Carbonium Ion Salts. XI. Convenient Preparations of Hydroxytropenylium Salts, Ditropenyl Ether, and Tropone[1]

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In the course of thermodynamic and infrared spectral studies,[3–5] we have prepared and characterized a number of anhydrous and hydrated hydroxytropenylium ion salts. Previous reports of the chloride,[6,7] bromide,[8–11] and iodide[12,13] have contained either no or inconvenient synthetic directions, and, of the salts discussed herein, only the perchlorate[14] has previously been satisfactorily characterized. The preparations given here use the single starting material tropone, are simple to carry out, and give good yields of stoichiometric salts.

At first we used tropone prepared by the acid-catalyzed disproportionation of ditropenyl ether after the method of ter Borg.[15] We found this distillative disproportionation to give considerable polymerization in the still, and the product tropone usually needed redistillation; however, the method is satisfactory for obtaining a sample of tropone quickly.

In the course of this work we have developed a convenient, large-scale preparation for the ditropenyl ether necessary for the synthesis of tropone. When methylene chloride solutions of either ditropenyl ether or tropenyl methyl ether were stored over molecular sieve drying agent, we observed the formation of tropone in the solutions; this suggested that the sieve acted as a mild acid catalyst to initiate disproportion. To test this a solution of ditropenyl ether in methylene chloride was stored in the cold over Linde 4A molecular sieve; aliquots of this solution were withdrawn at intervals and extracted with 50% sulfuric acid. Spectral analysis[16] of these acid extracts showed a steady increase in tropone content, and a concurrent decrease in tropenylium ion arising from extraction of ditropenyl ether into sulfuric acid. At the conclusion of the reaction, the nearly water-white methylene chloride solution contained quantitative yields of tropone and cycloheptatriene. We have found this reaction to be an excellent source of tropone; the solution can be concentrated and treated with acids to yield hydroxytropenylium salts, or tropone can be obtained in a pure state by concentration and distillation. The reaction is quite slow, however; a number of weeks are required for completion. We find it convenient to keep a large quantity of solution on hand at all times, stored in the refrigerator over molecular sieve.

Experimental Section

Cycloheptatriene,[17] cyclohexane,[17] acetonitrile,[16] methylene chloride,[16] ether,[18] and boron bromide[17] were prepared as previously described. Mallinckrodt reagent grade benzene, carbon tetrachloride, and ethyl acetate were dried over Linde 4A molecular sieve. U. S. I. absolute alcohol, Baker and Adamson reagent grade 71% perchloric acid, 48% hydrobromic acid, 47% hydriodic acid, and phosphorus pentachloride, Volk Radiochemical 99.8% deuterium oxide, and Matheson anhydrous hydrogen bromide were used without further treatment. Ultraviolet spectra were taken on the Cary 13 spectrophotometer; Baker and Adamson reagent grade 96% sulfuric acid was used for analytical spectra. Melting points were taken on a Fisher-Johns block and are corrected.

Tropone.—Tropone was prepared by a method adapted from that of ter Borg.[15] Ditropenyl ether was placed in a modified Hickman[19] still with a portion of a moist mixture of alumina and phosphorus pentoxide; the temperature was held at 56° at 150 torr until distillation of cycloheptatriene ceased, then was raised to 90° at 15 torr to effect distillation of tropone. Yields ranged between 60 and 70%. Tropone is extremely sensitive to oxygen and light and care must be taken to protect the product from both. Redistillation of the tropone fraction afforded a water-white liquid with an infrared spectrum identical with that reported[20] for tropone.

Hydroxytropenylium Perchlorate.[21]—Tropone (0.20 g, 1.89 mmol) was dissolved in acetonitrile (15 ml) and 71% perchloric acid (0.5 ml) was added. Ether (60 ml) was added slowly to afford a white precipitate. This material was recrystallized twice from acetonitrile by slow addition of ethyl acetate and dried *in vacuo* to yield 47.7% hydroxytropenylium perchorate (0.185 g 0.90 mmol) as white plates, mp 187° (lit.[14] mp 186°).

Anal. Calcd for $C_7H_7O_5Cl$: $HClO_4$, 48.87. Found: $HClO_4$, 48.94.

The ultraviolet spectrum of this compound was carefully determined in 96% sulfuric acid showing absorptions at λ_{max} 229 mμ (ϵ 41,700), 306 (10,300), and 312 (sh).

Hydroxytropenylium Chloride.—Tropone (0.26 g, 2.45 mmol) was dissolved in absolute ethanol (5 ml) and 38% hydrochloric acid (0.30 ml, 3.8 mmol) was added. Ether (150 ml) was added and the flask was stored at −10° overnight. The solvent was decanted while cold from a crop of fine white needles; these were washed with two 25-ml portions of ether, dried *in vacuo*, and sublimed to yield 71.8% hydroxytropenylium chloride (0.251 g, 1.76 mmol) as white needles, mp 78–82° dec.

Anal. Calcd for C_7H_7OCl: $C_7H_6OH^+$, 75.13; Cl^-, 24.87. Found: $C_7H_6OH^+$, 75.2;[22] Cl^-, 25.18.

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(1) Work supported by the National Science Foundation and the Petroleum Research Fund.

(2) Petroleum Research Fund Scholar, 1964–1965.

(3) K. M. Harmon and T. T. Coburn, *J. Amer. Chem. Soc.*, **87**, 2499 (1965).

(4) K. M. Harmon, T. T. Coburn, and J. M. Fisk, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p L50.

(5) K. M. Harmon and T. T. Coburn, *J. Phys. Chem.*, in press.

(6) The chloride was reported by Dauben and Ringold[7] as a deliquescent salt which was not characterized.

(7) H. J. Dauben, Jr., and H. J. Ringold, *J. Amer. Chem. Soc.*, **73**, 876 (1951).

(8) The bromide has been reported by Doering and Detert[9] from bromination of methoxycycloheptatriene (no analysis), by Dauben and Harmon[10] from solvolysis of halotropenylium salts, and by Zaitsev, *et al.*,[11] from addition of hydrogen bromide to tropone (no analysis).

(9) W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

(10) H. J. Dauben, Jr., and K. M. Harmon, Abstracts, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, p 35P; unpublished work in Ph.D. Thesis of K. M. H., University of Washington, Seattle, Wash., 1958; *Dissertation Abstr.*, **19**, 1563 (1959).

(11) B. E. Zaitsev, Yu. D. Koreshkov, M. E. Vol'pin, and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **139**, 1007 (1961).

(12) The iodide has been reported by Harmon, *et al.*,[13] by reaction of tropone with anhydrous hydrogen iodide; this yields material of good quality, but the reaction presents significant manipulative difficulty.

(13) K. M. Harmon, A. B. Harmon, S. D. Alderman, L. L. Hesse, and P. A. Gebauer, *J. Org. Chem.*, **32**, 2012 (1967).

(14) T. Nozoe, T. Mukai, and K. Takose, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **39**, 172 (1956).

(15) A. P. ter Borg, *et al.*, *Helv. Chim. Acta*, **43**, 457 (1960).

(16) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Amer. Chem. Soc.*, **84**, 3349 (1962).

(17) K. M. Harmon, A. B. Harmon, and F. E. Cummings, *ibid.*, **86**, 5511 (1964).

(18) K. M. Harmon, *et al.*, *ibid.*, **87**, 1700 (1965).

(19) K. C. D. Hickman, *Chem. Rev.*, **34**, 51 (1944).

(20) Y. Ikegami, *Bull. Chem. Soc. Jap.*, **35**, 967 (1962).

(21) Carbonium ion perchlorates should be prepared only in small amounts and handled with caution; detonation can occur on shock or ignition.

(22) Quantitative ultraviolet spectral analysis in 96% sulfuric acid affords the best technique for estimating carbonium ions: K. M. Harmon and A. B. Harmon, *J. Amer. Chem. Soc.*, **83**, 865 (1961).

Hydroxytropenylium Bromide.—Tropone (0.44 g, 4.15 mmol) was dissolved in absolute ethanol (10 ml) and 48% hydrobromic acid (1.18 g, 7.0 mmol) was added. Ether was added until turbidity persisted and the reaction was chilled at −10° overnight to afford a mass of white needles. The solvent was decanted and the crystals were washed with ether, dried *in vacuo*, and sublimed (80°, 1 torr) to yield 76.1% hydroxytropenylium bromide (0.59 g, 3.16 mmol) as pale yellow prisms. These crystals turn brilliant yellow at 125° and decompose above 170°.

Anal. Calcd for C_7H_7OBr: $C_7H_6OH^+$, 57.27; Br^-, 42.72. Found: $C_7H_6OH^+$, 56.9; Br^-, 42.91.

Hydroxytropenylium Bromide Monohydrate.—A freshly sublimed portion of hydroxytropenylium bromide was dissolved in oxygen-free water; this solution was allowed to evaporate to dryness in an oxygen-free glove box in which the vapor pressure of water was maintained at about 8 torr by a saturated solution of calcium chloride hexahydrate. This process affords hydroxytropenylium monohydrate as a mass of colorless, brittle spars and plates.

Anal. Calcd for $C_7H_9O_2Br$: $C_7H_6OH^+$, 52.20; Br^-, 38.95. Found: $C_7H_6OH^+$, 52.2; Br^-, 38.80.

Hydroxytropenylium Iodide.—Tropone (0.45 g, 4.25 mmol) was dissolved under nitrogen in deoxygenated absolute ethanol (10 ml) and 47% hydriodic acid (1.18 g, 4.4 mmol) was added. Anhydrous ether (80 ml) was added to precipitate a mixture of red and yellow crystals; these were washed with three 10-ml portions of ether, dried *in vacuo*, and sublimed (55°, 1 torr) to yield 86.0% hydroxytropenylium iodide (0.855 g, 3.66 mmol) as dark red prisms, mp 151–152° (lit.[13] mp 151°).

Hydroxytropenylium Iodide Monohydrate.—This material was prepared in the same manner as hydroxytropenylium bromide monohydrate, with the additional precaution that the preparation was carried out under red light. Evaporation of solvent water yielded hydroxytropenylium iodide monohydrate as orange spars which crush to a brilliant yellow powder.

Anal. Calcd for $C_7H_9O_2I$: $C_7H_6OH^+$, 42.50; I^-, 50.75. Found: $C_7H_6OH^+$, 42.4; I^-, 50.71.

Deuterioxytropenylium Bromide.—Boron bromide (1.06 g, 4.24 mmol) was placed in a small flask connected by a gas delivery tube to a second flask containing tropone (0.2 g, 1.9 mmol) in benzene (10 ml). Deuterium oxide (2 ml) was injected slowly into the boron bromide (*caution*) at a rate which maintained vigorous bubbling of deuterium bromide into the benzene solution. When the reaction was complete, the benzene was decanted from precipitated solids; these were washed with three 5-ml portions of benzene and dried *in vacuo* to yield deuterioxytropenylium bromide as a white microcrystalline powder. The infrared spectrum of this material was identical with that of hydroxytropenylium bromide with the exception of displacement of the O–H absorption.[3] This spectrum showed the sample to be contaminated with some hydroxytropenylium ion, even though the procedure had been carried out in a carefully dried glove box; this was shown to arise from residual water which is tenaciously retained by tropone, even on vacuum drying.[7,20]

Modified Preparation of Tropone. A. Ditropenyl Ether.[23–25]—Phosphorus pentachloride (108 g, 0.52 mol) was dissolved at reflux in carbon tetrachloride (800 ml) and a solution of cycloheptatriene (20 g, 0.22 mol) in carbon tetrachloride (400 ml) was added dropwise to this refluxing, vigorously stirred solution. The mixture was refluxed for 1 hr, then cooled, and allowed to stand overnight with protection from moisture; after this time, the flask was chilled in an efficient ice bath and distilled water (500 ml) added cautiously with stirring. The water layer was separated and retained; the carbon tetrachloride layer was discarded.

A 4-l., globe-shaped separatory funnel (Corning 6340) was clamped horizontally with the deep part in an ice bath on a magnetic stirrer; the neck of the funnel was fitted with a gas dispersion tube and a 60° funnel, both bent so as to reach the deepest part of the globe. A solution of 20% sodium hydroxide (500 g) was added and was deoxygenated by a stream of nitrogen; then the aqueous extract of tropenylium ion from the phosphorus pentachloride reaction was added slowly through the 60° funnel to the stirred, chilled base solution with continued bubbling of nitrogen. When addition was complete, the separatory funnel contained a snow-white emulsion of ditropenyl ether; this was extracted with three 200-ml portions of deoxygenated methylene chloride; magnesium sulfate was added to dry the methylene chloride extract; and this was again deoxygenated with a stream of nitrogen to remove air entrapped in the sulfate powder. The methylene chloride solution was brought to volume and an aliquot was extracted with 50% sulfuric acid; spectral analysis[16] of the acid extract showed the yield to be 77.8% ditropenyl ether (16.7 g, 0.084 mol) with a trace (less than 1%) of tropone.

B. Tropone and Cycloheptatriene.—The methylene chloride solution from the above preparation was placed over Linde 4A molecular sieve ($^1/_{16}$-in. pellets) and bubbled with nitrogen to remove air entrapped in the sieve. The flask was tightly stoppered, wrapped in foil, and stored in the refrigerator for 8 weeks. An aliquot was withdrawn and extracted with 50% sulfuric acid; spectral analysis[16] of this extract showed a yield of 97.5% tropone (8.69 g, 0.082 mol). Spectral analysis[16] of the methylene chloride remaining after acid extraction showed a yield of 97.2% cycloheptatriene (7.50 g, 0.0815 mol).

C. Hydroxytropenylium Ion Salts.—A portion of a methylene chloride solution prepared as above (100 ml) containing tropone (0.737 g, 6.9 mmol) and cycloheptatriene was concentrated to a volume of 20 ml, and hydrogen bromide passed over the surface of the stirred solution until precipitation ceased. Cyclohexane (50 ml) was added, the combined solvents were decanted, and the solid was washed with cyclohexane (50 ml) and dried *in vacuo* to yield 99.3% hydroxytropenylium bromide (1.28 g, 6.83 mmol) as a yellow powder.

Anal. Found: $C_7H_6OH^+$, 57.3.

A similar portion of the methylene chloride solution was concentrated at the rotary evaporator and the material not volatile at room temperature was taken up in deoxygenated absolute ethanol (15 ml) and 48% hydriodic acid (1.1 ml) was added. Dry ether (500 ml) was added and the mixed precipitate of red and yellow crystals was dried *in vacuo* to yield 67% hydroxytropenylium iodide (0.99 g, 4.2 mmol) as red crystals, mp 151°.

Registry No.—Hydroxytropenylium perchlorate, 16273-43-1; hydroxytropenylium chloride, 16273-44-2; hydroxytropenylium bromide, 16273-45-3; hydroxytropenylium iodide, 16273-46-4; ditropenyl ether, 16273-47-5; tropone, 539-80-0.

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[23] The preparation of tropenylium hexachlorophosphate is adapted from Kursanov,[24] and that of ditropenyl ether is adapted from Doering and Knox.[25] The specific procedures reported herein are designed to prevent losses from transfer operations, and discoloration and contamination from facile air oxidation.

[24] D. N. Kursanov and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, **113**, 339 (1957).

[25] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).

Lithium Aluminum Hydride Reduction of Benzoyldiferrocenylphenylmethane[1]

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In connection with our synthesis work on the diketone (**1**) we were led to investigate the products of Clemmensen reductions of several ferrocenyl ketones (**2**) including benzoylferrocene (**2**, R = Ph). We established that products corresponding to **5** and **6** were formed along with the previously recognized products corresponding to **3** and **4**. Isolation of the former pair raised intriguing questions as to their mode of formation, and we have continued investigations into

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[1] Presented at the 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, Abstracts, p 308.