A Derivative of cyclo*Heptatrienylium (Tropylium) Bromide.*

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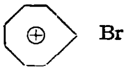
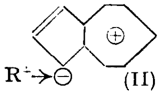
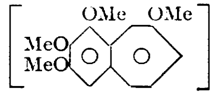
The action of bromine on β-*cyclo*heptatrienecarboxylic acid yields an adduct which loses hydrogen bromide when heated to give carboxy*cyclo*heptatrienylium bromide (VI), a polar compound containing ionic bromine. The properties of this product are similar to those of the parent *cyclo*heptatrienylium bromide (I) (Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203). Attempts to prepare the latter bromide (I) by Curtius degradation of α-*cyclo*heptatrienecarboxylic acid led to the formation of α-*cyclo*heptatrienylurethane, a non-polar compound in which the ring carbon–nitrogen bond is easily severed by hydrolysis.

The aromatic character of tropolones and tropones is attributed to the presence of the *cyclo*heptatrienylium cation in the molecules. Simple salts derived from this cation were unknown until quite recently although before this the aromatic stability and the course of the electrophilic substitution of the azulenes had been attributed to structures such as (II) (Heilbronner *et al.*, *Helv. Chim. Acta*, 1952, **35**, 1036, 1049, 2170; 1954, **37**, 2018; Anderson, Nelson, and Tazuma, *J. Amer. Chem. Soc.*, 1953, **75**, 4980; Reid, Stafford, *et al.*, *Chem. and Ind.*, 1954, 277, 724). The reduction of tetramethylpurpurogallin with lithium aluminium hydride and decomposition of the product with 25% sulphuric acid gave a salt formulated as a derivative of the substituted benzo*cyclo*heptatrienylium cation (III) (Eschenmoser *et al.*, *Helv. Chim. Acta*, 1953, **36**, 290, 1101).


(I)


(II)

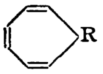

(III)

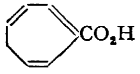
The preparation and some of the properties of *cyclo*heptatrienylium bromide (I) have recently been described by Doering and Knox (*J. Amer. Chem. Soc.*, 1954, **76**, 3203). It was obtained by heating the dibromide from *cyclo*heptatriene and was a deliquescent solid, m. p. 203°, insoluble in non-polar organic solvents and generally possessing properties consistent with its formulation as a salt. Actually its preparation had been described many years ago by Merling (*Ber.*, 1891, **24**, 3122), who, without appreciating its significance, had observed the formation of a crystalline residue in the distillation of *cyclo*heptatriene dibromide. The product as obtained by Doering and Knox (*loc. cit.*) contained ionic bromine, gave *cyclo*heptane on hydrogenation, and was converted, by reaction with aqueous sodium hydrogen carbonate, into di*cyclo*heptatrienyl ether. Dauben (Abs. Amer. Chem. Soc. 126th Meeting, 1954, p. 18-o) has also claimed to have prepared (I) from the dibromide of *cyclo*heptatriene.

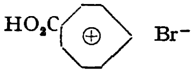
Several possible synthetic routes to (I) have been examined in our laboratories, *e.g.*, oxidation of *cyclo*heptatriene with *N*-bromosuccinimide (cf. Dryden and Burgert, *ibid.*, p. 22-o), reduction of tropone, and degradation of the various isomeric *cyclo*heptatrienecarboxylic acids. Reduction of 2 : 4 : 7-tribromotropone with lithium aluminium hydride gave an unsaturated dibromo-alcohol $C_7H_{10}OBr_2$ in which reduction of the ring had occurred (cf. Cook, Raphael, and Scott, *J.*, 1952, 4416). The structure of this product was not fully elucidated in view of the outcome of the experiments with the *cyclo*heptatrienecarboxylic acids.

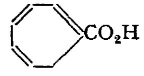
Buchner's classical work (*Ber.*, 1898, **31**, 2241; 1901, **34**, 897) on the ring expansion of benzene with diazoacetic ester has been re-examined by Grundmann and Ottmann (*Annalen*, 1953, **582**, 163) who, on the basis of ultraviolet spectra and mode of formation, revised the structures assigned by Buchner to the four *cyclo*heptatrienecarboxylic acids. Thus the structure of the α-isomer, m. p. 71° (IV; $R = CO_2H$), was deduced on the basis of the weak maximum in the absorption curve at 260 mμ (log ε 3·40), whereas the other double-bond isomers absorb at *ca.* 280 mμ (log ε 3·52—3·76).

α-*cyclo*Heptatrienecarboxylic acid was selected initially for experiments on the replacement of the carboxy-group because it was felt that the absence of double bonds conjugated with the substituent would lessen the tendency of the products to rearrange. However, attempts to replace the carboxy-group by bromine, by direct bromination of the silver salt or by use of silver trifluoroacetate and bromine, were unsuccessful, as were attempted Schmidt reactions. By the Curtius reaction the acid chloride (IV; $R = COCl$) gave the *iso*cyanate and urethane (IV; $R = NH{\cdot}CO_2Et$), the latter being a pale yellow oil, $C_{10}H_{13}O_2N$, b. p. 85—90°/0·4 mm. In order to show that no rearrangement of double bonds had occurred during the formation of the acid chloride it was converted into the amide (IV; $R = CO{\cdot}NH_2$), the ultraviolet absorption of which was very nearly identical with that of the original acid. The infrared spectrum of the urethane showed a strong band at 3322 cm.$^{-1}$, corresponding to the NH group and thus excluding the possibility of tautomerism. Although the volatility and physical nature of the urethane clearly indicated the covalent structure (IV; $R = NH{\cdot}CO_2Et$) (cf. the methyl ether, Doering and Knox, *loc. cit.*) rather than a polar structure of type (I), certain of the physical and chemical properties of the compound indicates that the carbon–nitrogen bond was quite weak. The ultraviolet absorption (max. at 270—271 mμ; log ε 3·88) was more intense than that of the original amide (IV; $R = CO{\cdot}NH_2$) (259—260 mμ; log ε 3·42) and somewhat resembled that of *cyclo*heptatrienylium bromide (275 mμ; log ε 3·65; Doering and Knox, *loc. cit.*).


(IV)


(V)


(VI)


(VII)

The strength of the carbon–nitrogen covalent bond in an amine or urethane can be gauged by the ease of its hydrolysis. Thus the simple aliphatic and aromatic amines resist hydrolysis under extreme conditions whereas (triphenylmethyl)amine gives 85% of the theoretical amount of ammonium chloride after hydrolysis with N/20-hydrochloric acid at 100° for 90 minutes (Kharasch and Howard, *J. Amer. Chem. Soc.*, 1934, **56**, 1370). Treatment of the urethane derived from α-*cyclo*heptatrienecarboxylic acid with N/100-acetic acid at 100° for 2 hours gave 30% of free urethane; even contact with moist solvents, especially alcohols at room temperature, yielded appreciable amounts of free urethane but other hydrolysis products have not been isolated. Triphenylmethylurethane, $Ph_3C{\cdot}NH{\cdot}CO_2Et$, with N/10-acetic acid at 100° for 4 hours gave only 9% of free urethane. The α-*cyclo*heptatrienylurethane darkened noticeably in air even at room temperature and when heated it was converted into a brown polymeric substance.

In experiments with β-*cyclo*heptatrienecarboxylic acid (V) (Grundmann and Ottmann, *loc. cit.*) it was found that it readily formed a colourless dibromide, m. p. 145—146° (Einhorn *et al.*, *Ber.*, 1893, **26**, 331, and *Annalen*, 1894, **280**, 124, give m. p. 135° for an isomeric dibromo*cyclo*heptadienecarboxylic acid) but, when the crude addition product was heated under reduced pressure, hydrogen bromide was liberated and carboxy*cyclo*heptatrienylium bromide (VI) was obtained in low yield [0·8%; the figure of 8% given by Johnson and Tisler (*Chem. and Ind.*, 1954, 1427) in a preliminary announcement was a typographical error]. The same product was obtained, although in even smaller yield, from γ-*cyclo*heptatrienecarboxylic acid (VII) (Grundmann and Ottmann, *loc. cit.*) by a similar process although not from the esters of (V) or (VII). The formation of (VI) from two isomers of *cyclo*heptatrienecarboxylic acid constitutes supporting evidence for the structure assigned to the product as double-bond rearrangement would not be expected under the experimental conditions employed.

The acid (VI) was a dull yellow crystalline solid, easily soluble in water and alcohols and insoluble in ether, benzene, and light petroleum. It was obtained anhydrous and as a monohydrate and was a strong acid (p*K* 3·3). It charred at about 180° but did not melt. Addition of silver nitrate to an aqueous solution of the acid caused an immediate precipitate of silver bromide and the structure (VI) followed from hydrogenation of the acid in the presence of platinum, four mols. of hydrogen being absorbed and *cyclo*heptanecarboxylic acid obtained. There was therefore a close relation between the properties of (VI) and those of the unsubstituted bromide (I) (Doering and Knox, *loc. cit.*). Other reactions of (VI) are being studied.

Of the various *cyclo*heptatrienyl derivatives, C_7H_7X, which have been prepared, only the halides ($X = Cl$ and Br) are polar compounds. The methyl ether, amine, and urethane as well as di*cyclo*heptatrienyl ether are all covalent compounds and it appears that the seven-membered alicyclic cation needs an anion derived from a relatively strong acid, HX, for the formation of a stable salt.

EXPERIMENTAL

Unless otherwise stated, ultraviolet spectra were determined in 95% EtOH, and infrared spectra on Nujol mulls.

Reduction of 2 : 4 : 7-*Tribromotropone.*—Lithium aluminium hydride (496 mg.) was suspended in dry tetrahydrofuran (10 c.c.) and cooled to −30°. A solution of 2 : 4 : 7-tribromotropone (1·06 g.) (Nozoe, Kitahara, Ando, Masumune, and Abe, *Sci. Rep. Tôhoku Univ.*, 1952, **36**, 166) in dry tetrahydrofuran (30 c.c.) was added dropwise with stirring during 30 min. and the mixture stirred for a further 2 hr. at −20° to −30°, then for 30 min. at room temperature. The product was decomposed by the addition of wet ether (50 c.c.), followed by water (10 c.c.), and then divided into equal portions A and B. Solution A was acidified with 4N-sulphuric acid (15 c.c.) and extracted with ether (3 × 20 c.c.). The ethereal extract was dried and the solvent removed, leaving a light brown oil (279 mg.) which slowly crystallised. The aqueous layer was made alkaline and again extracted with ether. This ethereal extract was dried and evaporated but left only a small amount (4 mg.) of brown gum. Solution B was made alkaline with sodium hydroxide (1·3 g.) and extracted with ether (3 × 20 c.c.). After drying of the ethereal extract and removal of the solvent, a light brown solid (337 mg.) remained. The aqueous layer was acidified with hydrochloric acid and again extracted with ether as before, but only a small quantity (7 mg.) of a brown gum was obtained. The two solid extracts were combined and distilled at 0·5 mm., a colourless solid *dibromide* (567 mg.) being obtained which after crystallisation from benzene-light petroleum (b. p. 60—80°) formed colourless needles, m. p. 98° (Found : C, 31·4; H, 3·8. $C_7H_{10}OBr_2$ requires C, 31·15; H, 3·7%).

α-cyclo*Heptatrienecarboxylic Acid* (IV; $R = CO_2H$) *and its Derivatives.*—The acid, m. p. 71°, was prepared according to Grundmann and Ottmann (*loc. cit.*). Light absorption : max. at 260 mμ (log ε 3·40); and in concentrated sulphuric acid : max. at 226, 284, and 330 mμ (log ε 4·37, 3·55, and 3·39 respectively). The infrared spectrum showed max. at 2632, 2532, 1701, 1605, 1414, 1326, 1294, 1277, 1212, 1179, 1095, 1047, 957, 926, 902, 880, 806, 775, 758, 717, and 676 cm.$^{-1}$.

The acid chloride, b. p. 74°/4 mm., was prepared by the action of thionyl chloride, and converted into the amide which formed colourless plates, m. p. 128—129° (Buchner, *Ber.*, 1897, **30**, 632, gives m. p. 129°), on sublimation and crystallisation from aqueous methanol. Light absorption: max. at 259—260 mμ (log ε 3·42). Infrared spectrum: max. at 3322, 3175, 1669, 1637, 1595, 1538, 1447, 1412, 1316, 1294, 1221, 1209, 1181, 1131, 1099, 1048, 1027, 996, 959, 944, 935, 905, 870, 812, 761, 728, and 706 cm.$^{-1}$.

Curtius Reaction with α-cyclo*Heptatrienecarboxylic Acid Chloride* (IV; R = COCl).—(*a*) Activated sodium azide (448 mg.) (Smith, *Org. Reactions*, 1946, **3**, 382) was added to a solution of the acid chloride (866 mg.) in dry xylene (7 c.c.). The mixture was heated at 114°, nitrogen (115 c.c., 92%) being evolved during 5 hr. The mixture was cooled, the inorganic salts were separated, and the filtrate and xylene washings (2 × 5 c.c.) treated with 10N-hydrochloric acid (1·7 c.c.) and heated at 100°. The solvent was removed *in vacuo*, leaving a yellow semicrystalline gum which gave a brown amorphous solid on attempted crystallisation from methanol–ether. The solid was dissolved in methanol and precipitated by addition of ether several times until a colourless powder (214 mg.) was obtained which proved to be ammonium chloride (71% calc. on the acid chloride).

(*b*) Sodium azide (570 mg.) was treated with α-*cyclo*heptatrienecarbonyl chloride (1·23 g.) in dry xylene (7 c.c.) as in the previous experiment. The salts were separated from the cooled solution and washed with dry ethanol (3 × 2 c.c.), and the combined filtrates heated at reflux temperature for 2 hr. with more dry ethanol (20 c.c.). After removal of the solvent *in vacuo* at 100°, there remained a light brown viscous oil which was distilled at 87° (bath temp.)/0·4 mm. A very volatile colourless solid was obtained together with a pale yellow oil and a dark brown solid residue. The volatile solid formed colourless plates (23 mg.), m. p. 48—49°, after crystallisation from light petroleum (b. p. 60—80°), and the m. p. was not depressed when the product was mixed with ethyl carbamate (Found : C, 40·65; H, 8·0; N, 15·9. Calc. for $C_3H_7O_2N$: C, 40·45; H, 7·9; N, 15·7%). The oily N-cyclo*heptatrienylurethane* (458 mg.) was redistilled for analysis (Found : C, 67·0; H, 7·5; N, 7·8. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8%). Light absorption : max. at 270—271 mμ (log ε 3·88); in sulphuric acid : max. at 226, 265, 344, and 392—393 mμ (log ε 3·97, 3·64, 3·16, and 3·22 respectively). The infrared spectrum of the liquid itself showed max. at 3322, 2985, 2890, 2841, 1715, 1634, 1524, 1481, 1445, 1379, 1316, 1235, 1171, 1095, 1056, 1005, 946, 923, 889, 852, 829, 797, 772, and 709 cm.$^{-1}$. The urethane was unstable in the presence of air or moisture but could be preserved at 0·3 mm. in a sealed tube. Moist solvents, especially methanol, caused hydrolysis to ethyl carbamate and a dark brown gum. The oil was soluble in most organic solvents except light petroleum, and insoluble in water, and with concentrated sulphuric acid it gave a strong yellow colour which disappeared on dilution with water.

(*c*) In other experiments the crude reaction products from sodium azide and α-*cyclo*heptatrienecarbonyl chloride in xylene solution were treated with ferric chloride in the presence of hydrogen chloride, hydrogen chloride alone, and 60% perchloric acid, but in no case were pure products isolated other than ammonium chloride.

Reactions of α-cyclo*Heptatrienylurethane* (IV; R = $NH{\cdot}CO_2Et$).—(a) *Hydrolysis*. Oxygen-free nitrogen was led through a suspension of the urethane in N/100-acetic acid at 100°. After 2 hr. a clear solution was obtained which was extracted with ether (3 × 20 c.c.). Evaporation of the aqueous phase at 100° in a vacuum gave a pale brown gum (2 mg.). The ethereal extract was dried and the solvent removed, to leave a yellow oil which on distillation at 107° (bath-temp.)/0·6 mm. gave a pale yellow oil (63 mg.) and colourless plates (19 mg., 30%), m. p. 49—50°, identical with ethyl carbamate.

(b) No solid products were obtained from reactions of the urethane in dry ether with 60% perchloric acid, concentrated sulphuric acid, anhydrous picric acid, anhydrous trifluoroacetic acid, or dry hydrogen chloride. Likewise no pure products were isolated from reactions of the urethane with 10% methanolic auric chloride alone or saturated with hydrogen chloride, methanolic picric acid, or 50% hydrobromic acid in acetic acid at 100°.

Triphenylmethylurethane.—A solution of triphenylmethylamine (5 g.) (Elbs, *Ber.*, 1884, **17**, 701) in dry ether (40 c.c.) was caused to react with ethyl chloroformate (1·1 g.) at the b. p. for 3 hr. during which a colourless precipitate formed. The ether was evaporated and the residue extracted with hot light petroleum (b. p. 60—80°; 3 × 50 c.c.), leaving (triphenylmethyl)amine hydrochloride as colourless crystals (2·67 g.), m. p. 243—244°. The solvent was removed from the petroleum extracts and the residue crystallised from aqueous methanol, to give colourless plates (2·81 g., 91% calc. on half the amount of triphenylmethylamine used), m. p. 110—111° (Found : C, 79·7; H, 6·2; N, 4·5. $C_{22}H_{21}O_2N$ requires C, 79·7; H, 6·4; N, 4·2%).

A solution of this *urethane* (282 mg.) in N/10-acetic acid (10 c.c.) and methanol (5 c.c.) was heated under reflux for 4 hr. The solvents were removed *in vacuo* and the glassy residue was sublimed at 0·5 mm., to give plates (7 mg., 9%), m. p. 49—50°, not depressed when mixed with ethyl carbamate. The residue from the sublimation was crystallised from aqueous methanol to give colourless plates (214 mg., 76%) of triphenylmethylurethane, m. p. 110—111°.

β-cyclo*Heptatrienecarboxylic Acid* (V) *and its Derivatives*.—The acid, m. p. 56°, was prepared according to Grundmann and Ottmann (*loc. cit.*). Light absorption : max. at 275—277 mμ (log ε 3·76). The infrared spectrum showed max. at 2653, 2532, 1695, 1616, 1538, 1408, 1335, 1282, 1235, 1186, 1099, 1049, 1021, 976, 965, 949, 905, 889, 798, 765, 733, and 668 cm.$^{-1}$.

The acid chloride, b. p. 93°/7 mm., n_D^{18} 1·5763, was prepared by the action of thionyl chloride and converted into the amide which sublimed at 90°/0·5 mm. and crystallised from ether as colourless plates, m. p. 97—98° (Buchner and Lingg, *Ber.*, 1898, **31**, 402, give m. p. 98°) (Found :

C, 71·1; H, 6·9. Calc. for C_8H_9ON: C, 71·1; H, 6·7%). Light absorption: max. at 274 mμ (log. ε 3·75).

The *dibromide*, prepared by the addition of bromine (1 mol.) to the acid in chloroform solution, formed colourless plates, m. p. 145—146° (decomp.) after crystallisation from ethanol (Found: C, 32·9; H, 2·6. $C_8H_8O_2Br_2$ requires C, 32·5; H, 2·7%). Hydrogenation of the product over platinum yielded *cyclo*heptanecarboxylic acid, identified as the amide, m. p. 195°, not depressed on admixture with an authentic specimen (Bartels-Keith, Johnson, and Langemann, *J.*, 1952, 4461).

*Carboxy*cyclo*heptatrienylium Bromide* (VI).—A solution of bromine (0·88 c.c., 0·8 mol.) in carbon tetrachloride (10 c.c.) was added dropwise to a cooled solution (ice) of β-*cyclo*heptatrienecarboxylic acid (3 g.) (Grundmann and Ottmann, *loc. cit.*) in carbon tetrachloride (20 c.c.). The solvent was then removed from the pale yellow solution under reduced pressure and the gummy residue heated at 80—90°/10^{-5} mm. for 2 hr. After cooling, dry ether (25 c.c.) was added and the solid insoluble *bromide* separated. It was dissolved in the least volume of dry ethanol and precipitated by addition of ether, being obtained as small dull yellow crystals (40 mg.) (Found: C, 41·0; H, 4·3. $C_8H_7O_2Br,H_2O$ requires C, 41·2; H, 3·9. Found, in a sample dried at 80—90°/0·01 mm.: C, 45·0; H, 3·6; Br, 36·95. $C_8H_7O_2Br$ requires C, 44·7; H, 3·3; Br, 37·15%). The bromide chars at about 180° but does not melt below 300°; pK_a 3·29. It is very soluble in water and alcohols but insoluble in non-polar organic solvents. Addition of silver nitrate to an aqueous solution gives an immediate precipitate of silver bromide. Light absorption in water: max. at 272—273 mμ (log ε 3·68) and min. at 246—247 mμ (log ε 3·52). The infrared spectrum (KBr plate) showed max. at 3279, 3003, 1980, 1715, 1631, 1563, 1531, 1477, 1443, 1387, 1366, 1280, 1258, 1239, 1212, 749, and 686 cm.$^{-1}$. Hydrogenation of an ethanolic solution of the bromide over a platinum catalyst caused the absorption of 4 mols. of hydrogen and the *cyclo*heptanecarboxylic acid so formed was identified as its amide, m. p. 195°, as above.

By a similar method, the liquid γ-*cyclo*heptatrienecarboxylic acid (VII) (1 g.) (Grundmann and Ottmann, *loc. cit.*) reacted with bromine (0·3 c.c., 0·8 mol.) and was treated as in the previous experiment. Carboxy*cyclo*heptatrienyl bromide (10 mg.), identical with that obtained as above, was isolated from the product.

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