derivatives and with cyanide ion to give tropyl cyanide which can be hydrolyzed to an amide identical with Buchner's norcaradiene carboxamide and which reacts with phenylmagnesium bromide to give desoxybenzoin. The tropylium ion is converted both by chromic acid and silver oxide to benzaldehyde. In a reaction of some theoretical significance because it probably proceeds by way of the cycloheptatrienyl (tropyl) free radical, tropylium ion is reduced by zinc dust to ditropyl.

Cycloheptatrienylium or tropylium ion, the parent of the heptagonal aromatic system, was discovered two years ago among the products of the decomposition of dibromotropilidene.[2] Shortly thereafter a derivative, carboxycycloheptatrienylium ion, was synthesized in England by the same type of reaction.[3] Last year saw an original synthesis of the tropylium ion by the Curtius rearrangement of norcaradiene carboxazide[4] and the preparation of the benzotropylium ion.[5] The D_{7h} structure of the tropylium ion has now been put on an essentially "absolute" basis by the definitive infrared–Raman investigation of Lippincott and Fateley.[6] The present work reports additional characterization of the chemical behavior of the tropylium ion.

The previously described method of preparation[2] of tropylium bromide has been improved and standardized so that isolation of the intermediate dibromotropilidene is now avoided and the yield has been raised to 60% of theory. Tropylium bromide is well crystallized from absolute ethanol but contains solvent of crystallization. Unless this ethanol is removed by thorough drying in

(1) Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

(2) (a) G. Merling, Ber., 24, 3108 (1891); (b) W. von E. Doering and L. H. Knox, This Journal, 76, 3203 (1954); (c) compare also H. J. Dauben, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York City, September 12, 1954, p. 18-O: "Cycloheptatrienylium ('tropenium') salts (II) have been derived (D. L. Pearson) from 1,3,5-cycloheptatriene and its 1,6-dibromo and 7-(N-succinimidyl) derivatives."

(3) A. W. Johnson and M. Tisler, Chemistry and Industry, 1427 (1954).

(4) M. J. S. Dewar and R. Pettit, ibid., 199 (1955).

(5) H. H. Rennhard, E. Heilbronner and A. Eschenmoser, ibid., 415 (1955).

(6) W. G. Fateley and E. P. Lippincott, This Journal, 77, 249 (1955).

vacuo before the tropylium bromide is used in reaction with bases, tropyl ethyl ether is always formed as a disturbing by-product. An attempt to convert tropilidene dibromide directly to tropyl methyl ether by refluxing with sodium methoxide failed in its intended purpose but did lead, in an unexpected oxidative rearrangement, to a small amount of benzaldehyde. Tropylium iodide can be prepared easily by passing hydrogen iodide into an ethanolic solution of the bromide. Although the aqueous solution of the iodide is colorless or slightly yellow depending on the concentration, the crystals are dark red. This sequence of color in the crystals of the halide salts, chloride essentially colorless, bromide yellow and iodide red suggests a charge transfer spectrum.

In the reaction of tropylium ion with water, hydronium ion can be titrated and, assuming the other product to be tropyl alcohol, an equilibrium constant can be calculated.[2] Very intensive efforts to isolate tropyl alcohol from tropylium ion and hydroxide ion under a variety of conditions have led uniformly to ditropyl ether[2] alone. With dilute alkali some time is required for ditropyl ether to precipitate from relatively concentrated solutions. In the very dilute solutions used for titration, the reaction is completely reversible so that, with no apparent drift in pH, tropylium ion can first be titrated with 0.1 N hydroxide ion and then be brought back to its original state by titration with 0.1 N hydrochloric acid, the second titration curve being the mirror image of the first within experimental error. Presumably tropyl alcohol is formed initially and, being in equilibrium with tropylium ion, reacts further to give the less soluble ether.

Similarly with hydrogen sulfide and ammonia it

has not been possible to isolate the expected primary products. Hydrogen sulfide and aqueous tropylium bromide react rapidly to give ditropyl sulfide having essentially the same ultraviolet absorption spectrum in isoöctane [λ_{min} 234 mμ (log ϵ 3.66), λ_{max} 254–258 mμ (log ϵ 3.81)] as that of ditropyl ether in isoöctane [λ_{min} 234 mμ (log ϵ 3.80), λ_{max} 256–260 mμ (log ϵ 4.02)]. The thought that ditropyl sulfide might have the sandwich structure is thus incorrect. With saturated aqueous ammonia, tropylium bromide reacts similarly to give the secondary amine, ditropylamine. With saturated ethereal ammonia the tertiary amine, tritropylamine, is the only product. Dimethylamine reacts normally to give dimethyltropylamine.

Derivatives of the still non-existent tropylamine can be prepared from tropylium ion and amides. Thus succinimide reacts in pyridine solution to give N-tropylsuccinimide, a substance which Dryden and Burgert prepared previously from the reaction of tropilidene and N-bromosuccinimide and whose structure had been proved by hydrolysis and by hydrogenation to N-cycloheptylsuccinamic acid, synthesized independently.[7] Benzamide and acetamide react similarly with tropylium ion to give N-tropylbenzamide and N-tropylacetamide, respectively. These structures are assigned on the basis of analogy and elementary analysis. The reactions are reminiscent of the formation of N-substituted amides from alkyl halides and amides.[8] It is of interest that N-tropylbenzamide also results as the product of the reaction of ditropylamine and benzoyl chloride.

Tropylium bromide reacts very smoothly with aqueous potassium cyanide giving a liquid product, C_8H_7N, in excellent yield. The assigned structure of 7-cyanotropilidene is consistent with the method of preparation and the ultraviolet absorption spectrum in isoöctane [λ_{min} 218 mμ (log ϵ 2.09) and λ_{max} 255 mμ (log ϵ 3.57)] which is essentially identical with that of tropilidene itself, [λ_{min} 224 mμ (log ϵ 2.94) and λ_{max} 261 mμ (log ϵ 3.54)] or with that of "norcaradiene carboxamide" in 95% ethanol [λ_{min} 225 mμ (log ϵ 3.08) and λ_{max} 259 mμ (log ϵ 3.50)]. Hydrolysis of the nitrile with alkaline hydrogen peroxide proceeds smoothly to an amide, m.p. 140–141°, which gives no depression of m.p. when mixed with "norcaradiene carboxamide"[9] and has an identical infrared spectrum.

This observation bears on the structure of the Buchner acids[10,11] in the following way. From the reaction of tropylium ion and cyanide ion followed by hydrolysis, one might reasonably have expected cycloheptatriene-7-carboxamide to have resulted. From the reaction of benzene and methyl diazoacetate followed by treatment with ammonia, one might expect norcaradiene carboxamide (as has been generally accepted.)[12] In fact, both reactions

lead to the same substance. Since no one of the Buchner acids (α, β, γ and δ) has ever been reconverted to the "norcaradiene" acid or its derivatives, the "norcaradiene" series must be thermodynamically unstable relative to the others. We con-

clude that two amides of structures a and b cannot exist side by side, that the problem of valency tautomerism in the "norcaradiene" and "cycloheptatriene" series is unsolved in the sense that the nonplanar cycloheptatriene (a) and norcaradiene (b) structures as well as the planar, "tropilidene" structure (pseudo aromatic and most provocative) must again be considered and finally that the previous assignment of structure a to the δ-acid series[10] and to the α-acid series[11] are both incorrect.[13]

Tropyl cyanide reacts with phenylmagnesium bromide to give desoxybenzoin in 42% of the theoretical yield. This is an example of a rearrangement of the tropilidene ring system in which the driving force is the resonance energy of the benzene aromatic system.[14]

When methoxytropilidene is brominated, as with tropilidene itself, one mole of bromine is added easily to give a crystalline dibromo methyl ether in 49% yield. The close similarity of the ultraviolet absorption spectrum of this derivative [λ_{max} 267 mμ (log ϵ 2.72)] and that of dibromotropilidene both in isoöctane [λ_{max} 269 mμ (log ϵ 2.76)] leaves little doubt that both dibromides contain a conjugated diene. Heating the dibromomethoxytropilidene under reduced pressure at 95–100° leads to the rapid evolution of gas, solidification of the mixture and finally to the slow sublimation of tropone hydrogen bromide, obtained in quantitative yield. In the usual way this salt can be converted in good yield to tropone, having an infrared spectrum identical with that of a sample prepared according to Doering and Detert.[15]

Tropylium ion can be oxidized either by chromic acid in acetic acid or by silver oxide in water to

(7) H. L. Dryden and B. E. Burgert, 126th Meeting of the American Chemical Society, New York, New York, September 12, 1954, Abstracts of Papers, p. 22-O; THIS JOURNAL, 77, 5633 (1955).

(8) J. Houben, "Die Methoden der Organischen Chemie," Vol. IV, Georg Thieme Verlag, Leipzig, 1941, p. 380.

(9) E. Buchner, Ber., 30, 632 (1897).

(10) E. Buchner, ibid., 31, 2241 (1898).
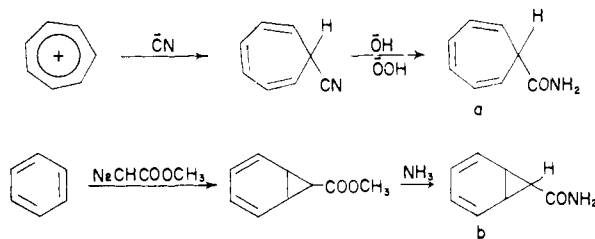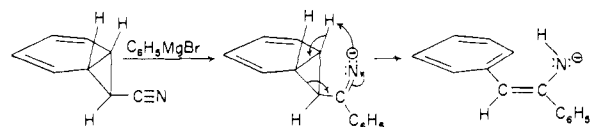
(11) C. Grundmann and G. Ottmann, Ann., 582, 163 (1953).

(12) See, however, E. J. Corey, H. J. Burke and W. A. Remers, THIS JOURNAL, 77, 4941 (1955).

(13) This final conclusion is confirmed by W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, THIS JOURNAL, 78, 5448 (1956), in which the following structural assignments (neglecting questions of valency tautomerism) are supported: α-acid, cycloheptatriene-2-carboxylic acid; β-acid, cycloheptatriene-3-carboxylic acid; γ-acid, cycloheptatriene-1-carboxylic acid; and, of course, "norcaradiene carboxylic acid" or pseudo phenyl acetic acid, cycloheptatriene-7-carboxylic acid.

(14) There being no further evidence on the matter, the following rationalization of the rearrangement should suffice

(15) W. von E. Doering and F. L. Detert, THIS JOURNAL, 73, 876 (1951).

Hydrolysis of 7-Cyanotropilidene.—To a solution of 0.600 g. of nitrile in 3 ml. of 30% hydrogen peroxide and 5 ml. of acetone, 3 ml. of 10% sodium carbonate was added. The mixture became warm and oxygen was evolved slowly. After standing overnight at room temperature, the mixture

(21) E. Buchner, Ber., 29, 106 (1896).

with 6 N hydrochloric acid and exhaustive extraction with pentane afforded 0.516 g. (42.3%) of benzoic acid as a light yellow, crystalline residue, m.p. 121–122° after sublimation and recrystallization from isohexane, undepressed
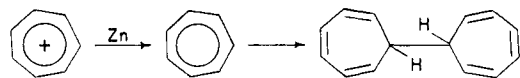
(22) Prepared by Dr. R. Vonderwahl from ethyl "norcaradiene"-carboxylate and aqueous ammonia as previously described.[9]

benzaldehyde in good yield. The oxidation by chromic acid can be rationalized by extending the mechanism of Westheimer[16] to include a rearrangement. Like the other aromatizing rearrangements in the tropilidene and tropolone field, expression in terms of the norcaradiene valence tautomer, although never necessary, is simplest. The oxidation by silver oxide presumably proceeds via tropyl alcohol, but there is no evidence relating to the mechanism.
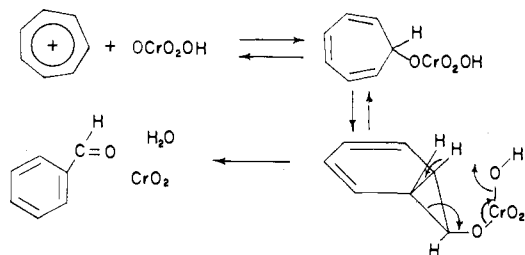
Finally, the remarkably smooth reduction of tropylium ion in aqueous solution by zinc dust should be mentioned. The product is ditropyl which may be catalytically hydrogenated to dicycloheptyl, identical with an authentic sample.[17] The symmetrical formulation of the hydrocarbon is in accord with its ultraviolet absorption spectrum in isoöctane [λ_{min} 227 mμ (log ϵ 2.82) and λ_{max} 255 mμ (log ϵ 3.85)] which is essentially identical with that of tropilidene.

By making the reasonable assumption that the zinc reduction proceeds by a one-electron transfer producing as intermediate, the radical cycloheptatrienyl,[18] one concludes from the isolation of di-

tropyl that the radical is not thermodynamically stable at room temperature relative to its dimer. Despite its high calculated resonance energy (2.54 β vs. 2.99 β for tropylium ion itself),[19] it is apparent that one can never expect to detect the free radical in appreciable concentrations in equilibrium with its dimer.

Experimental[20]

Improved Procedure for Cycloheptatrienylium Bromide.— To a solution of 46.0 g. of tropilidene (b.p. 114°, n^{25}D 1.5215) dissolved in 400 ml. of carbon tetrachloride cooled to 0°, 80.0 g. of bromine dissolved in 250 ml. of carbon tetrachloride was added dropwise with stirring in 3.5 hr. Solvent was removed under reduced pressure at room temperature leaving dibromotropilidene which was heated at 55–60° and 15–20 mm. for 72 hr. The solid, greenish-yellow

(16) Cf. F. Holloway, M. Cohen and F. H. Westheimer, This Journal, **73**, 65 (1951).

(17) Kindly prepared and furnished by Dr. J. R. Mayer. To be published in This Journal.

(18) It is hard to believe that the carbanion resulting from a two-electron transfer could survive long enough to give (a high yield of) ditropyl by reacting with tropylium ion without at the same time forming large amounts of tropylidene by reacting with water.

(19) (a) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatische Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71–85; (b) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, This Journal, **74**, 4579 (1952); (c) J. L. Franklin and F. H. Field, ibid., **75**, 2819 (1953).

(20) Microanalyses are by the Schwarzkopf Microanalytical Laboratory, 56–19 37th Avenue, Woodside 77, N. Y. All melting points are corrected.

cake was ground in a mortar under carbon tetrachloride, filtered, washed with carbon tetrachloride and dried in vacuo at room temperature over calcium chloride. The crude product, 79.0 g. (92%), m.p. 163–165° dec., was placed in a glass-stoppered flask with 700 ml. of absolute ethanol added at its boiling point and shaken vigorously until solution was complete. The dark solution was set aside at −50° for several hours, filtered rapidly by suction, washed with 50 ml. of cold (−50°) absolute ethanol. In this manner 50.6 g. (59%) of pure cycloheptatrienylium bromide, m.p. 203° dec., is obtained. The initial crystals from ethanol contain ethanol of crystallization which has to be removed by drying in vacuo either at room temperature for 3–4 days or at 100° for 3–4 hr.

A similar preparation in which the bromination was carried out in methylene chloride at −70° to −80°, afforded 51.5 g. (60.2%) of once-recrystallized product, m.p. 203° dec.

Tropylium bromide can be crystallized from acetonitrile without solvent of crystallization, but the losses due to an adverse temperature coefficient of solubility are prohibitive.

Tropylium chloride[2] can be recrystallized well from acetonitrile, m.p. 106° dec.

Cycloheptatrienylium Iodide.— To a solution of 0.860 g. of tropylium bromide in 40 ml. of absolute ethanol, 3 ml. of 57% aqueous hydriodic acid was added with stirring. An immediate bright red precipitate separated. The mixture was cooled to −4°, filtered, washed with cold absolute ethanol followed by dry ether and dried in vacuo at room temperature to give 0.900 g. (83%) of tropylium iodide, m.p. 127° dec.

Anal. Calcd. for C_7H_7I: C, 38.6; H, 3.2; I, 58.2. Found: C, 38.8; H, 3.4; I, 58.2.

Despite the red color of crystalline tropylium iodide, its solution in water is only faintly yellow. Silver nitrate causes an immediate precipitation of silver iodide. Tropylium iodide is soluble in warm methanol or ethanol. Crystallization from absolute ethanol, however, affords red needles of unchanged melting point but of lower carbon and hydrogen and higher iodine values.

Dibromotropilidene and Methoxide Ion.— A mixture of 1.647 g. of dibromotropilidene in 15 ml. of absolute methanol and 0.35 g. of sodium methoxide in 15 ml. of absolute methanol was refluxed. The initially yellow solution changed to red and finally violet. The solution was concentrated in vacuo, dissolved in water and extracted with ether. Drying and concentration of the ether extract gave 0.218 g. of oil. The infrared spectrum indicated the presence mainly of benzaldehyde. Treatment with 2,4-dinitrophenylhydrazine afforded benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 239–240°, showing no depression of m.p. on admixture with authentic material.

Cycloheptatrienylium Bromide and Hydrogen Sulfide.— Saturation of a solution of 5.13 g. of tropylium bromide in 50 ml. of water with hydrogen sulfide led to the precipitation of an oil which was extracted with ether. Drying over magnesium sulfate and concentration afforded ditropyl sulfide in practically quantitative yield as a light yellow oil that crystallized on cooling. Two recrystallizations from pentane afforded ditropyl sulfide as colorless crystals, m.p. 37–38°.

Anal. Calcd. for $C_{14}H_{14}S$: C, 78.5; H, 6.6; S, 15.0. Found: C, 78.5; H, 6.6; S, 14.9.

The sulfide decomposes slowly at room temperature and can be stored at −20° for several weeks without decomposition.

Cycloheptatrienylium Bromide and Aqueous Ammonia.— A solution of 1.71 g. of tropylium bromide in 2 ml. of water was added dropwise with stirring to 10 ml. of cold, concentrated aqueous ammonia. An oil separated which was isolated by extraction with pentane followed by evaporation. The crude oil, 0.791 g., crystallized on cooling and was recrystallized twice from pentane at −20° to yield ditropylamine as colorless crystals, m.p. 28–30°.

Anal. Calcd. for $C_{14}H_{15}N$: C, 85.2; H, 7.7; N, 7.2. Found: C, 85.2; H, 7.3; N, 7.5.

The secondary amine, 0.181 g., on treatment with benzoyl chloride in benzene–pyridine solution gave 0.144 g. of dark, crystalline product. Two recrystallizations from absolute ethanol afforded colorless crystals of N-tropylbenzamide, m.p. 160–161° alone and in admixture with an authentic sample of amide m.p. 161° (vide infra).

Cycloheptatrienylium Bromide and Ethereal Ammonia.—
Tropylium bromide, 1.71 g., was added all at once to 100 ml. of dry ether which had been saturated with ammonia at 0°. The mixture was stirred for 30 min. while ammonia was continuously passed through the mixture. The reaction mixture was filtered from ammonium bromide, concentrated and cooled to give 0.384 g. of light yellow crystals, m.p. 112–116°. Concentration of the mother liquor and cooling furnished an additional 0.223 g. of material raising the yield to 63.2% of theory (calculated as $C_{21}H_{21}N$). Two recrystallizations from ether afforded tritropylamine as colorless, transparent prisms, m.p. 124–125°.

Anal. Calcd. for $C_{21}H_{21}N$: C, 87.8; H, 7.4; N, 4.9. Found: C, 88.1; H, 7.6; N, 4.8.

Cycloheptatrienylium Bromide and Dimethylamine (Experiment by Dr. Donald B. Denney).—To a solution of 0.850 g. of tropylium bromide in 5 ml. of water, 5 ml. of a 25% aqueous solution of dimethylamine was added. The colorless oil which separated immediately was isolated by extraction with pentane, drying over magnesium sulfate and evaporation of the solvent. The oily product, 0.675 g. (94.5%), was evaporatively distilled at 55–65° at 1 mm. to give 0.527 g. of dimethyltropylamine, $n^{25}D$ 1.5182.

Anal. Calcd. for $C_9H_{13}N$: C, 80.0; H, 9.7. Found: C, 80.0; H, 9.6.

Cycloheptatrienylium Bromide and Amides. (a) Benzamide.—A solution of 0.171 g. of tropylium bromide in 1 ml. of water was added to a solution of 0.121 g. of benzamide in 2 ml. of hot water. On cooling to room temperature, 0.117 g. of N-tropylbenzamide slowly separated as colorless needles, m.p. 161° after two recrystallizations from absolute ethanol.

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.6; H, 6.2; N, 6.6. Found: C, 79.7; H, 6.1; N, 6.5.

(b) Acetamide.—A solution of 1.77 g. of acetamide in 10 ml. of dry pyridine was added to 5.13 g. of tropylium bromide. Boiling and stirring completed the solution of the bromide within 5 min. The dark mixture was cooled, diluted with 100 ml. of water and extracted with three 25-ml. portions of ether. The ether extract was washed with water, 2 N sodium bicarbonate until neutral, dried over magnesium sulfate and evaporated to give 1.443 g. of dark crystalline solid from which pure N-tropylacetamide was obtained by recrystallization from a small amount of benzene as colorless crystals, m.p. 104–105°.

Anal. Calcd. for $C_9H_{11}NO$: C, 72.5; H, 7.4; N, 9.4. Found: C, 72.8; H, 7.5; N, 9.6.

(c) Succinimide.—A solution of 0.099 g. of succinimide in 1 ml. of warm dry pyridine was added to 0.171 g. of tropylium bromide and heated several minutes on the steam-bath with stirring. The reaction mixture was cooled, diluted with 4 ml. of water and extracted with ether to give 0.110 g. of a colored crystalline residue. Two recrystallizations from absolute ethanol afforded pure N-tropylsuccinimide as colorless platelets, m.p. 148° (reported[7] m.p. 148°).

Anal. Calcd. for $C_{11}H_{12}NO_2$: C, 69.8; H, 5.9; N, 7.4. Found: C, 69.9; H, 5.9; N, 7.3.

7-Cyanotropilidene.—A solution of 1.97 g. of tropylium bromide in 5 ml. of water was shaken with a solution of 1.30 g. of potassium cyanide in 5 ml. of water. Heat was liberated and an oil separated which was extracted with three 5-ml. portions of ether. The extract was dried over magnesium sulfate and evaporated to an orange oil. Evaporative distillation afforded 1.174 g. (87%) of the nitrile as a colorless oil, $n^{25}D$ 1.5330, for a middle cut.

Anal. Calcd. for C_8H_7N: C, 82.0; H, 6.0; N, 12.0. Found: C, 82.2; H, 6.1; N, 11.7.

It dissolves in concentrated sulfuric acid giving the same color reaction, red gradually changing to blue, as reported for norcaradienecarboxylic acid and its derivatives.[21]

The ultraviolet spectrum in 95% ethanol [λ_{min} 218 (log ε 2.09), λ_{max} 255 (log ε 3.57)] closely resembles that of norcaradiene carboxamide.

Hydrolysis of 7-Cyanotropilidene.—To a solution of 0.600 g. of nitrile in 3 ml. of 30% hydrogen peroxide and 5 ml. of acetone, 3 ml. of 10% sodium carbonate was added. The mixture became warm and oxygen was evolved slowly. After standing overnight at room temperature, the mixture

(21) E. Büchner, *Ber.*, **29**, 106 (1896).

was filtered from a small amount of precipitated sodium carbonate and concentrated in a current of nitrogen. Extraction with 40 ml. of ether and concentration of the dried (magnesium sulfate) ether solution gave a colorless crystalline residue of "norcaradiene" carboxamide, 0.436 g. (64.1%), m.p. 140–141° after two recrystallizations from ether; m.p. 140.5–142° in admixture with an authentic sample of the so-called "norcaradiene" carboxamide,[22] m.p. 140–141°. The infrared and ultraviolet spectra of this product and the authentic sample were identical.

Reaction of 7-Cyanotropilidene with Phenylmagnesium Bromide.—To the gently refluxing Grignard solution prepared from 1.22 g. of magnesium, 7.85 g. of bromobenzene and 75 ml. of ether, a solution of 3.51 g. of 7-cyanotropilidene in 25 ml. of ether was added dropwise in 30 min. After being stirred for 3 more hr. under gentle reflux, the solution was treated cautiously with 50 ml. of 2 N hydrochloric acid. After removal of the ether by distillation, the aqueous residue was heated 30 min. on the steam-bath. Extraction with ether afforded 4.20 g. of a brown oil which was evaporatively distilled at 0.4 mm. and 115° to give 0.792 g. of a light yellow oil, followed at 115–138° by 2.60 g. of a crystalline sublimate. The oil partially crystallized on standing at 0° and yielded an additional 0.220 g. of colorless crystals on centrifugation. From the residual oil, diluted with a little isohexane and cooled to 0°, 0.082 g. of additional crystalline material was obtained. Recrystallization from isohexane afforded 2.472 g. (42%) of desoxybenzoin, m.p. 54–55°, having an infrared spectrum identical with that of an authentic sample.

Dibromomethoxytropilidene.—A solution of 4.80 g. of bromine in 20 ml. of carbon tetrachloride was added dropwise with stirring in 20 min. to a solution of 3.66 g. of methyl tropyl ether[2b] in 20 ml. of carbon tetrachloride maintained at 0° by means of an ice–water-bath. After filtration of some amorphous yellow material which separated during the bromine addition, removal of the solvent under reduced pressure at room temperature afforded 6.87 g. of an oily crystalline residue of dibromides from which, by crystallization from absolute methanol, 4.122 g. (48.7%) of dibromomethoxytropilidene was obtained as colorless crystals, m.p. 74–76° and m.p. 77–78° after one additional recrystallization from absolute methanol.

Anal. Calcd. for $C_8H_{10}Br_2O$: C, 34.1; H, 3.6; Br, 56.7; CH_3O, 11.0. Found: C, 34.2; H, 3.7; Br, 56.8; CH_3O, 11.2.

Cycloheptatrienylium Oxide (Tropone) from Dibromomethoxytropilidene.—Dibromomethoxytropilidene, 1.410 g., was heated at 95–100° at 15–20 mm. under a water-cooled condenser. Evolution of gas ceased after 30 min. and the resulting, completely solid, light brown residue sublimed completely in 12 hr. affording tropone hydrobromide as a light yellow crystalline sublimate in quantitative yield.

A solution of 0.300 g. of hydrobromide in 1 ml. of water was covered with 25 ml. of ether, neutralized with solid sodium bicarbonate, filtered, diluted to 100 ml. with ether and dried (magnesium sulfate). Distillation of the ether and removal of the last traces under reduced pressure at room temperature afforded tropone in quantitative yield as a practically colorless, mobile liquid. Evaporative distillation at 68° at 1 mm. gave 0.127 g. (74.7%) of a colorless product, identical infrared-spectroscopically with a sample prepared as described by Doering and Detert.[15]

Chromic Acid Oxidation of Cycloheptatrienylium Bromide.—A solution of 1.0 g. of chromic oxide in 10 ml. of glacial acetic acid was added to a solution of 1.71 g. of tropylium bromide in 30 ml. of 50% aqueous acetic acid. After standing for 24 hr. at room temperature, the mixture was extracted with four 25-ml. portions of ether. The ether extract was washed with three 30-ml. portions of 10% aqueous sodium hydroxide and then with water until neutral, dried over magnesium sulfate and evaporated to give 0.522 g. (49.2%) of benzaldehyde as a light yellow oil, identified by comparison of its infrared spectrum and 2,4-dinitrophenylhydrazone with those of an authentic sample.

Acidification of the combined alkaline and water washings with 6 N hydrochloric acid and exhaustive extraction with pentane afforded 0.516 g. (42.3%) of benzoic acid as a light yellow, crystalline residue, m.p. 121–122° after sublimation and recrystallization from isohexane, undepressed

(22) Prepared by Dr. R. Vonderwahl from ethyl "norcaradiene"-carboxylate and aqueous ammonia as previously described.[9]

in admixture with an authentic sample and having an infrared spectrum identical with that of an authentic sample.

In a parallel experiment in which 1.71 g. of tropylium bromide in 30 ml. of water was treated with 1.0 g. of chromic oxide in 10 ml. of water and allowed to stand for 48 hr., benzaldehyde was isolated in 71% yield. No benzoic acid was isolated.

Reaction of Cycloheptatrienylium Bromide with Silver Oxide.—A solution of 1.71 g. of tropylium bromide in 50 ml. of water was stirred for 24 hr. with 2.0 g. of silver oxide. Filtration followed by ether extraction afforded 0.491 g. (46.3%) of benzaldehyde which was identified by comparison of its infrared spectrum and 2,4-dinitrophenylhydrazone with those of an authentic sample.

Dihydroheptafulvalene (Ditropyl). (a).—A solution of 0.513 g. of tropylium bromide (purified by crystallization from absolute ethanol) in 6 ml. of water was shaken vigorously with 0.200 g. of zinc dust. The mixture became warm and the yellow color of the solution was rapidly discharged. Extraction with four 5-ml. portions of pentane, followed by evaporation of the solvent, afforded a colorless crystalline residue of dihydroheptafulvalene, 0.266 g. (97.4%), m.p. 61° after one recrystallization from pentane. Sublimation at 65–75° at 0.5 mm. gave a colorless crystalline sublimate of unchanged melting point.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.7.

(b).—A solution of 28.8 g. of bromine in 120 ml. of carbon tetrachloride was added in 45 min., with stirring, to a solution of 16.6 g. of tropilidene in 180 ml. of carbon tetrachloride cooled in ice-water. Solvent was removed at room temperature under reduced pressure and the residual crude dibromotropilidene was heated at 70–80° at 20 mm. for 24 hr. The resulting yellow-brown cake was dissolved in 100 ml. of water, filtered from a small amount of insoluble tar and shaken vigorously with 12.0 g. of zinc dust. Slight warming occurred, but on addition of 10 ml. of pentane and shaking, the reaction became strongly exothermic. After being shaken intermittently over a period of 15 min., the mixture was extracted with three 50-ml. portions of pentane. Concentration of the extract to 25 ml. and cooling overnight at −40° afforded 11.4 g. of ditropyl as a heavy, slightly discolored crystalline mass, m.p. 56–58°, for a total yield of 39% based on tropilidene.

Hydrogenation of Dihydroheptafulvalene.—Ditropyl, 0.182 g., was hydrogenated in 10 ml. of glacial acetic acid over 50 mg. of platinum oxide. Four molar equivalents of hydrogen was absorbed in 40 min. Filtration of the catalyst and dilution with water precipitated the hydrocarbon which was extracted with four 10-ml. portions of pentane. The pentane extract was washed twice with 2 N sodium bicarbonate and twice with water. Evaporation of the dried (magnesium sulfate) pentane extract and evaporative distillation of the residual oil at 80–90° at 0.5 mm. afforded dicycloheptyl as a colorless oil, $n^{25}D$ 1.4910, having an infrared spectrum identical with that of an authentic sample (prepared by Dr. J. R. Mayer[17]).

KATONAH, NEW YORK

Constituents of *Heliopsis* Species. V. Heliopsin, a Second Insecticidal Amide from the Roots of *H. helianthoides* var. *scabra.*

BY MARTIN JACOBSON

Heliopsin, an unsaturated isobutylamide closely related to scabrin, has been isolated from the roots of *Heliopsis helianthoides* var. *scabra*. It is a powerful sialagogue as toxic as pyrethrins to house flies. Hydrogenation, hydrolysis, oxidation, and ultraviolet and infrared absorption spectra of heliopsin show it to be the N-isobutylamide of either 2,4,8,10,12,16- or 2,4,8,12,14,16-octadecahexaenoic acid. The geometrical configuration of heliopsin has been partially determined.

In Part I of this series[1] the isolation of scabrin, an unsaturated insecticidal amide from the roots of *Heliopsis helianthoides* (L.) B.S.P. var. *scabra* Dunal. (formerly *H. scabra*), was reported, and reference was made to the presence in the roots of a second highly insecticidal material. The latter has now been obtained in the pure state and its structure has been elucidated.

A petroleum ether extract of the roots,[2] after purification by solvent partition with nitromethane, was chromatographed on adsorption alumina (80 to 200 mesh). The scabrin was readily removed by elution with benzene,[1] and elution with benzene–ethyl ether (1:1) removed the second toxic fraction (corresponding to fraction B) as a yellow oil showing blue fluorescence in ultraviolet light. Repeated attempts to purify the fraction on ordinary adsorption alumina and on silicic acid columns were unsuccessful, but purification was finally achieved by chromatography on neutral alumina (Woelm) and elution with benzene–ethyl ether (9:1) to give a pale yellow, non-fluorescent, viscous oil for which the name "heliopsin" is proposed.

Heliopsin, obtained in 0.06% yield (based on dry root), distilled at 198–200° (0.08 mm.) accompanied by extensive decomposition, and could not be induced to crystallize. A trace of the material, when placed on the tongue, produced an intense paralytic effect on the tongue and lips after an induction period of approximately 20 minutes, whereas scabrin gave a similar effect in 10 minutes.[3] It proved to be as toxic as the pyrethrins to house flies.[4] It is quite unstable at room temperature, changing to a red inactive resin after about a week, but it is stable in the cold for several months under nitrogen or in sealed ampoules, particularly when kept in solution.

Analysis and molecular-weight determination indicated the formula $C_{22}H_{33}NO$ for heliopsin. Acid hydrolysis yielded an acid which was too unstable to be characterized, and a nitrogenous base which was identified as isobutylamine. On reduction with platinum it absorbed hydrogen equivalent to 5.8 double bonds to give N-isobutylstearamide, m.p. 77–78°. Heliopsin was thus established as the N-isobutylamide of an unsaturated

(1) M. Jacobson, THIS JOURNAL, **73**, 100 (1951).

(2) The plant material was very kindly collected on the Mescalero Indian Reservation in the White Mountains of New Mexico by A. H. Berkman, Texas Western College, El Paso.

(3) Because of this induction period, heliopsin was previously mistakenly reported as being without sialagogue effect.

(4) The tests against house flies were carried out by W. A. Gersdorff and P. G. Piquett, of the Entomology Research Branch.