

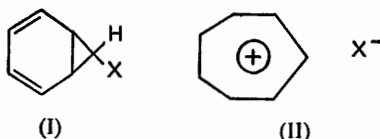
397. *The Tropylium Ion. Part II.* A Further Synthesis and Some Reactions of Tropylium Salts.*

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Diazoacetonitrile adds readily to benzene, to give cyanonorcaradiene (I; X = CN). This product does not exhibit properties associated with tropylium compounds but on treatment with boron trifluoride or aluminium chloride forms tropylium salts. Evidence is given for the ready interconversion of compounds having a norcaradiene or tropylium structure. Tropylium bromide forms an addition product with bromine which readily rearranges in water to give benzaldehyde. A possible mechanism is given for this reaction.

In the preceding paper we described how norcaradiene *isocyanate* (I; X = $\cdot\text{NCO}$), a mobile liquid, was converted by heat in polar solvents into the isomeric ionic compound, tropylium *isocyanate* (II; X = $\cdot\text{NCO}$). Further, when norcaradienyl *isocyanate* was treated with anhydrous hydrogen bromide, practically quantitative yields of tropylium bromide and cyanuric acid were obtained. These results suggested that any substituted norcaradiene derivative of type (I) where X is a sufficiently electronegative group could be converted into the isomeric tropylium salt or could give rise to tropylium bromide on treatment with hydrogen bromide.

We have explored this route to tropylium compounds. Very few substituted norcaradiene derivatives of the type (I) are known. As a result of Buchner's¹ classical work with



diazoacetic ester and aromatic hydrocarbons the most efficacious way of making compounds of type (I) appears to be by reaction of benzene with an appropriately substituted diazomethane. The present paper deals with the synthesis of cyanonorcaradiene (I; X = CN) from benzene and diazoacetonitrile, and its conversion into tropylium salts.

Harper and Sleep² had treated diazoacetonitrile with a molecule containing an olefinic bond and obtained the expected *cyclopropane* derivative. No record appears of a reaction between diazoacetonitrile and an aromatic compound. We have now found that this diazo-compound reacts smoothly with benzene to give cyanonorcaradiene. The reaction proceeds much more readily and gives a considerably higher yield of product than does the corresponding reaction with diazoacetic ester.

Cyanonorcaradiene was a stable mobile liquid, soluble in non-polar solvents, and did not react with silver nitrate. Like norcaradienecarboxylic acid and its derivatives the material gave an intensely blue solution in concentrated sulphuric acid. This material obviously possessed the covalent structure (I; X = CN) and not (II; X = CN). Cyanonorcaradiene was unaffected by heat in polar solvents. Further, treatment of the material with hydrogen bromide did not give the expected tropylium bromide, as did norcaradiene *isocyanate* (I; X = $\cdot\text{NCO}$). Instead, a white solid was formed which readily decomposed in water and regenerated the starting material and presumably was merely a salt of the nitrile and hydrogen bromide. Nevertheless an indication of the potentially ionic character of the nitrile group was obtained from formation of sodium cyanide when cyanonorcaradiene was heated with concentrated sodium hydroxide solutions.

When cyanonorcaradiene and boron trifluoride-ether complex containing some free

* Part I, preceding paper.

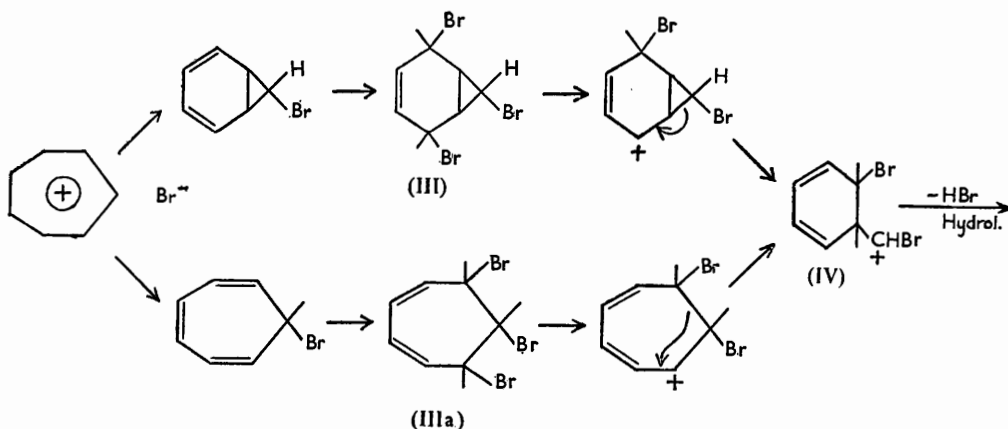
¹ Buchner, *Ber.*, 1903, **36**, 3515, and references therein.

² Harper and Sleep, *J. Sci. Food Agric.*, 1955, **6**, 116.

fluoroboric acid were heated for a short time, hydrogen cyanide was liberated. Addition of ether precipitated tropylium fluoroborate, a white, water-soluble solid, identical with the material prepared from the double decomposition of tropylium bromide and sodium fluoroborate. Another white crystalline tropylium salt, presumably one containing the anion $[\text{AlCl}_3\text{CN}]^-$, was obtained when cyanonorcaradiene and aluminium chloride were heated in nitrobenzene. This salt was soluble in water and with aqueous picric acid gave tropylium picrate. After a nitrobenzene solution of cyanonorcaradiene and aluminium chloride had been heated and treated with methyl iodide, addition of ether precipitated tropylium iodide.

Doering and his collaborators³ found that treatment of tropylium bromide in water with sodium cyanide gave a covalent compound, presumably cyanonorcaradiene, and not, as might be expected, tropylium cyanide. We have repeated this and find that the material is identical with cyanonorcaradiene obtained from the reaction of diazoacetonitrile and benzene. It is apparent that there is very easy interconversion of structures (I) and (II), the structure preferred for a particular compound being determined by the nucleophilic properties of the anion X^- . Because of the strong nucleophilic properties of the cyanide ion our initial choice of diazoacetonitrile was perhaps unfortunate. Nevertheless the synthesis of tropylium salts from cyanonorcaradiene is still a superior method to that using diazoacetic ester;⁴ this should prove to be especially true for the synthesis of substituted tropylium derivatives.

An interesting example of the equilibrium between structures (I) and (II) is shown when tropylium fluoroborate is treated with sodium cyanate. When an equimolecular amount of cyanate is slowly added to a solution of tropylium fluoroborate, tropylium *isocyanate* (II; $\text{X} = \cdot\text{NCO}$) is gradually precipitated. However, when a large excess of cyanate is rapidly added to the tropylium solution, the covalent liquid isomer, norcaradiene *isocyanate* (I; $\text{X} = \cdot\text{NCO}$) separates. The two products are identical with those obtained by heating norcaradienecarboxyl azide.⁴ In the first case the more thermodynamically stable ionic isomer is formed by normal double decomposition, whereas in the second the presence of excess of cyanate ions produces a mass-action effect on the equilibrium and the covalent compound is produced.



The tropylium ring system can undergo an interesting rearrangement, to give benzaldehyde under two different conditions, though the mechanism of the rearrangement is probably similar in each case. When tropylium bromide in absolute alcohol is treated with one mol. of bromine a yellow tribromo-product separates. This immediately decomposes in water to yield benzaldehyde. The same compound is produced when tropylium salts are oxidised with dilute neutral permanganate solution. In view of the difficulty in

³ Doering, personal communication.

⁴ Dewar and Pettit, preceding paper.

establishing the structure of *cycloheptatriene* derivatives⁵ one can arrive at two possible structures (III or IIIa) for the tribromo-compound. As shown in the annexed scheme, a compound with either structure could give rise to the ion (IV) by loss of a bromine anion to form a carbonium ion, followed by a Wagner–Meerwein rearrangement. The ion (IV) would, on loss of hydrogen bromide and hydrolysis, yield benzaldehyde. A similar mechanism, involving an intermediate glycol, probably operates during the oxidation of tropylium bromide to benzaldehyde. It is interesting that the product obtained from the addition of one mol. of bromine to cyanonorcaradiene, which presumably has a structure similar to (III), does not rearrange under similar conditions to give mandelonitrile. However, the nitrile group might influence such a rearrangement.

EXPERIMENTAL

Diazoacetoneitrile.—Aminoacetoneitrile hydrochloride⁶ (92.5 g.) in water (150 ml.) was contained in a 2 l. separatory funnel fitted with a stirrer. Ether (100 ml.) and a solution (15 ml.) of sodium nitrite (69 g.) in water (100 ml.) were added, and the mixture stirred vigorously. After 30 sec. the ether layer was run off and transferred to a large flask containing 2*N*-sodium carbonate (100 c.c.) at 0°. The aqueous solution was replaced and stirred with ether (2 × 50 ml.), the extracts being collected as before. Another portion (15 ml.) of the sodium nitrite solution was added and the extraction repeated as before. Ice chips were added periodically to keep the temperature below 15°. The remainder of the nitrite solution was then added, followed by ether (100 ml.) and 4*N*-sulphuric acid (10 ml.); the mixture was then extracted with three lots of ether. The process was repeated for eight additions of acid; then a further amount of sodium nitrite (30 g.) in water (50 ml.) was added. Addition of acid followed by ether-extraction was further continued until finally the reaction was completed when about 120 ml. of acid had been used and the aqueous solution was acid to Congo-red. The combined ether extracts (approx. 4 l.) were washed with 2*N*-sodium carbonate (100 ml.) and water (200 ml.) and dried (Na₂SO₄). The above method is similar to that used by Grundmann and Ottmann⁷ for the preparation of diazoacetic ester, but the greater solubility of diazoacetoneitrile in water necessitates a much larger amount of ether for the extraction. The diazoacetoneitrile thus prepared is quite suitable for use in the following reactions without further purification. In the first preparation the solvent was removed and the product distilled but this led to a violent explosion: in solution the material is quite safe to handle. The yield determined by the volume of nitrogen liberated when an aliquot portion of the ether solution was shaken with dilute acid was usually between 60% and 70%.

Cyanonorcaradiene.—The above ether solution of diazoacetoneitrile was slowly run into benzene (1½ l.), and the ether continuously removed under reduced pressure. After removal of the ether the benzene solution was refluxed before a 1 kw ultraviolet lamp. In 6 hr., 9 l. of nitrogen were evolved and the reaction was complete. The dark solution was cooled, filtered from small amounts of decomposition products, and washed with dilute sulphuric acid to remove traces of unchanged diazo-compound. Removal of excess of benzene, followed by vacuum-distillation, gave *cyanonorcaradiene* (32 g.), a pale yellow oil, b. p. 48–50°/0.5 mm. (Found: C, 81.9; H, 6.1; N, 12.3. C₈H₇N requires C, 82.1; H, 6.0; N, 12.0%).

Tropylium Fluoroborate.—Cyanonorcaradiene (1.0 g.), boron trifluoride–ether complex (3 ml.), and water (0.1 g.) were refluxed vigorously for 7 min. The solution was cooled, dry ether (40 ml.) added, and the light brown precipitate collected and washed with a little ether–acetone (yield, 1.0 g., 65%). Tropylium fluoroborate recrystallised from alcohol in white prisms, m. p. 242° (decomp.), alone or mixed with a sample obtained from equimolecular amounts of tropylium bromide and sodium fluoroborate in a little water. Tropylium fluoroborate dissolves readily in water to give a colourless solution. Concentrated solutions, when mixed with concentrated sodium iodide solution, gave a red precipitate of tropylium iodide. With picric acid, *tropylium picrate* was formed as yellow needles, m. p. 114–115° (Found: C, 49.3; H, 3.0; N, 13.0. C₁₃H₉O₇N₃ requires C, 48.9; H, 2.8; N, 13.2%). An initial experiment with a very old sample of boron trifluoride–ether complex, presumably containing some hydrolysed products, gave almost quantitative yields of tropylium fluoroborate from cyanonorcaradiene, but this has

⁵ Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203; Dryden and Burgert, *ibid.*, 1955, **77**, 5633.

⁶ Curtius, *Ber.*, 1898, **31**, 2490.

⁷ Grundmann and Ottmann, *Annalen*, 1953, **582**, 163.

not been repeated with purer materials. The yield appears to be the same when the reaction is carried out in a polar solvent such as trichloroacetic acid. Aluminium chloride (1.5 g.), nitrobenzene (10 ml.), and cyanonorcaradiene (1.2 g.) were heated at 70° for 15 min. The mixture was cooled, anhydrous ether (200 ml.) added, and the fine white precipitate collected (1.0 g.). This tropylium salt was dissolved in water (8 ml.) and filtered from a small amount of nitrobenzene, and aqueous picric acid was added. Tropylium picrate (0.8 g.) was collected (yellow needles, m. p. 113—114°).

Tropylium isoCyanate and Norcaradiene isoCyanate.—(a) To a stirred solution of tropylium fluoroborate (0.55 g.) in water (10 ml.) a solution of sodium cyanate (0.15 g.) in water (10 ml.) was added dropwise during 10 min. After 3 hr. the precipitate of tropylium isocyanate was collected and washed with a little water (yield, 0.39, 75%; m. p. and mixed m. p. 186—188°).

(b) To a solution of tropylium fluoroborate (1.0 g.) in water (10 ml.) was added sodium cyanate (1.5 g.) in water (10 ml.). An evil-smelling liquid immediately separated. This was taken up in ether and dried (Na_2SO_4), and the solvent removed, leaving norcaradiene isocyanate (0.65 g., 86%). Each isomer gave tropylium bromide and cyanuric acid when treated with hydrogen bromide as described in Part I.

Rearrangement of Tropylium Salts.—A solution of bromine (0.3 g.) in absolute alcohol (6 ml.) was added slowly and with stirring to tropylium bromide (0.3 g.) in absolute alcohol. The bromo-adduct (0.55 g.) separated at once. It crystallised from absolute alcohol in yellow plates, m. p. 118° (Found: C, 25.7; H, 2.4; Br, 71.5. $\text{C}_7\text{H}_7\text{Br}_3$ requires C, 25.4; H, 2.1; Br, 72.5%). The material immediately decomposed when shaken with water, to give benzaldehyde, identified by its smell and its 2:4-dinitrohydrazone.

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