489. *The Tropylium Ion. Part IV.*[1] *Conversion of Cyclohepta-2,4,6-trienecarboxylic Acid into Tropylium Salts.*

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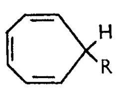
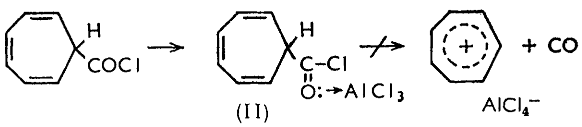
The Hunsdiecker reaction with silver cyclohepta-2,4,6-trienecarboxylate gives a tropylium halide. Tropylium salts are obtained by reaction of cyclohepta-2,4,6-trienecarbonyl chloride with acetyl fluoroborate or silver perchlorate. The perchlorate with 7-cyanocyclohepta-1,3,5-triene gives tropylium perchlorate. Bromine and cyclohepta-2,4,6-trienecarboxylic acid give two dibromo-adducts; one of these can be dehydrobrominated to carboxytropylium bromide, the other is stable.

Oxidation of cyclohepta-2,4,6-trienecarboxylic acid (I; R = CO_2H) into the tropylium cation, reported in Part III,[1] suggests that this acid should be readily decarboxylated or decarbonylated to yield tropylium salts directly; several methods for effecting such a conversion are described below.

Treatment of silver cyclohepta-2,4,6-trienecarboxylate with bromine in carbon tetrachloride, or iodine in benzene, as in the normal Hunsdiecker reaction,[2] liberated carbon dioxide, and the resulting silver halide was precipitated in intimate mixture with the insoluble tropylium halide. Only a small proportion of the tropylium salt in this precipitate was extracted by water or ethanol, but it was all converted into biscycloheptatrienyl ether by vigorous agitation with aqueous sodium hydroxide. This ether was then extracted and converted into tropylium bromide with hydrogen bromide.



(I)



(II)

The tropylium salt was, however, retained in solution when cyclohepta-2,4,6-trienecarbonyl chloride (I; R = COCl) was decarbonylated with silver perchlorate in nitromethane to give silver chloride, which was removed by filtration, and tropylium perchlorate which was then precipitated from the filtrate by the addition of ether. An analogous reaction has been described[3] in which the treatment of pivaloyl chloride with aluminium chloride results in loss of carbon monoxide. A similar reaction with cyclohepta-2,4,6-trienecarbonyl chloride gave a solid organic product which contained aluminium but displayed none of the characteristic properties of the tropylium cation. It is possible that this product is a complex of the form (II): this type of complex has been obtained[4] on reaction of benzoyl chloride with aluminium chloride. In a similar way 7-cyanocyclohepta-1,3,5-triene[5] (I; R = CN) with silver perchlorate in nitromethane produced silver cyanide: this was filtered off and addition of ether to the filtrate precipitated tropylium perchlorate.

Acetyl fluoroborate[6] with compounds containing an active chlorine atom gives acetyl chloride and a fluoroborate; however, there is no recorded use of this reagent with acid chlorides. The reaction with cyclohepta-2,4,6-trienecarbonyl chloride in chloroform proceeded with elimination of carbon monoxide to give tropylium fluoroborate which was

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[1] Part III, *J.*, 1958, 55.

[2] See Johnson and Ingham, *Chem. Rev.*, 1956, **56**, 219.

[3] Grundy, Rothstein, and Hsü, *J.*, 1956, 4558.

[4] Brown and Jensen, *J. Amer. Chem. Soc.*, 1958, **80**, 2291.

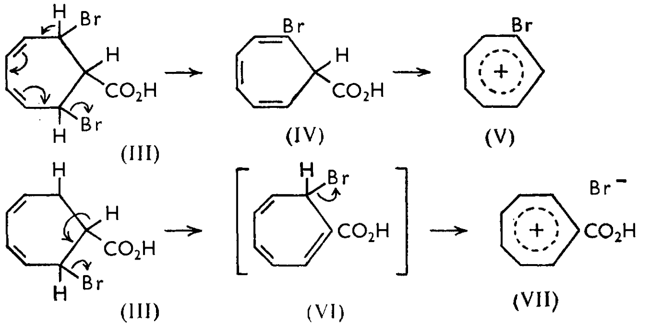
[5] Dewar and Pettit, *J.*, 1956, 2021, 2026.

[6] Seel, *Z. anorg. Chem.*, 1943, **250**, 331.

precipitated on addition of ether. A similar reaction with cyclohepta-2,4,6-trienecarboxylic acid gave acetic acid and carbon monoxide, the yield of tropylium fluoroborate being increased to almost 100%.

All the above reactions remove the group R from the cycloheptatriene derivatives (I; R = CO_2H, COCl, or CN) to give tropylium salts. An alternative reaction, whereby the hydrogen atom α to the group R is removed, would give a tropylium cation containing a functional substituent. Such a reaction was described recently by Johnson, Langemann, and Tisler,[7] who obtained carboxytropylium bromide in low yields from β- or γ-cycloheptatrienecarboxylic acid by the bromination procedure of Doering and Knox.[8]

Braren and Buchner [9] stated that the action of bromine on cyclohepta-2,4,6-trienecarboxylic acid [10] gave a crystalline dibromide which did not lose hydrogen bromide and could be reduced back to cyclohepta-2,4,6-trienecarboxylic acid with zinc. This suggested that it might be possible to dehydrohalogenate the dibromide to bromocyclohepta-2,4,6-trienecarboxylic acid, and then to convert this by our procedure into a bromotropylium salt and so into tropone; this is illustrated below for a possible structure (III) of the dibromide and the corresponding structure (IV) for the monobromo-acid. It would of course be equally possible in principle for dehydrobromination to give carboxytropylium bromide (VII) *via* (VI).



(III) (IV) (V)

(III) (VI) (VII)

On repeating the addition of bromine to cyclohepta-2,4,6-trienecarboxylic acid we obtained two products, one of which was the solid dibromocarboxylic acid described by the earlier workers. This acid did not eliminate hydrogen bromide when heated alone *in vacuo* or with anhydrous pyridine, and in the presence of hydroxyl ions the bromine atoms were readily hydrolysed. The other product was obtained as a pale yellow viscous liquid when the filtrate from the reaction mixture was evaporated. This was too unstable to be purified and eliminated hydrogen bromide with extreme ease, even at room temperature, to give carboxytropylium bromide. It is possible that the two bromo-acid products are configurational isomers in which either both bromine atoms are *trans*, or one is *trans*, to the carboxyl group. Only the latter isomer satisfies the requirement for *trans*-elimination of hydrogen bromide, whilst participation of the hydrogen atom adjacent to the carboxyl group is favoured by the inductive (+*I*) effect of the latter.

Carboxytropylium bromide was unstable in aqueous or alcoholic solution and was much more susceptible to nucleophilic substitution than the parent tropylium cation; thus a solution in water, or dilute acid, afforded a brown solid within a few minutes; this was a mixture and we were unable to purify it, but it appeared to contain formyl- and hydroxymethyl-benzoic acid. In solutions containing a high concentration of bromide ions the cation was much more stable. In the presence of different halide ions the colour of the

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[7] Johnson, Langemann, and Tisler, *J.*, 1955, 1622.

[8] Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **54**, 925.

[9] Braren and Buchner, *Ber.*, 1901, **34**, 995.

[10] This acid was formerly formulated as norcaradienecarboxylic acid; see Doering, Chamberlain, Laber, Vonderwahl, and Williams, *J. Amer. Chem. Soc.*, 1956, **78**, 5448.

solution changed in a way similar to that observed for the tropylium cation. A concentrated aqueous solution of carboxytropylium bromide was yellow; the addition of sodium chloride solution removed the colour, whilst with sodium iodide it was deep red. With saturated aqueous picric acid this compound formed a yellow crystalline picrate, which also was unstable in aqueous solution.

EXPERIMENTAL

Hunsdiecker Reaction.—Cyclohepta-2,4,6-trienecarboxylic acid[8] was neutralised with 0·5N-sodium hydroxide; an equivalent amount of silver nitrate was then added. The resulting white precipitate of silver cyclohepta-2,4,6-trienecarboxylate was filtered off, was washed with water, then acetone, partially dried at 100° for 30 min., and finally dried *in vacuo* over phosphoric oxide (yield, 90%).

(*a*) To a suspension of the silver salt (10·0 g., 0·041 mole) in dry, refluxing carbon tetrachloride (700 ml.), bromine (6·6 g., 0·041 mole) was added dropwise with vigorous stirring. Carbon dioxide (250 c.c., 25%) was liberated, and refluxing was continued for 10 min. After filtration, the yellow precipitate (10 g.), consisting of a mixture of silver and tropylium bromides, was agitated for 30 min. with 2N-sodium hydroxide. The resulting mixture was extracted with ether (3 × 100 ml.), and the combined extracts were washed once with water, dried ($MgSO_4$), and evaporated. The residue of biscycloheptatrienyl ether was dissolved in dry ether (50 ml.) and treated with hydrogen bromide to give tropylium bromide (0·40 g., 5%). Evaporation of the carbon tetrachloride filtrate gave polymeric material. Variation of the initial reaction temperature did not improve the yield of tropylium bromide.

(*b*) The above silver salt (18·5 g., 0·076 mole) was added portionwise during 1 hr. to a dry, refluxing solution of iodine (19·3 g., 0·076 mole) in benzene (2 l.). Carbon dioxide was evolved and refluxing was continued for 1 hr. The red precipitate (23·0 g.), consisting of a mixture of silver and tropylium iodides, was filtered off and treated as described above, to give tropylium bromide (1·7 g., 13%). The yield was not improved by varying the order of addition or the initial temperature of reaction.

*Reaction of Acetyl Fluoroborate with Cyclohepta-*2,4,6*-trienecarboxylic Acid.*—Excess of acetyl fluoroborate[6] (1·5—2 g.) was added to the carboxylic acid (1·00 g.) in chloroform (5 ml.) at −70°, and the mixture was allowed to reach 20° (the initial reaction occurred at approx. −20°). More acetyl fluoroborate (0·5 g.) was added and, after 30 min., the mixture was heated at 40—50° for 1 hr. The mixture was cooled, dry ether (50 ml.) added, and the resulting pale brown precipitate was collected and dried (1·21 g., 93%). Trituration, followed by crystallisation from ethanol, gave pure tropylium fluoroborate as prisms (Found: C, 47·3; H, 4·3. Calc. for $C_7H_7BF_4$: C, 47·2; H, 4·0%).

*Reactions with Cyclohepta-*2,4,6*-trienecarbonyl Chloride.*—(*a*) A solution of the acid chloride[5] (1·13 g., 0·0073 mole) in dry nitromethane (10 ml.) was added dropwise, during 45 min., to a stirred solution of silver perchlorate (1·74 g., 0·0084 mole) in dry nitromethane (20 ml.) at 90°. After a further 75 min. the precipitate of silver chloride was filtered off and dry ether (300 ml.) was added to the filtrate to precipitate tropylium perchlorate (0·39 g., 28%). This tropylium salt crystallised from nitromethane as prisms (Found: C, 43·8; H, 4·0. Calc. for $C_7H_7ClO_4$: C, 44·1; H, 3·7%).

(*b*) A solution of aluminium chloride (0·73 g., 0·0054 mole) in dry nitromethane (3 ml.) was added to the acid chloride (0·92 g., 0·0059 mole) with cooling, and the mixture was heated to 80°. After 20 min. the mixture was cooled, dry ether (200 ml.) was added, and the resulting pale yellow precipitate was collected (0·61 g.). This substance was soluble in ethanol, acetone, or chloroform, but insoluble in benzene or water. The addition of alkali did not produce biscycloheptatrienyl ether.

(*c*) Excess of acetyl fluoroborate was added to the acid chloride (0·70 g.) in chloroform (5 ml.) at −70°, and the mixture was allowed to reach 20°. After 30 min., dry ether was added to precipitate tropylium fluoroborate (0·25 g., 41%).

Reaction of Silver Perchlorate with 7*-Cyanocyclohepta-*1,3,5*-triene.*—The cyanide[5] (1·00 g., 0·0085 mole) was heated with silver perchlorate (3·6 g., 0·017 mole) in dry nitromethane (50 ml.) at 85° for 5½ hr. After removal of the silver cyanide (0·51 g., 58%), dry ether (100 ml.) was added and the white precipitate of tropylium perchlorate was collected (0·72 g., 45%).

*Bromination of Cyclohepta-*2,4,6*-trienecarboxylic Acid.*—(*a*) To a stirred solution of cyclohepta-2,4,6-trienecarboxylic acid (2·5 g., 0·018 mole) in carbon disulphide (10 ml.) at 0°, bromine

(2·9 g., 0·018 mole) in carbon disulphide (10 ml.) was added dropwise during 10 min. Dibromocycloheptadienecarboxylic acid (0·8 g., 15%), which separated as a white solid, was filtered off and, after three crystallisations from benzene, had m. p. 139—139·5° (decomp.) (lit.,[9] 159—160°). Several further crystallisations from benzene or light petroleum did not raise the m. p. which was extremely sensitive to the rate of heating (the value recorded above was obtained after slow heating from room temperature) (Found: C, 32·6; H, 2·7; Br, 54·1. Calc. for $C_8H_8O_2Br_2$: C, 32·5; H, 2·7; Br, 54·0%). The colour reactions of this product with sulphuric acid, and its behaviour towards permanganate or bromine, were identical with those previously described.[9]

Evaporation of the carbon disulphide filtrate left a pale yellow viscous residue which evolved hydrogen bromide and deposited yellow needles. This was heated for 30 min. at 80°/14 mm., then dry ether (50 ml.) precipitated carboxytropylium bromide as dull yellow needles (0·73 g., 19%). Evaporation of the ethereal filtrate left a residue which, on crystallisation from benzene, gave a further crop of dibromocycloheptadienecarboxylic acid (1·0 g., 19%).

Several other solvents were investigated: the highest yield of carboxytropylium bromide was obtained by using chlorobenzene.

(*b*) To a stirred solution of cyclohepta-2,4,6-trienecarboxylic acid (10·0 g., 0·074 mole) in chlorobenzene (60 ml.) at 80°, bromine (11·8 g., 0·074 mole) in chlorobenzene (20 ml.) was added dropwise during 30 min. Hydrogen bromide was evolved and carboxytropylium bromide separated as yellow prismatic needles which, after a further 1 hr. at 80°, were filtered off (2·4 g., 15%). The residue obtained on evaporation of the filtrate was heated at 80°/14 mm. for 2 hr., to give carboxytropylium bromide (3·2 g., 20%) and a small amount of dibromocycloheptadienecarboxylic acid.

Carboxytropylium bromide, obtained as above, had the properties described by Johnson *et al.*[7] (Found: C, 44·5; H, 3·7; Br, 38·0. Calc. for $C_8H_7O_2Br$: C, 44·7; H, 3·3; Br, 37·2%). This salt was sparingly soluble in ethanol at 0° and was precipitated with dry ether; however, after being warmed in ethanol, the salt dissolved and was not reprecipitated by ether. Addition of saturated aqueous picric acid to a concentrated aqueous solution of carboxytropylium bromide gave a yellow ***picrate*** (prisms), m. p. 135—137° (decomp.), which decomposed in warm water, aqueous picric acid, or ethanol (Found: C, 45·7; H, 2·8; N, 11·1. $C_{14}H_9O_9N_3,\frac{1}{2}H_2O$ requires C, 45·3; H, 2·7; N, 11·3%).

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