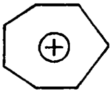
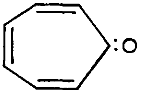
396. *The Tropylium Ion. Part I. Synthesis of Tropylium and Methyltropylium Salts.*

By M. J. S. Dewar and R. Pettit.

By the Curtius reaction norcaradienecarboxylic acid (IV; $R = CO_2H$) gives the isomers, tropylium and norcaradienyl *iso*cyanate. Both products yield tropylium (*cyclo*heptatrienyl) bromide and cyanuric acid when treated with hydrogen bromide. None of the three *cyclo*heptatrienecarboxylic acids yields tropylium salts when similarly treated, so the previous assignments of structures to these acids are probably in error. Methyltropylium bromide has been made by a similar Curtius reaction. The introduction of a methyl group into the tropylium ring produces a hypsochromic shift in the ultra-violet absorption.

In his classical work on molecular-orbital theory Hückel [1] in 1938 showed that the *cyclo*heptatrienyl cation (I) should, in common with benzene and the *cyclo*pentadienyl anion, possess considerable resonance stabilisation energy. Some time later Doering and Detert [2] recognised the existence of such a structure in organic chemistry when they found that tropone (*cyclo*heptatrienone) (II*a*) showed no ketonic activity and formed stable salts with acids. To accommodate these facts they assigned the *cyclo*heptatrienylium oxide formula (II*b*) to tropone. Tropolone also is best regarded as a 2-hydroxy-derivative of this, and the name tropylium has been used for the ion (I).


(I)



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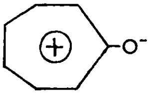
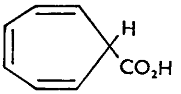


(II*b*)



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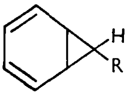

(IV)

It therefore seemed to be of theoretical and practical interest to attempt the synthesis of simple tropylium salts. Our initial attempts were governed by the idea that if tropylium possessed considerable resonance energy, then *cyclo*hepta-2 : 4 : 6-triene-1-carboxylic acid (III) should be readily decarboxylated or decarbonylated to give salts of the required ion. However, liberation of carbon dioxide did not occur when the silver salt of " α-*cyclo*heptatrienecarboxylic acid " [considered to be (III); see below] was treated with iodine perchlorate, or with iodine or bromine as in the normal Hunsdiecker reaction, or when the acid chloride was treated with silver perchlorate. In each case the main product was a tar. Oxidation of the acid with lead tetra-acetate appeared to destroy most of it; similar experiments [3] with triphenylacetic acid, which also forms a comparatively stable cation, gave good yields of triphenylmethyl acetate. Finally, anodic oxidation of the acid (III) gave small amounts of polymer and mainly unchanged starting material (cf. Linstead and Weedon [4]). All of these experiments were tried in various solvent media under various conditions but with only unpromising results.

However, synthesis of tropylium salts was attained (Dewar and Pettit [5]) during an attempt to make norcaradieneol (IV; $R = OH$) : it was hoped that this alcohol might rearrange in the presence of strong acids to form tropylium salts. As reported, ethyl norcaradienecarboxylate (IV; $R = CO_2Et$) was hydrolysed by mild alkali to the corresponding acid. The acid was then converted, *via* the chloride, into the azide which was heated in benzene. During the last operation approx. 40% of white crystals separated and, as *iso*cyanates of low molecular weight are normally mobile liquids and freely soluble in benzene, it was suspected that this material was the isomeric tropylium *iso*cyanate. The

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[1] E. Hückel, " Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

[2] Doering and Detert, *J. Amer. Chem. Soc.*, 1951, **73**, 876.

[3] Mosher and Kehr, *ibid.*, 1953, **75**, 3172.

[4] Linstead and Weedon, *J.*, 1952, 3626.

[5] Dewar and Pettit, *Chem. and Ind.*, 1955, 199.

ionic nature of the material was also indicated by its high melting point, reaction with silver nitrate, and insolubility in non-polar solvents. The structure was confirmed by conversion of the material, with hydrogen bromide, into cyanuric acid and tropylium bromide, the latter identical with that reported by Doering and Knox [6] just before our own synthesis.

The norcaradienecarboxylic acid used was obtained by mild alkaline hydrolysis of the ester and could conceivably have contained some amount of *cyclo*hepta-2 : 4 : 6-triene-1-carboxylic acid (III); the latter acid is obtained in good yield from the caradiene acid or ester (IV; R = CO_2Et or CO_2H) in more vigorous alkaline conditions. We could not then assert definitely that norcaradienecarboxylic acid was the precursor of the tropylium *iso*cyanate. We have now found that direct acid hydrolysis of the ester (IV; R = CO_2Et) gives good yields of pure norcaradienecarboxylic acid (cf. Buchner [7]). When the Curtius rearrangement is performed on the pure acid two *iso*cyanates are obtained. One is the crystalline material identical with tropylium *iso*cyanate. The second, obtained by removal of the solvent followed by distillation in a vacuum, is a mobile, evil-smelling liquid which, when kept at 0°, or more quickly when heated, rearranges to tropylium *iso*cyanate. Solutions of the liquid *iso*cyanate when treated with hydrogen bromide gave practically quantitative yields of cyanuric acid and tropylium bromide. Apparently the mobile compound is the covalent norcaradienyl *iso*cyanate (IV; R = ·NCO).

In several experiments the total yield of *iso*cyanates was about 60% based on norcaradienecarboxylic acid used, but the individual yields of the solid isomer varied from 0% to 50%. This is possibly due to traces of acid chloride carried over in the reaction which might catalyse the conversion of the covalent compound into its ionic isomer. It is significant in this respect that the conversion of norcaradienyl *iso*cyanate into tropylium *iso*cyanate is very much faster in polar than in non-polar solvents.

Tropylium or norcaradienyl *iso*cyanate can be converted into the other halide salts by treatment in nitromethane with the corresponding hydrogen halide. The chloride thus obtained is identical with that previously reported.[6] The iodide forms red needles from absolute alcohol, and, unlike the other halide salts, is not deliquescent and is quite stable in air.

In order to establish definitely that the synthesis of tropylium *iso*cyanate proceeded *via* the norcaradiene acid it was necessary to repeat the procedure starting from *cyclo*hepta-2 : 4 : 6-triene-1-carboxylic acid (III). This had previously been done by Johnson and Tisler [8] who had obtained a urethane from α-*cyclo*heptatrienecarboxylic acid but could not convert it into tropylium salts. Of the four possible isomeric *cyclo*heptatrienecarboxylic acids only that of structure (III) could be expected to yield tropylium salts. We have repeated the Curtius reaction on the acid (III) and obtained a mobile *iso*cyanate which did not yield tropylium bromide when treated with hydrogen bromide or react with aqueous silver nitrate. Further, hydrolysis of the *iso*cyanate obtained gave *cyclo*heptadienone which, on catalytic reduction, absorbed two mols. of hydrogen to give suberone. The same *iso*cyanate was obtained when the acid (III) was subjected to the Lossen rearrangement. In view of its inability to form tropylium salts the *iso*cyanate cannot have the structure (V); therefore, if the structure of acid (III) is correct, a rearrangement of double bonds must have occurred during the Curtius reaction : this is, however, unlikely, especially in view of the known stability of tropylium *iso*cyanate. It seemed to us much more probable that the structure ascribed to the α-acid was wrong.

Buchner [9] first assigned structures to the four possible *cyclo*heptatrienecarboxylic acids but these assignments were recently revised by Grundmann and Ottmann [10] on spectroscopic and chemical evidence. Following the direction of the latter workers we have made the other two *cyclo*heptatrienecarboxylic acids which can be obtained from norcaradienecarboxylic acid, *viz.*, the β- and the γ-isomer, to which Grundmann and Ottmann assigned structures (VI) and (VII) respectively. The azide of each of

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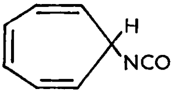
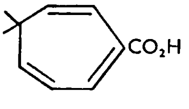
[6] Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203.
[7] Buchner, *Ber.*, 1901, **34**, 989.
[8] Johnson and Tisler, personal communication.
[9] Buchner, *Ber.*, 1898, **31**, 2241.
[10] Grundmann and Ottmann, *Annalen*, 1953, **582**, 163.

these, when heated in benzene, gave a covalent *iso*cyanate which could not be converted into tropylium salts. Further, the *iso*cyanate derived from each of the α-, β-, and γ-acids gave the same phenylurea on treatment with aniline, and the same ketone on acid hydrolysis. We have not prepared the fourth *cyclo*heptatrienecarboxylic acid, but there is little doubt from previous work [11] that it has not the structure (III). From these results we must conclude that the previous assignment of structures to these acids is incorrect. Doering and his co-workers [12] have also come to this conclusion and are studying the structures of the acids. It seems clear that our failure to obtain tropylium derivatives by attempted decarboxylation or decarbonylation of α-*cyclo*heptatrienecarboxylic acid was due to its not having the structure assigned by Grundmann and Ottmann.

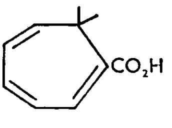
We have also synthesised a methyltropylium salt (VIII) in a similar manner. Following the classical work of Buchner [13] we obtained methyl norcaradienecarboxylate from toluene and ethyl diazoacetate. Acid hydrolysis then gave the acid which was converted *via* the chloride into the azide. When the azide was heated in benzene no solid separated but distillation afforded methylnorcaradiene *iso*cyanate which, when treated with hydrogen bromide, gave methyltropylium bromide. Like the parent compound this material was very soluble in water, and its solution immediately gave a precipitate of silver bromide when treated with silver nitrate. Methyltropylium bromide showed a hypsochromic shift of about 200 Å in the long-wavelength region of the ultraviolet absorption spectrum, when compared with the unsubstituted salt. Such large hypsochromic shifts, produced by the introduction of a methyl substituent, are observed only in other non-alternant hydrocarbons, *e.g.*, in 2-, 4-, and 6-methylazulene. They are unknown in the alternant hydrocarbon series except in a few cases where steric effects operate. We are investigating the effects of other substituents on the light absorption of the tropylium ion.



(V)



(VI)



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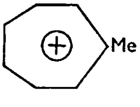

(VIII)

EXPERIMENTAL

Ethyl Norcaradienecarboxylate.—In the absence of a large autoclave (cf. Grundmann and Ottmann [10]) the following method was developed. Ethyl diazoacetate (230 g.), in benzene (4 l.), was refluxed and irradiated continuously with a 1 kw ultraviolet lamp until evolution of nitrogen ceased (6—7 days; *ca.* 35 l. of nitrogen collected). Evaporation of the benzene, followed by distillation *in vacuo*, afforded the crude ester (90 g.), b. p. 82—95°/2·5 mm. Large amounts of high-boiling by-products remained. Redistillation gave small amounts of unchanged diazoacetic ester and pure ethyl norcaradienecarboxylate (82 g., 25%), b. p. 86—88°/2·5 mm. (Found: C, 72·9; H, 7·1. Calc. for $C_{10}H_{12}O_2$: C, 73·2; H, 7·5%). The ester with concentrated sulphuric acid gave an intense blue solution with a red fluorescence.

Norcaradienecarboxylic Acid.—(*a*) A mixture of ethyl norcaradienecarboxylate (50 g.), water (250 ml.), acetone (250 ml.), and concentrated sulphuric acid (40 ml.) was refluxed with vigorous stirring for 2½ hr. The mixture was cooled and made alkaline with sodium hydroxide. After extraction with ether (3 × 100 ml.) the solution was acidified and extracted with ether (4 × 150 ml.). The combined extracts were dried (Na_2SO_4). Removal of the solvent followed by vacuum-distillation gave norcaradienecarboxylic acid (33 g., 80%), b. p. 95—98°/0·4 mm., which solidified. Crystallisation from light petroleum gave white needles, m. p. 20° (Found: C, 70·8; H, 6·0. Calc. for $C_8H_8O_2$: C, 70·6; H, 5·9%). This material also gave an intensely blue solution in sulphuric acid.

[11] Ref. 10 and references therein.
[12] Doering, personal communication.
[13] Buchner, *Ber.*, 1903, **36**, 3515.

(*b*) Ethyl norcaradienecarboxylate (20 g.) was dissolved in absolute alcohol (240 ml.) containing sodium (3·2 g.) and water (5 ml.), and the mixture kept in the refrigerator for 2 days. The solvent was distilled off below 20° and the residue dissolved in water (100 ml.) and extracted with ether. The norcaradienecarboxylic acid was liberated from the alkaline solution with hydrochloric acid, extracted with ether, and collected by distillation (yield, 9·0 g., 55%).

Curtius Reaction.—Norcaradienecarboxylic acid (40 g.) was refluxed in ether (200 ml.) with thionyl chloride (38 g.) and six drops of pyridine for 2½ hr. Removal of the solvent and excess of thionyl chloride followed by vacuum-distillation gave the acid chloride (40 g.) as a pale yellow oil, b. p. 46—47°/0·5 mm. (90%). With ammonia the acid chloride gave norcaradienecarboxyamide, white plates (from alcohol), m. p. 141° (Found : C, 70·7; H, 6·4; N, 10·1. Calc. for C_8H_9ON : C, 71·1; H, 6·7; N, 10·4%).

To a solution of the acid chloride (30 g.) in acetone (250 ml.) was slowly added, with vigorous stirring at $<0°$, a solution of sodium azide (15 g.) in water (60 ml.). The mixture was shaken vigorously for 10 min. in a separatory funnel. Benzene (200 ml.) and water (200 ml.) were added. The benzene solution of the acid azide was separated, washed with water, dried (Na_2SO_4), and evaporated at $<20°$. Dry benzene (300 ml.) was added to the residue and the solution gently refluxed on a steam-bath. After 15 min. white crystals began to separate and the evolution of nitrogen ceased after 45 min. After cooling, *tropylium* iso*cyanate* was collected and washed with dry benzene, forming needles (4·8 g.), m. p. 198° (Found : C, 72·5; H, 5·2; N, 10·1. C_8H_7ON requires C, 72·2; H, 5·3; N, 10·5%). *Norcaradienyl* iso*cyanate* (18·7 g.), b. p. 33°/0·25 mm. was obtained by distillation of the filtrate after the removal of the solvent (Found : C, 7·32; H, 5·2; N, 10·1%); on exposure to the air this material rapidly became yellow.

Tropylium Salts.—Norcaradienyl *iso*cyanate (5 g.) was dissolved in dry nitromethane (80 ml.) and the solution, while contained in a cold-water bath, was saturated with dry hydrogen bromide. The white precipitate of cyanuric acid was filtered off (1·6 g., 95%) and dry ether (800 c.c.) added to the filtrate. In order to free it from adhering hydrogen bromide the yellow precipitate was collected, quickly taken up in absolute alcohol (30 ml.), and reprecipitated with dry ether. The microcrystalline tropylium bromide (5·8 g., 90%) was collected and stored in a dry atmosphere. Crystallisation from warm absolute alcohol gave yellow needles, m. p. 203°, having the properties reported by Doering and Knox[6] (Found: Br, 47·0. Calc. for C_7H_7Br: Br, 46·7%). Tropylium *iso*cyanate was converted in an identical manner into tropylium bromide.

Using hydrogen chloride and iodide respectively gave similarly *tropylium chloride*, white needles (from absolute alcohol), m. p. 189° (decomp.) (Found : Cl, 27·9. C_7H_7Cl requires Cl, 28·1%), and *iodide*, red needles (from absolute alcohol), m. p. 117° (Found : I, 58·2. C_7H_7I requires I, 58·3%).

α-cyclo*Heptatrienecarboxylic Acid.*—Ethyl norcaradienecarboxylate (20 g.) was refluxed vigorously for 1½ hr. with 10% sodium hydroxide solution (200 ml.), then cooled to 0°, treated with charcoal, and acidified. The crystalline acid (13 g.), m. p. 65—68°, was collected; from light petroleum it gave white plates, m. p. 70—71° (Found : C, 70·4; H, 5·7. Calc. for $C_8H_8O_2$: C, 70·6; H, 5·9%).

The acid was converted into the chloride (95% yield), b. p. 60—61°/0·6 mm. The *anilide* formed white plates (from alcohol), m. p. 115—117° (Found : C, 79·8; H, 6·2; N, 7·0. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2; N, 6·6%).

α-*cyclo*Heptatrienecarboxyl chloride (6·0 g.) was converted into the azide as described for norcaradienecarboxyl chloride. The azide was refluxed in dry benzene (80 ml.) for 1 hr.; the solvent was removed and the residue distilled. α-cyclo*Heptatrienyl* iso*cyanate* (4·5 g., 84%) was obtained as a colourless oil, b. p. 30—32°/0·3 mm. (Found : C, 72·5; H, 5·2; N, 10·1. C_8H_7ON requires C, 72·2; H, 5·3; N, 10·5%). With aniline it formed a *phenylurea*, white needles (from nitromethane), m. p. 196° (Found : C, 74·0; H, 6·0; N, 12·2. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2; N, 12·4%).

This *iso*cyanate (4·5 g.) in benzene (50 ml.) was refluxed with vigorous stirring with 5% hydrochloric acid (100 ml.) for 2 hr. The benzene layer was separated, washed with water, and dried. Removal of the solvent followed by distillation afforded *cyclo*heptadienone (2·9 g., 80%), b. p. 28°/0·7 mm. (Found : C, 77·5; H, 7·5. Calc. for C_7H_6O : C, 77·8; H, 7·4%), whose 2 : 4-*dinitrophenylhydrazone* formed red plates, m. p. 149—150°, from alcohol (Found : N, 19·2. $C_{13}H_{10}O_4N_4$ requires N, 19·4%). When catalytically reduced in alcohol with palladised charcoal, *cyclo*heptadienone absorbed 2 mols. of hydrogen to give suberone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 148°).

Lossen Rearrangement.—α-*cyclo*Heptatrienecarboxyl chloride (13·3 g.) in dry benzene (60 c.c.) was added slowly to a stirred solution of hydroxylamine (69 g.) in dry benzene (50 c.c.). After

1½ hr. the solution was cooled to 0° and the white precipitate collected and extracted with hot ethyl acetate (2 × 300 ml.). Evaporation of the extracts gave α-cyclo*heptatrienecarboxyhydroxamic acid* (8·0 g., 62%), white plates (from ethyl acetate), m. p. 123—124°, giving a violet-red colour with ferric chloride (Found : C, 63·3; H, 6·2; N, 9·0. $C_8H_9O_2N$ requires C, 63·6; H, 6·0; N, 9·2%).

The hydroxamic acid (7·0 g.) was treated, in a mixture of acetic acid (50 ml.) and saturated sodium acetate solution (50 ml.), with benzoyl chloride, slowly with vigorous stirring. After 1 hr. the N-*benzoyl derivative* was collected (8·5 g.); it formed white needles, m. p. 132—134°, from benzene (Found : C, 71·0; H, 5·3; N, 5·2. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1; N, 5·5%).

A solution of the benzoate (8·0 g.) in warm acetone (100 ml.) was added slowly with stirring to a solution of potassium (1·25 g.) in absolute methanol (15 ml.). Anhydrous ether (80 ml.) was then added and the microcrystalline potassium salt of the benzoyl derivative collected and dried (8·5 g.). This material was refluxed in dry benzene (150 ml.) for 1 hr. After collection of the potassium benzoate the benzene was removed and the residue distilled. α-*cyclo*Heptatrienyl *iso*cyanate (3·6 g., 90%) was obtained which was identical with the same material described above.

β-cyclo*Heptatrienecarboxylic Acid*.—The β-acid (8·0 g.), prepared as described by Grundmann and Ottmann, was converted in the usual manner into the acid chloride, a pale yellow oil (8·0 g., 90%), b. p. 54°/0·5 mm. This (7·0 g.) was converted into the *iso*cyanate (4·7 g.), a colourless oil, b. p. 34°/0·5 mm. The phenylurea formed white needles (from nitromethane), m. p. 196° alone or mixed with this derivative obtained from α-*cyclo*heptatrienyl *iso*cyanate. Hydrolysis of the *iso*cyanate with acid also gave the same ketone as was derived from the α-isomer.

γ-cyclo*Heptatrienecarboxylic Acid*.—Prepared as described by Grundmann and Ottman the γ-acid (5·5 g.) was converted into the chloride (5·5 g.), b. p. 50—51°/0·4 mm., and thence into the *iso*cyanate (3·7 g.), b. p. 36°/0·5 mm., in the usual manner. The *iso*cyanate gave the preceding phenylurea and ketone.

Methyltropylium Bromide.—Methyl norcaradienecarboxylate (34 g.) (prepared from toluene and diazoacetic acid [13]) was hydrolysed with sulphuric acid as given above for ethyl norcaradienecarboxylate. The crude acid was a pale yellow oil, b. p. 93—97°/0·15 mm. (15 g., 52%) (Found : C, 71·4; H, 6·7. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%). The acid (14·5 g.) was refluxed for 1½ hr. with dry ether (120 ml.), thionyl chloride (9·0 ml.), and pyridine (6 drops). Distillation afforded methyl norcaradienecarbonyl chloride (13·5 g.), b. p. 53—55°/0·15 mm. With ammonia this compound gave the amide, white plates (from light petroleum), m. p. 128° (Found : C, 72·5; H, 7·1; N, 9·1. Calc. for $C_9H_{11}ON$: C, 72·5; H, 7·4; N, 9·4%).

Methyl norcaradienecarboxyl chloride (7·5 g.) was converted into the azide in the usual manner and this was refluxed in dry benzene for 45 min. Removal of the solvent followed by distillation gave *methylnorcaradienyl* iso*cyanate* (2·3 g.), b. p. 53—56°/0·2 mm. (Found : C, 73·0; H, 6·0; N, 9·3. C_9H_9ON requires C, 73·5; H, 6·1; N, 9·5%). The residue (2·0 g.) consisted of polymer.

A solution of this *iso*cyanate (2·0 g.) in dry nitromethane (40 ml.) was saturated with hydrogen bromide. The mixture was filtered and dry ether (800 c.c.) was added. The white precipitate (0·7 g.) was filtered off. Recrystallisation from nitromethane gave *methyltropylium bromide monohydrate* as white needles, melting over a large range above 140° (Found : C, 47·3; H, 5·7. Br, 39·6. C_8H_9Br,H_2O requires C, 47·3; H, 5·4; Br, 39·4%). Ultraviolet absorption max. at 2570 Å (log ε 3·4). The compound was readily soluble in water and gave an immediate precipitate when treated with silver nitrate solution.

One of us (R. P.) is indebted to the University of London for the award of an I.C.I. Research Fellowship. We thank the Central Research Fund for a research grant and Professor Doering for helpful discussion.

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[*Received, December* 29*th*, 1955.]