mol. wt., 367. Found: C, 78.4; H, 4.7; N, 3.6; mol. wt. (micro-Rast), 360.

The photo-product, namely, 1-benzamido-2-naphthylbenzoate (XIVa), is not depressed when admixed with an authentic specimen of XIVa.[16] It is soluble in benzene, but difficultly soluble in light petroleum. It is insoluble in cold, aqueous sodium hydroxide solution but soluble in alcoholic sodium hydroxide and gives no color with concentrated sulfuric acid.

When a solution of 1 g. of XIVa in 15 ml. of alcoholic sodium hydroxide (15%) was refluxed for ten minutes followed by cooling and acidification with dilute hydrochloric acid, a solid separated out. It was filtered off, washed thoroughly with water and crystallized from alcohol as colorless crystals, m.p. 248°; identified as 1-benzamido-2-naphthol (V) (m.p. and mixed m.p.[16]); yield is almost quantitative. It is readily converted in an almost quantitative yield, to XIVa by the action of benzoyl chloride in presence of aqueous sodium hydroxide solution (10%).

(b) *p*-**Tolualdehyde.**—A mixture of 1.5 g. of III, 1 ml. of *p*-tolualdehyde and 30 ml. of benzene was exposed to sunlight for 10 days (August). The reaction mixture was worked up as described above and the colorless crystals (*ca.* 0.39 g.), so obtained, were recrystallized from a mixture of benzene and light petroleum, m.p. 186°. It was identified by m.p. and mixed m.p. determination with a sample of 2-naphthyl *p*-tolyl (XIVb) (prepared as below). It is easily soluble in benzene and hot ethyl alcohol, but sparingly soluble in petroleum ether and is insoluble in cold aqueous sodium hydroxide solution.

XIVb was prepared from 1 g. of V and 1 ml. of *p*-toluoyl chloride (prepared by the action of thionyl chloride on *p*-toluic acid) in presence of aqueous sodium hydroxide (15 ml.; 10%). It was obtained as colorless crystals from ethyl alcohol, m.p. 186°, in almost quantitative yield.

Anal. Calcd. for $C_{25}H_{19}NO_3$: C, 78.7; H, 5.0; N, 3.7; mol. wt., 381. Found: C, 78.8; H, 4.8; N, 3.6; mol. wt. (micro-Rast), 374.

(c) *p*-**Methoxybenzaldehyde.**—One and one-half grams of III and 1 ml. of *p*-methoxybenzaldehyde in 30 ml. of benzene was exposed for 10 days (August). The dark brown benzene solution was evaporated and the oily residue was washed several times with cold light petroleum (*ca.* 60 ml.), then followed by washing with cold, dilute aqueous sodium hydroxide solution (5%) (*ca.* 10 ml.). The insoluble mass was extracted with ether, washed with water, dried and evaporated and the resulting oil dissolved in a few ml. of benzene. The benzene solution was allowed to evaporate slowly and the colorless crystals obtained were collected and recrystallized from light petroleum as colorless crystals (*ca.* 0.29 g.), m.p. 181°. The photo-addition product XIVc was identified as 2-naphthyl *p*-tolyl (m.p. and mixed m.p.[16]).

GIZA, CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Reaction of N-Bromosuccinimide with Cycloheptatriene[1]

BY HUGH L. DRYDEN, JR., AND BILL E. BURGERT

RECEIVED FEBRUARY 14, 1955

Cycloheptatriene reacts with N-bromosuccinimide to give N-(cyclohepta-2,4,6-trienyl)-succinimide, succinimide and a dibromide of cycloheptatriene. A new synthesis of cycloheptatriene from bicyclo[3.2.0]hept-2-ene-6-one is described. A comparison of the reactivities of cycloheptatriene and ethyl norcaradiene carboxylate toward maleic anhydride strongly suggests that cycloheptatriene exists largely if not entirely as the monocyclic triene rather than as its valency tautomer norcaradiene.

In an attempt to prepare cycloheptatrienylium bromide (I)[2] the reaction of cycloheptatriene (II) with N-bromosuccinimide (NBS) was investigated. When equimolar quantities of the two reagents were heated in boiling carbon tetrachloride containing a little benzoyl peroxide, a reaction occurred during several hours. None of the expected bromide I could be isolated from the reaction mixture. Instead a bromine-free nitrogen containing solid III corresponding in analysis to a cycloheptatrienylsuccinimide was obtained. That III was an N-substituted succinimide was indicated by the presence of two carbonyl bands in the infrared spectrum at 5.59 μ (m) and 5.82 μ (s). These bands seem to be characteristic of N-substituted succinimides since they have been reported[3] in the spectrum of N-(*n*-amyl)-succinimide and we have observed them in the spectra of N-phenyl and N-allylsuccinimides. A comparison of the ultraviolet spectrum of III (λ_{max} 256 mμ) with that of II (λ_{max} 260 mμ) showed that the succinimido group was on the allylic carbon atom of the cycloheptatriene ring. The chemical reactions described below confirmed that III was N-(cyclohepta-2,4,6-trienyl)-succinimide.

Hydrogenation of III in a variety of solvents using either platinum or palladium catalysts proceeded with the absorption of more than three mole equivalents of hydrogen presumably because of hydrogenolysis of the allylic carbon–nitrogen bond. It was not possible to isolate N-cycloheptylsuccinimide from any of the reduction mixtures.

The partial hydrolysis of III afforded N-cycloheptatrienylsuccinamic acid (IV). Although the hydrogenation of IV under a variety of conditions proceeded with concurrent hydrogenolysis, the hydrogenation of the sodium salt of IV in aqueous solution proceeded without cleavage three mole equivalents of hydrogen being absorbed. The N-cycloheptylsuccinamic acid (V) isolated from the reduction mixture was identical with a sample prepared from cycloheptylamine and succinic anhydride. V could also be isolated from the hydrogenation products of III following their partial hydrolysis.

In addition to III and succinimide a dibromide of II was isolated from the reaction mixture. This dibromide was unstable and evolved hydrogen bromide upon standing. Presumably it was identical with the cycloheptatriene dibromide described by

---

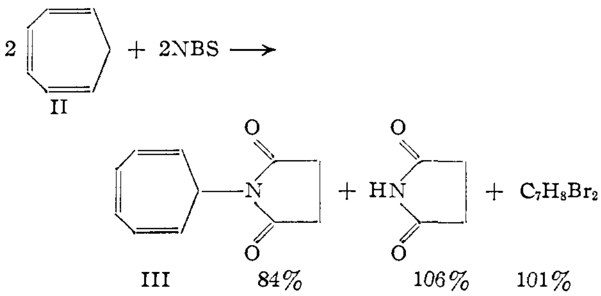
[1] Presented at the 126th National Meeting of the American Chemical Society, New York, N. Y., September 12–17, 1954.

[2] Since this work was completed successful syntheses of this compound have been reported (ref. 4 and 5).

[3] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 172.

Doering and Knox[4] and Dauben and Pearson[5] and reported by the latter authors to be 1,6-dibromocyclohepta-2,4-diene.

On the basis of the nature and yields of the products obtained, the over-all equation for the reaction between cycloheptatriene and NBS may be written as shown.



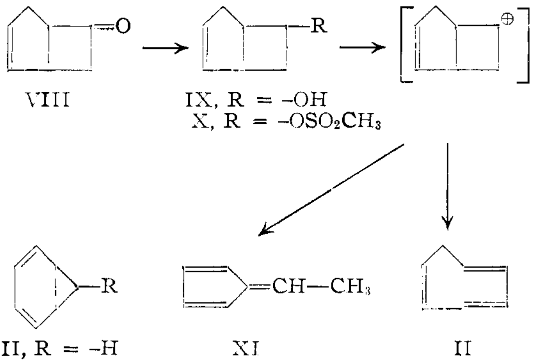
Although direct evidence on the point is lacking, it is possible that the formation of III involves the intermediate formation of cycloheptatrienylium bromide followed by its reaction with NBS or succinimide. Alternate reaction paths would appear to lead to the formation of at least some vinyl-type imides such as N-(cyclohepta-1,3,5-trienyl)-succinimide in addition to III. However III, obtained in 84% yield based on the foregoing equation, was the only substituted succinimide isolated.

Regardless of the detailed reaction path the formation of III from II and NBS involved a formal elimination of the elements of hydrogen bromide. Since NBS is known[6] to oxidize hydrogen bromide to bromine, it is apparent that bromine would ultimately be produced during the reaction either as such or more probably in incipient form as $Br^{\oplus}$. The elements of bromine liberated added selectively to unreacted II rather than to the seemingly unsaturated imide III as well. In support of such a selective addition we observed that a solution of II in chloroform decolorized bromine instantly whereas a solution of III did so only after standing for several minutes.[7]

The complete hydrolysis of III with 10% sodium hydroxide solution afforded a low yield of an amine VII which may have been cycloheptatrienylamine. Because of the sensitivity of the amine to air oxidation a satisfactory analysis of it could not be obtained. Benzoylation of the amine gave N-cycloheptatrienylbenzamide which upon hydrogenation absorbed three mole equivalents of hydrogen. The N-cycloheptylbenzamide thus formed was identical with an authentic sample.

A portion of the cycloheptatriene required for this work was prepared by a modification of the Willstätter[8] synthesis. Cycloheptene was found to react with two moles of NBS forming an unstable dibromo compound which may have been identical with the one obtained[8] by the addition of one mole of bromine to cyclohepta-1,3-diene. Dehydrobromination of this bromo compound with quinoline afforded impure II. Following purification II was obtained in 20% yield based upon the cycloheptene initially taken.

The major portion of the cycloheptatriene used was prepared by our recently described procedure[9] starting with the available[10] bicyclo[3.2.0]hept-2-ene-6-one (VIII). Reduction of VIII with lithium aluminum hydride afforded the alcohol IX which was converted to the corresponding methane sulfonate ester X. Solvolysis of X in hot acetic acid containing sodium dihydrogen phosphate proceeded rapidly giving cycloheptatriene in 50% yield based upon IX. In addition to II an ester fraction of undetermined composition was obtained. If the sodium dihydrogen phosphate was replaced by sodium acetate, the yield of the ester was increased at the expense of II (30%). The cycloheptatriene obtained by this method was contaminated with a yellow impurity which was probably methylfulvene (XI) arising from an alternate mode of opening of the cyclobutane ring in X. Although XI could be removed from II by fractional distillation, it was present in too small an amount to be detected spectroscopically and it did not interfere with the reactions of II.



Cycloheptatriene obtained by either of the above procedures had physical constants identical with those reported previously[8b,11] and formed a maleic anhydride adduct having the reported[8b] melting point. Doering and Knox[4] have suggested that the structure of cycloheptatriene cannot be expressed as II with certainty but that it may be formulated equally well as the valency tautomer norcaradiene (XII). Although the Willstätter synthesis[8a] would be expected to lead to the structure II, both the photochemical reaction of diazomethane with benzene[11] and the solvolysis of X could lead to either II

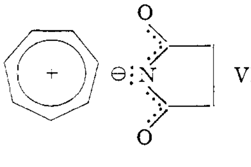
---

[4] W. von E. Doering and L. M. Knox, THIS JOURNAL, **76**, 3203 (1954).

[5] H. J. Dauben, Jr., and D. L. Pearson, 126th meeting of the American Chemical Society, New York, Sept. 13, 1954, Abstracts of Papers, p. 8M.

[6] P. Wieland and K. Miescher, *Helv. Chim. Acta*, **30**, 1879 (1947).

[7] N-Allylsuccinimide was found to react with bromine equally slowly. The sluggish addition of bromine to these olefinic imides may be rationalized best in terms of inductive effects. Although it is tempting to attribute the slow rate of reaction of III with bromine to a significant contribution of resonance structures of the type VI, the fact that the infrared carbonyl frequencies of III are "normal" seems to preclude any significant contribution of such structures.



VI

[8] (a) R. Willstätter, *Ann.*, **317**, 204 (1901); (b) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1057 (1939).

[9] H. L. Dryden, Jr., *ibid.*, **76**, 2841 (1954).

[10] A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

[11] W. von E. Doering and L. H. Knox, *ibid.*, **72**, 2305 (1950).

or XII.[12] XII as a 1,3-cyclohexadiene would be expected to display the relatively high degree of reactivity toward maleic anhydride which is characteristic of this system whereas II would be expected to show a lower order of reactivity. In this regard it is significant that Cope and his co-workers[13] have found that bicyclo[4.2.0]octa-2,4-diene reacted nearly quantitatively with maleic anhydride at 10° whereas its monocyclic valency tautomer 1,3,5-cycloöctatriene failed to form an adduct under the same conditions. We have found that ethyl norcaradiene carboxylate[14] (XIII) afforded an 80% yield of its maleic anhydride adduct at 5°. It seems reasonable that XII would form a maleic anhydride adduct with similar ease. Cycloheptatriene did not react with maleic anhydride to an appreciable extent at 5° and therefore its formulation as norcaradiene seems precluded.[15] Admittedly our findings do not exclude the possibility that cycloheptatriene as ordinarily obtained is an equilibrium mixture of II and XII containing only a small percentage of XII and that the rate of equilibrium of II and XII is negligibly small at 5°.[16] However, our findings do suggest strongly that cycloheptatriene exists largely and perhaps entirely as the monocyclic valency tautomer II.

Experimental[17]

Reaction of Cycloheptatriene with NBS.—A mixture of cycloheptatriene (25.0 g., 0.272 mole), NBS (48.5 g., 0.272 mole), benzoyl peroxide (3.29 g., 0.0136 mole) and 900 ml. of carbon tetrachloride was refluxed under nitrogen for four hours. The mixture was filtered and the precipitate washed with several portions of hot carbon tetrachloride. The precipitate of succinimide weighed 14.15 g. (106%) after drying in air.

When the combined carbon tetrachloride filtrates were concentrated under reduced pressure a solid separated. This was removed by filtration, washed with cold carbon tetrachloride, and crystallized (Norite) from ethyl acetate giving 21.75 g. (84%) of III, m.p. 144–146°. An analytical sample was prepared by several recrystallizations from ethyl acetate, m.p. 145.5–146.5°.

Anal. Calcd. for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.14; H, 5.78; N, 7.73.

Removal of the carbon tetrachloride from the combined filtrate left an unstable oil, wt. 34.45 g. (101%). It evolved hydrogen bromide and turned black on keeping. The oil from another preparation was evaporatively distilled at 80–90° (2 mm.) affording a nearly colorless liquid (45%) which decomposed vigorously if the distillation was carried out at a higher temperature.

Anal. Calcd. for $C_7H_8Br_2$: C, 33.36; H, 3.20. Found: C, 34.40; H, 3.48.

The cycloheptatrienylsuccinimide (III) had infrared maxima at 5.59 μ (m) and 5.82 μ (s). N-Allyl- and N-phenylsuccinimides were found to have similar bands at 5.60 μ (m), 5.82 μ (s) and 5.58 μ (m), 5.73 μ (s), respectively. N-(*n*)-Amylsuccinimide has been reported[3] to have carbonyl absorptions at 5.66 μ (m) and 5.86 μ (s). A solution of III in 95% ethanol had λ_{max} 256 mμ (log ε 3.54).

When III was hydrogenated using platinum oxide or 5% palladium–charcoal catalysts and ethanol, acetic acid or ethyl acetate as solvents, the hydrogen absorption varied from 122–161% of that calculated for three mole equivalents.

N-Cycloheptatrienylsuccinamic Acid (IV).—A mixture of 300 mg. (1.58 mmoles) of III, 10 ml. of 0.7994 *N* sodium hydroxide solution, and 3 ml of 95% ethanol was heated on a steam-bath for five minutes during which time the *p*H changed from 12 to 7. An additional 2.6 ml. of the sodium hydroxide solution was added (1.28 mmoles total) and the mixture warmed for another five minutes. The solution (*p*H 7) was treated with several drops of alkali and extracted with ether to remove neutral material. The aqueous layer was separated, acidified with hydrochloric acid, and the precipitated solid was filtered. The N-cycloheptatrienylsuccinamic acid obtained weighed 175 mg. (53%), m.p. 145–146°. An analytical sample was crystallized from ethyl acetate, m.p. 147–148°.

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.33; N, 6.77; neut. equiv., 207. Found[18]: C, 64.00; H, 6.14; N, 7.26; neut. equiv., 200.

IV had $\lambda_{max.}$ 27 mμ (log ε 3.52) in 95% ethanol.

Reduction of N-Cycloheptatrienylsuccinamic Acid to N-Cycloheptylsuccinamic Acid (V).—A solution of 48.1 mg. (0.222 mmole) of IV in 15 ml. of water and 3 ml. of 0.07994 *N* sodium hydroxide was hydrogenated at atmospheric pressure using 50 mg. of 5% Pd–C catalyst. At the end of 75 minutes 101% of three mole equivalents of hydrogen had been absorbed and the reduction had ceased. After removal of the catalyst the solution was acidified and the product was extracted with ether. After drying the extracts over magnesium sulfate and removing the ether a residue of N-cycloheptyl succinamic acid was obtained, m.p. 127.5–128.5°. Crystallization from ethyl acetate–carbon tetrachloride did not change the melting point. A mixture melting point with an authentic sample (see below) was 127–128°. The infrared spectrum of the reduction product (measured in a potassium bromide pellet) was identical with that of the authentic material when both samples had been crystallized from ethyl acetate–carbon tetrachloride. Significant differences were observed in the spectra in the 6–12 μ region when one of the samples had been crystallized from ethyl acetate alone.

When IV was hydrogenated in ethanol or ethyl acetate–hexane as solvents, the hydrogen absorption corresponded to 130–150% of three mole equivalents.

Hydrolysis of N-Cycloheptatrienylsuccinimide (III) with 10% Sodium Hydroxide. N-Cycloheptatrienylbenzamide.—A mixture of 4 g. (0.022 mole) of III and 120 ml. of 10% sodium hydroxide solution was distilled into 140 ml. of 0.42 *N* hydrochloric acid until about 60 ml. of water had distilled. The acidic distillate was concentrated under reduced pressure and then made strongly basic by the addition of solid sodium hydroxide. The organic material was extracted with ether, the extract dried over solid potassium hydroxide and the solvent removed. The residual dark oil (0.88 g., 39%) was distilled in a short path apparatus at 60–120° (0.25 mm.) giving a pale yellow oil (n^{25}D 1.5780) which darkened at once upon contact with air. Owing to its ease of oxidation a satisfactory analysis could not be obtained. The crude distillate showed $\lambda_{max.}$ 252.5 mμ in 95% ethanol and absorbed 62% of three mole equivalents of hydrogen using 5% Pd–C catalyst.

The crude amine obtained from a similar hydrolysis of III was not distilled but was treated with benzoyl chloride and dilute sodium hydroxide solution. The white solid which formed was removed by filtration, m.p. 130–145°.

---

(12) The formation of cyclopropanes from diazomethane and olefinic compounds is well known. However G. Schenck and H. Ziegler (*Ann.*, **584**, 221 (1953)) have reported that ethyl norcaradienecarboxylate is partially converted to a monocyclic isomer by irradiation with ultraviolet light. J. D. Roberts and R. H. Mazur (This Journal, **73**, 2509 (1951)) have shown that the cyclobutylcarbonium ion is equivalent to the cyclopropyl carbinyl and allylcarbinyl-carbonium ions and can give rise to products derived from any or all of these three carbon skeletons.

(13) A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *ibid.*, **74**, 4867 (1952).

(14) C. Grundmann and G. Ottmann, *Ann.*, **582**, 163 (1953). As shown in the Experimental section the material which we obtained contained only 69% of XIII as determined by maleic anhydride assay. The remainder of the material, presumably monocyclic, did not react with maleic anhydride at 25°.

(15) K. Alder and G. Jacobs (*Ber.*, **86**, 1528 (1953)) have shown however that the maleic anhydride adduct of cycloheptatriene has the structure derived from norcaradiene. This finding implies that a rapid equilibrium between II and XII is established at elevated temperatures as is the case with 1,3,5-cycloöctatriene. Alternatively the bridging of the monocyclic system may occur as an integral part of the Diels–Alder reaction.

(16) The rate of equilibration of bicyclo[4.2.0]octa-2,4-diene and 1,3,5-cycloöctatriene is small at temperatures below 40° (ref. 13).

(17) Melting and boiling points are uncorrected. We wish to thank Miss H. Beck for the analyses.

(18) CH analysis by Micro-Tech Laboratories, Skokie, Illinois.

After several recrystallizations from ethyl acetate–hexane the N-cycloheptatrienylbenzamide melted at 162–163°.

Anal. Calcd. for $C_{14}H_{13}NO$: N, 6.64. Found: N, 6.74.

Upon hydrogenation in absolute ethanol using Pd–C catalyst, the N-cycloheptatrienylbenzamide absorbed exactly three mole equivalents of hydrogen. After removal of the catalyst and solvent a solid, m.p. 128–130°, was obtained. Recrystallization from ethyl acetate–hexane raised the melting point to 130.0–130.5°. A mixture melting point with authentic N-cycloheptylbenzamide (see below) was 131–132° and the infrared spectra (KBr pellet) of the two samples were identical.

N-Cycloheptylsuccinamic Acid.—Cycloheptylamine (3.73 g., 0.033 mole), succinic anhydride (4.73 g., 0.0473 mole) and glacial acetic acid (60 ml.) were refluxed for 50 minutes. Water (450 ml.) was added, the solution was cooled, and the product extracted with ether (175 ml.). The combined extracts were washed with 50 ml. of water, the solution dried over magnesium sulfate, and the solvent removed. The residual solid (2 g.) melted at 123–125° and repeated recrystallization from ethyl acetate gave material melting at 128.5–129.5°.

Anal. Calcd. for $C_{11}H_{19}O_3N$: C, 61.94; H, 8.98. Found: C, 62.20; H, 9.02.

N-Cycloheptylbenzamide.—This compound was prepared from cycloheptylamine by the usual Schotten–Baumann technique. After several recrystallizations from ethyl acetate–hexane the compound melted at 131.5–132.5°.

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.61. Found: C, 77.47; H, 8.35.

Preparation of Cycloheptatriene from Cycloheptene.—A mixture of 34.5 g. (0.36 mole) of cycloheptene,[8b] 140.8 g. (0.79 mole) of NBS and a few granules of benzoyl peroxide was heated in 400 ml. of carbon tetrachloride until the reaction was complete (2–4 hours). The succinimide was removed by filtration and the solvent removed from the filtrate under reduced pressure at 25°. Without further purification the remaining liquid was added dropwise to quinoline heated to 140° and held at a pressure (45 mm.) such that it was just below the boiling point. The hydrocarbon distilled and was taken up in pentane. The solution was washed with 10% hydrochloric acid and water and dried over magnesium sulfate. After removal of the solvent the residue was distilled giving 14.78 g. (45%) of material boiling at 110–116°, $n^{25}\mathrm{D}$ 1.5093–1.5178.

The products from several runs were combined and distilled through a Piros–Glover spinning band column at a reflux ratio equivalent to approximately 90 theoretical plates. About 47% of the material distilled at 116° ($n^{25}\mathrm{D}$ 1.5203–1.5209) and was pure cycloheptatriene (lit.[8b] b.p. 116–117°, $n^{20}\mathrm{D}$ 1.5243); 27% of the material distilled at 111.5–116° ($n^{25}\mathrm{D}$ 1.5028–1.5188) and was probably II containing some cycloheptene; the remainder of the material boiled up to 121.5° or was lost as column holdup. The yield of pure cycloheptatriene was approximately 20% based on the cycloheptene initially taken.

Bicyclo[3.2.0]hept-2-ene-6-one.—This compound was prepared as described[10] previously. The yields of pure ketone varied erratically from 5.9–15% based on ketene. The crude ketone fraction could be purified more conveniently *via* the sodium bisulfite adduct rather than the semicarbazone as follows.

The crude ketone fraction (612 g.) obtained from 9.1 moles of cyclopentadiene and 12 moles of ketene was added to 190 g. of sodium metabisulfite dissolved in a mixture of 200 ml. of water and 200 ml. of methanol. The solution was stirred for one hour, cooled in an ice-bath, and the white solid separated by filtration. The solid was slurried three times with 500-ml. portions of ether and filtered in order to remove dicyclopentadiene. The washed solid was suspended in 500 ml. of water, a solution of 90 g. of potassium carbonate in 100 ml. of water was added and the mixture was distilled until no more ketone could be seen in the distillate. The ketone was extracted with ether and distillation of the extract afforded 76.2 g. (8.6% based upon cyclopentadiene) of pure ketone, b.p. 52–54° (12 mm.), $n^{25}\mathrm{D}$ 1.4797.

Bicyclo[3.2.0]hept-2-ene-6-ol.—Bicyclo[3.2.0]hept-2-ene-one (101.3 g., 0.94 mole) dissolved in 100 ml. of dry ether was added to a stirred suspension of 37.91 g. (0.47 mole) of lithium aluminum hydride in 600 ml. of ether. Following the addition the mixture was stirred for several hours, allowed to stand overnight, and then hydrolyzed by the successive cautious addition of 18.8 ml. of water, 14.1 ml. of 20% sodium hydroxide solution and 66 ml. of water. The solution was filtered, the solvent removed from the filtrate and the residue distilled. The alcohol was collected at 66–70° (9 mm.), wt. 93.85 g. (91%). An analytical sample had b.p. 96–98° (38 mm.), $n^{25}\mathrm{D}$ 1.4987.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.20; H, 8.87.

Cycloheptatriene from Bicyclo[3.2.0]hept-2-ene-6-ol.—A mixture of 129.2 g. (1.17 moles) of bicyclo[3.2.0]hept-2-ene-6-ol and 350 ml. of dry pyridine was cooled to about −20° in a Dry Ice–acetone bath. To this mixture was added 135.0 g. (1.18 moles) of methanesulfonyl chloride. The mixture was removed from the bath and its temperature kept below 30° by cooling as required. When the initial exothermic reaction was over the mixture was kept at room temperature for several hours and then poured into a mixture of 1100 g. of ice and 450 ml. of concentrated hydrochloric acid. The methanesulfonate was extracted with chloroform, the combined extracts washed with several portions of water, and the bulk of the solvent removed on a steam-bath at reduced pressure. The temperature of the ester was not allowed to exceed 60°.[19] The last traces of solvent were removed at 50° (0.5 mm.).

The crude methanesulfonate (207 g., 94%) was solvolyzed by adding it gradually during 45 minutes to a distilling mixture of 600 ml. of water, 600 ml. glacial acetic acid and 390 g. (2.8 moles) of sodium dihydrogen phosphate monohydrate. The solvolysis was rapid[20] and the crude yellow cycloheptatriene distilled as it formed. It was necessary to add an additional 100 ml. of acetic acid and 150 ml. of water to the reaction flask after about one-half of the sulfonate had been added. The distillation was continued until a negligible amount of water insoluble material was steam distilling. The distillate was cooled in an ice-bath and made alkaline by the addition of 50% sodium hydroxide solution. The organic material was taken up in pentane, the extracts washed with water, dried over magnesium sulfate, and the solvent was removed. Distillation of the residue gave 55.8 g. (51.7%) of yellow cycloheptatriene, b.p. 70.5–75° (145 mm.), $n^{25}\mathrm{D}$ 1.5181. Higher boiling material containing acetate esters was also obtained. When the sodium dihydrogen phosphate was replaced by an equivalent amount of sodium acetate the yield of II decreased to 30% and the amount of high boiling material was increased.

The cycloheptatriene obtained as above could be obtained free of the yellow impurity (probably methylfulvene) by distillation through a Piros–Glover spinning band column. However, the amount of impurity present was small since the infrared spectrum of the yellow material was essentially identical with that of the pure colorless hydrocarbon. Also no maximum absorption could be detected at 350–360 mμ where methylfulvene would be expected to absorb strongly.[21] Since the yellow impurity did not interfere with the reactions of the hydrocarbon it normally was not removed. Several means of removing the contaminant other than fractional distillation were investigated but none was successful. In particular we were unable to obtain a silver nitrate adduct of cycloheptatriene.

The cycloheptatriene prepared by solvolysis was identical in all respects with that obtained from cycloheptene. Both samples gave the same maleic anhydride adduct in 64% yield as follows: one gram (0.0109 mole) of cycloheptatriene was heated in refluxing benzene with 1.3 g. (0.0133 mole) of sublimed maleic anhydride for 40 hours. The solid obtained after removal of the solvent was heated at 50° (0.3 mm.) to remove excess maleic anhydride. The adduct was then sublimed at 100° (0.3 mm.) giving 1.33 g. (64%) of product, m.p. 93–101° Crystallization from ethyl acetate–hexane raised the melting point to 104.2–105.0° (reported[8b] 102–104°).

Ethyl Norcaradiene Carboxylate (XIII) and its Maleic Anhydride Adduct.—The XIII was made in a glass liner contained in a steel autoclave by the procedure of Grundmann and Ottmann.[14] By means of a thermocouple immersed in the liquid it was possible to maintain the liquid temperature between 136–139°. The product isolated had b.p. 62–66°

---

[19] In an experiment in which cycloheptatriene contaminated with the methanesulfonate was being distilled, the residue of the ester decomposed explosively at 130° destroying the distillation apparatus.

[20] A kinetic study is planned.

[21] J. H. Day, *Chem. Revs.*, **53**, 167 (1953).

(1 mm.), n^{25}_D 1.5056. Spectral examination indicated that the material was not homogeneous. The infrared spectrum had carbonyl absorptions at 5.81 and 5.87 μ. In 95% ethanol the material had $\lambda_{max.}$ 267 mμ. The isomeric ester obtained by heating the above material at 150° for four hours[14] absorbed at 5.87 μ in the infrared with only slight absorption at 5.81 μ and had $\lambda_{max.}$ 276 mμ. The XIII thus was contaminated with the thermally rearranged ester.

A mixture of the impure XIII (5.6 g., 0.034 mole) and 3.29 g. (0.034 mole) of sublimed maleic anhydride was kept overnight at 25°. The mixture was initially liquid but gradually became solid. The solid was triturated with pentane to remove unreacted ester, filtered and then heated at 50° (0.3 mm.) to remove maleic anhydride. The product (6.1 g., 69%) melted at 120–125°. Several recrystallizations from ethyl acetate–hexane raised the melting point to 138–139°.

Anal. Calcd.: C, 64.12; H, 5.38. Found: C, 64.54; H, 5.63.

The unreacted ester recovered from the pentane washings had a carbonyl absorption at 5.87 μ but none at 5.81 μ and had $\lambda_{max.}$ 277 mμ with no evidence of a shoulder at 267 mμ.

Treatment of Ethyl Norcaradiene Carboxylate (XIII) and Cycloheptatriene with Maleic Anhydride at 5°.—One gram (0.00616 mole) of impure XIII was mixed with 0.66 g. (0.00673 mole) of sublimed maleic anhydride and kept at 5° for 24 hours. The adduct was isolated as before giving 0.89 g. of crude material, m.p. 133–137.5°. Since the ester used was 69% ethyl norcaradiene carboxylate this is equivalent to an 80% yield of adduct.

When 1 g. (0.01085 mole) of cycloheptatriene was treated with 1.2 g. (0.0122 mole) of maleic anhydride under similar conditions, 89% of the maleic anhydride (m.p. 50–52°) was recovered. Only a trace of material sublimed at 100° (0.3 mm.) and a small amount of non-volatile residue remained behind.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

Reaction of 2-Naphthol with Formaldehyde and 2-Naphthylamine. Isolation of 1-(2-Naphthylaminomethyl)-2-naphthol

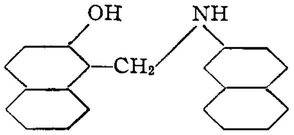
BY W. J. BURKE, LEO G. ADAMS, K. CHADWICK MURDOCK AND SVEN H. RUETMAN

RECEIVED JUNE 23, 1955

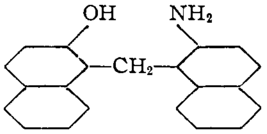
Further investigation of the reaction of 2-naphthol with formaldehyde and 2-naphthylamine resulted in the isolation of 1-(2-naphthylaminomethyl)-2-naphthol, which has been postulated as the precursor of the several products derived from this system. Two new compounds, 2,3-dihydro-2-(2-naphthyl)-1H-naphth[1,2-*e*]-*m*-oxazine and 1-(2-methyleneimino-1-naphthylmethyl)-2-naphthol were also obtained. The interrelationships of the products were studied.

The condensation of equimolar quantities of 2-naphthol with formaldehyde and 2-naphthylamine in refluxing toluene was reported by Hardman[1] to yield 1-(2-naphthylaminomethyl)-2-naphthol (I). Shortly afterward, Corley and Blout in a detailed study[2] of this condensation showed that in refluxing benzene the resulting product was not I but the isomeric 1-(2-amino-1-naphthylmethyl)-2-naphthol II.[2a] These investigators prepared I by reduction of the Schiff base III from 2-hydroxy-1-naphthaldehyde and 2-naphthylamine and demonstrated that I was readily convertible to II by heating in benzene.[2b] When the condensation was effected in toluene or xylene, good yields of 1,2,7,8-dibenzacridine and Morgan's base (a molecular compound of 1,2,7,8-dibenzacridine and its 9,10-dihydro derivative) were isolated along with only traces of II.[2c] Morgan's base, 1-methyl-2-naphthol and 1,2,7,8-dibenzacridine were formed when II was heated to its melting point.[2a]

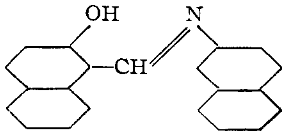
Corley and Blout proposed a sequence of reactions involving I as the initial product of the condensation of 2-naphthol with formaldehyde and 2-naphthylamine to explain the relationship of the several compounds formed.[2c] They were not able to isolate I from the condensation reaction and suggested that I was an intermediate in the formation of II. They stated that the temperature necessary for reaction to occur, as evidenced by the evolution of water (*ca.* 80°), was also sufficient for isomerization to II.[2b]



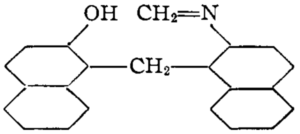
I



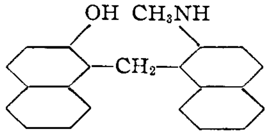
II



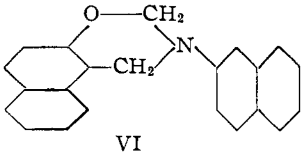
III



IV



V



VI

In connection with related work[3] it was observed that aniline and certain of its ring substituted derivatives reacted readily with formaldehyde and 2-naphthol in a molar ratio of 1:2:1 at 5° to form 2,3-dihydro-2-aryl-1H-naphth[1,2-*e*]-*m*-oxazines. These results suggested the feasibility of investigating the reaction of 2-naphthol with formaldehyde and 2-naphthylamine under conditions which might permit the isolation of I should it actually be a condensation product. Reaction of equimolar quantities of these reagents in methanol at 2° for seven days resulted in a 63% yield of I. When the condensation was effected at 25° for seven days, a 9% yield of I was obtained along with a 23% yield of II and an orange crystalline

---

[1] A. F. Hardman, U. S. Patent 2,411,427 (1946).

[2] (a) R. S. Corley and E. R. Blout, THIS JOURNAL, **69**, 755 (1947); (b) R. S. Corley and E. R. Blout, *ibid.*, **69**, 761 (1947); (c) E. R. Blout and R. S. Corley, *ibid.*, **69**, 763 (1947).

[3] W. J. Burke, K. C. Murdock and G. Ec, *ibid.*, **76**, 1677 (1954).