methanol, gave a crystalline precipitate which was collected and recrystallized from water–methanol (yields: 6 hr, 6 mg; 12 hr, 30 mg; 24 hr, 130 mg), mp 240–250° dec (diaminocarboxylic acid sulfate of biotin lit.[5] mp 245–255°). The infrared spectra were completely identical with that of an authentic sample of diaminocarboxylic acid sulfate of biotin.

Anal. Calcd for $C_9H_{20}N_2O_6S_2$: C, 34.16; H, 6.37; N, 8.85; S, 20.27. Found: C, 34.29; H, 6.47; N, 8.69; S, 20.21.

In a similar way, fractions 90–105 of the 6-hr experiment were applied to a Dowex-50 column and eluted with 1 *M* NH_4OH, the solvent was evaporated, and the product was recrystallized from water. A product (30 mg) melting at 228–230° was obtained (biotin lit.[10] mp 230–232°). The infrared spectrum of this product was identical with that of an authentic sample of biotin.

Biotin.—Carboxyl-^{14}C-biotin (200 mg, 0.01 μcurie/mg) in 4 ml of 2 *N* HCl was refluxed for 12 hr under N_2. The material was treated further as given for hydrolysis of biotin *d*-sulfoxide. The elution pattern of the Dowex-1 column showed that less than 1% of the biotin was hydrolyzed to its diaminocarboxylic acid.

Biotin Sulfone.—Carboxyl-^{14}C-biotin sulfone (80 mg, 0.01 μcurie/mg) in 4 ml of 2 *N* HCl was refluxed under N_2 for 12 hr. The solvent was evaporated and the remaining material was recrystallized from water. Biotin sulfone (71 mg) of unchanged melting point was recovered.

Registry No.—Biotin, 58-85-5; biotin sulfone, 786-79-8; biotin *d*-sulfoxide, 10406-89-0; biotin *l*-sulfoxide, 10406-90-3; diaminocarboxylic acid sulfate of biotin, 10349-21-0.

[10] V. du Vigneaud, K. Hofmann, D. B. Melville, and J. R. Rachele, *J. Biol. Chem.*, **141**, 763 (1941).

The Iodine–Cycloheptatriene System[1,2]

Kenneth M. Harmon, Ann B. Harmon,
Sharon Davis Alderman, Peter A. Gebauer,
and Lee-Louise Hesse

*Department of Chemistry, Harvey Mudd College,
Claremont, California 91711*

Received November 22, 1966

Oxidation of cycloheptatriene with iodine in ether solvent affords excellent yields of tropenium salts; iodine alone gives tropenium triiodide of high purity; and if mercuric iodide is also present tropenium triiodomercurate or pentaiododimercurate salts are obtained.

Dauben and Harmon[3] have reported the preparation of a tropenium triiodomercurate[4] by reaction of *t*-butyl iodide, mercuric iodide, and cycloheptatriene in ether. They proposed a mechanism involving ionization of *t*-butyl iodide by mercuric iodide, followed by hydride transfer from cycloheptatriene to the trimethylcarbonium ion so formed, but were unable to isolate isobutane from the reaction. We now find that this reaction is not an ionization–hydride transfer process, but proceeds *via* oxidation of cycloheptatriene by iodine produced by photochemical decomposition of *t*-butyl iodide. Mixtures of *t*-butyl iodide, mercuric iodide, and cycloheptatriene react to a very limited extent in the dark, but reaction proceeds quantitatively when the solution is exposed to sunlight. A series of controlled-atmosphere experiments confirms that no appreciable reaction occurs in the absence of light or oxygen, and that light is the more potent catalyst (Table I).

TABLE I

REACTIONS OF CYCLOHEPTATRIENE WITH *t*-BUTYL IODIDE AND MERCURIC IODIDE IN ETHER UNDER CONTROLLED CONDITIONS[a]

Reaction	Light	Oxygen	Water	% yield of $C_7H_7^+$
1	0	0	0	0.39
2	Trace	0	0	1.04
3	0	+	0	1.63
4	+	0	0	5.50
5	+	+	0	17.5[b]

[a] Identical concentrations, temperature, and times. [b] Yield (5)/yield (1) = 45.

We have recently found that tropenium ion is reduced to cycloheptatriene by hydrogen iodide in nonpolar solvents[5] with concurrent formation of iodine; this reduction was unexpected in light of the oxidations noted above. These conflicting observations are in accord with the existence of a mobile oxidation–reduction equilibrium (eq a). In ether solvent the reaction

$$C_7H_8 + I_2 = C_7H_7^+ + I^- + HI \qquad \text{(a)}$$

would normally be shifted to the right by formation of insoluble tropenium salts; however, treatment of tropenium ion with excess hydrogen iodide would drive the reaction to the left by mass action. In contrast to tropenium ion, hydroxytropenium ion is not reduced by hydrogen iodide; presumably resonance interaction of nonbonding oxygen electrons with the π system of the ring lends sufficient stabilization to prevent such reduction.

In a solvent where tropenium salts are soluble, the equilibrium should be directly observed. In methylene chloride solution the reaction between iodine and cycloheptatriene proceeds rapidly to produce a limited amount of tropenium ion; after this time no further change occurs. The reaction is more complex in methylene chloride than is represented by eq a, since an additional, colorless, iodine-containing species is also present (see the Experimental Section). The nature of this species is not known at this time; one possibility is a diene–diiodide similar to the diene–dibromide which occurs as an intermediate in the oxidation of cycloheptatriene by bromine.[7,8] Whatever the nature of this colorless compound, its formation does not irreversibly remove cycloheptatriene from the reaction system, since addition of mercuric iodide to methylene chloride solutions of cycloheptatriene and iodine greatly increases the yield of tropenium ion by formation of insoluble, complex mercuric iodide salts.

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[1] Work supported by the Petroleum Research Fund and the National Science Foundation.

[2] Reported in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 9, 1964.

[3] (a) H. J. Dauben, Jr., and K. M. Harmon, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 8, 1958, Abstracts, p 35P; (b) Ph.D. Thesis of K. M. H., University of Washington, 1958; *Dissertation Abstr.*, **19**, 1563 (1959).

[4] This material was a less stable, lower melting (157°) crystal modification of that reported herein; on long standing it slowly changed to the higher melting form.

[5] Hydrogen iodide does not reduce tropenium ion in sulfuric acid, in accord with the conclusion of Deno[6] that in this solvent hydrogen iodide only reduces carbonium ions with a pK_{R+} less than -5; pK_{R+} for tropenium ion is 4.75.

[6] N. C. Deno, *et al.*, *J. Am. Chem. Soc.*, **84**, 4713 (1962).

[7] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954); **79**, 352 (1957).

[8] H. J. Dauben, Jr., and D. L. Pearson, unpublished work in Ph.D. Thesis of D. L. P., University of Washington, 1955; *Dissertation Abstr.*, **15**, 978 (1955).

Experimental Section

Purification and treatment of methylene chloride and cycloheptatriene have been described.[9] Baker and Adamson reagent grade anhydrous ether was stored over sodium wire in brown bottles and transferred by siphon or pipet. Baker and Adamson reagent grade 96% sulfuric acid, mercuric iodide, and iodine, and Matheson anhydrous hydrogen iodide were used without further treatment. Spectra were recorded on the Cary Model 13 spectrophotometer; melting points were determined on a Fisher-Johns block, and are corrected. The oxygen-free glove box and the methods of freeing glassware and solvents from oxygen have been described.[10] Solid reagents were freed of oxygen when indicated by pumping followed by exposure to the glove box atmosphere.

Reaction of Cycloheptatriene with Iodine in Ether.—Cycloheptatriene (1.17 g, 10.6 mmoles) was added to a solution of iodine (0.28 g, 1.10 mmoles) in ether (400 ml). Red needles formed slowly from a clear solution. After 10 days the solvent was decanted and the crystals were washed with ether (two 50-ml portions) and dried *in vacuo* to yield 77.2% tropenium triiodide (0.20 g, 0.425 mmole) as deep red single needles, mp 134°.[11] *Anal.* Calcd for $C_7H_7I_3$: $C_7H_7^+$, 19.31; Found: $C_7H_7^+$, 19.4.

Reaction of Cycloheptatriene and Iodine with Mercuric Iodide in Ether.—Cycloheptatriene (0.027 g, 0.26 mmole) and iodine (0.060 g, 0.24 mmole) were added to a solution of mercuric iodide (0.20 g, 0.44 mmole) in ether (100 ml). After 14 days the light blue mother liquor was decanted from a mass of yellow needles; these were washed with ether (two 25-ml portions) and dried *in vacuo* to yield 91.4% tropenium pentaiododimercurate[14] (0.226 g, 0.201 mmole) as yellow needles, mp 151°. *Anal.* Calcd for $C_7H_7Hg_2I_5$: C, 7.46; H, 0.63; I, 56.31; $C_7H_7^+$, 8.09. Found: C, 7.50; H, 1.08; I, 56.90; $C_7H_7^+$, 8.05.

Reaction of Cycloheptatriene with *t*-Butyl Iodide and Mercuric Iodide in Ether.—Cycloheptatriene (0.36 g, 3.5 mmoles) and *t*-butyl iodide (0.78 g, 4.2 mmoles) were added to a solution of mercuric iodide (1.00 g, 2.20 mmoles) in ether (500 ml). The flask was wrapped with foil, and showed only a trace of precipitate formation in 3 days. The flask was then allowed to stand in diffuse sunlight for 7 days; considerable reaction occurred during this time. The solvent was decanted and the yellow-orange precipitate was washed with ether (two 50-ml portions) and dried *in vacuo* to yield 98.8% tropenium triiodomercurate (1.46 g, 2.17 mmoles) as an orange powder, mp 165–167°, *Anal.* Calcd for $C_7H_7HgI_3$: C, 12.50; H, 1.05; I, 56.61; $C_7H_7^+$, 13.55. Found: C, 12.72; H, 1.06; I, 56.10; $C_7H_7^+$, 13.7. This material recrystallized from acetonitrile to give a mixture of orange plates and yellow needles; both crystal forms melted sharply at 167°. *Anal.* Found: $C_7H_7^+$, 13.3 (orange), 13.9 (yellow).

Reaction of Cycloheptatriene with *t*-Butyl Iodide and Mercuric Iodide under Controlled Conditions.[17]—Five identical reaction mixtures were prepared, each containing a solution of cycloheptatriene (0.0225 g, 0.220 mmole), *t*-butyl iodide (0.0472 g, 0.256 mmole), and mercuric iodide (0.100, 0.220 mmole) in ether (50 ml). Each flask was treated as indicated, allowed to stand for 10 days, then worked up by decantation, washing the product with ether, drying, and spectral analysis. Results were as follows—(a) treatment, (b) appearance of product, (c) mg of $C_7H_7^+$, (d) μmoles of $C_7H_7^+$, (e) per cent yield of $C_7H_7^+$: (1) (a) stored in glove box in the dark, (b) film on flask, (c) 0.078, (d) 0.862, (e) 0.39;[18] (2) (a) stored in glove box with exposure to diffuse artificial light through thick glass, (b) red microcrystals, (c) 0.209, (d) 2.30, (e) 1.04; (3) (a) saturated with oxygen and stored in dark, (b) red crystals, (c) 0.326, (d) 3.58, (e) 1.63; (4) (a) oxygen-free, exposed to diffuse sunlight, (b) yellow needles, (c) 1.10, (d) 12.1, (e) 5.50; (5) exposed to air, then in diffuse sunlight, (b) orange plates and yellow needles, (c) 3.50, (d) 38.5, (e) 17.5.

Reaction of Tropenium Iodide with Hydrogen Iodide in Methylene Chloride.[17]—Tropenium iodide[7] (0.27 g, 1.24 mmoles) was covered with methylene chloride (70 ml) and the mixture was stirred for 1 hr to effect saturation. Hydrogen iodide was then passed over the stirred solution; the bright blue charge-transfer color[9] of the tropenium iodide solution was rapidly replaced by the red color of iodine, and the scarlet tropenium iodide crystals dissolved with concurrent formation of black dendroidal crystals. The methylene chloride was decanted, extracted with distilled water (three 70-ml portions), and rendered colorless by contact with mercury. Spectral analysis[9] showed this solution to contain a 49.6% yield of cycloheptatriene (0.0568 g, 0.616 mmole), λ_{max} 263.5 mμ. The black polyiodide precipitate was shown by spectral analysis to contain 38.4% of the original tropenium ion (0.0428 g, 0.472 mmole).

Reaction of Tropone with Hydrogen Iodide in Methylene Chloride.[17]—Methylene chloride (20 ml) was saturated with hydrogen iodide; then tropone[19] (0.58 g, 5.46 mmoles) dissolved in methylene chloride (5 ml) was injected under the surface of the stirred solution with continued passage of hydrogen iodide. Red crystals formed at once; the mother liquor was decanted and the solid was washed with methylene chloride (two 5-ml portions) and cyclohexane (one 5-ml portion) and dried *in vacuo* to yield 73.5% hydroxytropenium iodide (0.94 g, 4.01 mmoles) as brilliant red needles, mp 151°. *Anal.* Calcd for C_7H_7IO: I, 54.23; $C_7H_6OH^+$; 45.77. Found: I, 54.24; $C_7H_6OH^+$, 45.9.

Reaction of Cycloheptatriene with Iodine in Methylene Chloride.[17]—Cycloheptatriene (0.35 g, 3.42 mmoles) was added to a solution of iodine (0.20 g, 0.787 mmole) in methylene chloride (225 ml). The deep red solution became significantly lighter[20] in a short time; no further observable change occurred. After 10 days the solution was washed with dilute sulfuric acid; spectral analysis of the acid solution showed the presence of a 6.35% yield of tropenium ion (0.0198 g, 0.217 mmole). The mother liquor was shaken with mercury to discharge the color of iodine, dried over Linde 4 A molecular sieve, and concentrated *in vacuo* to leave a colorless, mobile oil. This oil showed λ_{max} 258 mμ in methylene chloride, ethanol, or pentane, with a shoulder at 308 mμ. It gave an instantaneous precipitate with alcoholic silver nitrate, and on exposure to the air polymerized with liberation of molecular iodine.

A reaction solution was prepared as above containing cycloheptatriene (0.045 g, 0.44 mmole) and iodine (0.14 g, 0.53 mmole) in methylene chloride (50 ml). When mercuric iodide (0.20 g, 0.44 mmole) was added a precipitate of orange crystals began to form. When reaction appeared to have ceased (3 days) the solvent was decanted and the crystals were washed with methylene chloride (three 10-ml portions) and dried *in vacuo* to yield 64.5% tropenium triiodomercurate (0.1909 g, 0.284 mmole) as an orange powder, mp 168°. *Anal.* Found: $C_7H_7^+$, 13.9.

Registry No.—Cycloheptatriene, 544-25-2.

Acknowledgment.—We wish to thank Professor H. J. Dauben, Jr., for encouragement in the early stages of this work.

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(9) K. M. Harmon, *et al.*, *J. Am. Chem. Soc.*, **84**, 3349 (1962).

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

(11) The melting point of the triiode has been reported as 127°[12] and 132–133°.[13] We find that traces of excess iodine render the salt black and lower the melting point.

(12) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(13) D. H. Reid, *et al.*, *Tetrahedron Letters*, 530 (1961).

(14) Salts of this ion, for example pyridinium pentaiododimercurate,[15] have been reported; more recently the dissociation constant has been measured in acetonitrile.[16]

(15) M. Francois, *Compt. Rend.*, **140**, 862 (1905).

(16) K. Ellendt and G. Cruse, *Z. Phys. Chem.*, **201**, 130 (1962).

(17) Oxygen-free conditions under red light except as noted.

(18) The decanted reaction mixture did not produce any additional tropenium ion after 10 additional days.

(19) T. Ikemi, T. Nozoe, and H. Sugiyama, *Chem. Ind.* (London), 962 (1960).

(20) Since only about 20% of the original iodine would have been removed as I_3^- or HI_3, the solution should have remained a deep red; the residual color was much too light to account for as unreacted iodine.

A Selective Reduction Using Tris(triphenylphosphine)chlororhodium(I)

MORRIS BROWN AND LEONARD W. PISZKIEWICZ

Contribution No. 3460 from Gates and Crellin Laboratories, California Institute of Technology, Pasadena, California 91109

Received January 12, 1967

In the course of some synthetic studies on eremophilone (I), we needed the 13,14-dihydro derivative