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.

---

(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

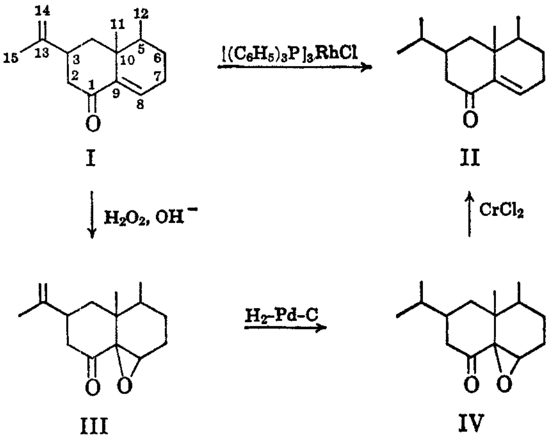
Received January 12, 1967

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

(II). Attempted selective hydrogenation of eremophilone (I) with palladium on a variety of supports and in various solvents all led to the same result, namely, more rapid reduction of the conjugated double bond.

Bromination and dehydrobromination of tetrahydroeremophilone gave mixtures of compounds. Reduction of eremophilone (I) with diborane was also attempted, but again without success. The three-step procedure (I → III → IV → II) was then devised and found to proceed satisfactorily in 63% over-all yield (see Scheme I).

SCHEME I



Subsequently, we tried direct reduction of eremophilone using the new, homogenous hydrogenation catalyst, tris(triphenylphosphine)chlororhodium(I).[1] The hydrogenation proceeded very well using this catalyst and in this manner dihydroeremophilone was obtained in 94% yield. We have also looked at the reduction of other compounds, and in general we find that a terminal double bond can be selectively reduced in the presence of other more substituted double bonds.[2,3]

Experimental Section

Melting points were determined on a Kofler micro hot stage and are corrected. The infrared spectra were determined on a Perkin-Elmer Infracord, Model 137, and nmr spectra were obtained with a Varian A-60 spectrometer on solutions in carbon tetrachloride.

Eremophilone oxide (III) was prepared by the published procedure[4] in 78% yield: mp 60–61° (lit.[1] mp 63–64°); $\lambda_{max}^{CHCl_3}$ 5.82, 11.18 μ; nmr δ 2.83 m (epoxy-ring hydrogen), 4.75 ($>C{=}CH_2$).

Dihydroeremophilone Oxide (IV).—A solution of 2.16 g of eremophilone oxide (III) was hydrogenated over 0.050 g of 5% palladium on carbon. Removal of the catalyst and evaporation of the solvent afforded the product 2.08 g (95% yield): mp 50–51° (lit.[1] mp 53–54°), $\lambda_{max}^{CHCl_3}$ 5.82 μ, nmr δ 2.80 m (epoxy-ring hydrogen).

13,14-Dihydroeremophilone (II).—A solution of 2.0 g of dihydroeremophilone oxide (III) in 40 ml of acetic acid was stirred at room temperature under nitrogen while 60 ml of 0.5 *M* chromous chloride[5] was added. After stirring for 2.5 hr the solution was then poured into water and isolated in the usual manner by extraction with methylene chloride. Distillation afforded 1.65 g (85% yield) of dihydroeremophilone (II): bp 100° (1 mm); n^{25}D 1.5015; $[\alpha]$D −175° (*c* 0.411, methanol); λ_{max}^{film} 5.92 μ (conjugated C=O), 6.16 (conjugated C=C); λ_{max}^{EtOH} 242 mμ (ϵ 6500); mass spectrum *m/e* 220 (M^+), 205, 178 (base peak), 153, 149, 135, 121, 109, 107.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.69; H, 11.08.

Dihydroeremophilone (II) by Direct Reduction.—A solution of 0.102 g of eremophilone and 0.070 g of tris(triphenylphosphine)-chlororhodium(I)[5] in 15 ml of benzene was stirred under an atmosphere of hydrogen for 8 hr. The solution was then passed through an alumina column (3 g), which, on evaporation of the solvent and distillation, afforded 0.097 g (94% yield) of pure 13,14-dihydroeremophilone (II).

Registry No.—II, 10316-33-3; III, 10316-34-4; IV, 10316-35-5.

Acknowledgment.—The authors appreciate greatly support by a grant from the Eli Lilly Foundation.

---

(1) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Comm.*, **131** (1965).

(2) M. Brown, unpublished results.

(3) For other reductions using this catalyst, see C. Djerassi and J. Gutzwiller, *J. Am. Chem. Soc.*, **88**, 4538 (1966); A. J. Birch and K. A. M. Walker, *Tetrahedron Letters*, 4939 (1966).

(4) A. E. Bradfield, A. R. Penfold, and J. L. Simonsen, *J. Chem. Soc.*, 2749 (1932). The eremophilone was isolated from the wood oil of *Eremophilia mitchelli*. The oil was kindly supplied by the Museum of Applied Arts and Sciences, Sydney, Australia.

(5) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *J. Am. Chem. Soc.*, **72**, 4077 (1950).

Preparation of Alkoxysulfonium Salts by Oxidation of Sulfides with Positive Halogen Compounds[1,2a]

CARL R. JOHNSON[2b] AND MICHAEL P. JONES

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received December 27, 1966

The first and most widely investigated method of preparation of alkoxysulfonium salts consists of O alkylation of the respective sulfoxides (synthesis of the oxygen–carbon bond).[3] Synthesis of the sulfur–oxygen bond, on the other hand, has received little attention. Only the reaction of dimethylchlorosulfonium salts with ethanol, propyl alcohol, and isopropyl alcohol to give the respective alkoxysulfonium salts have been reported.[4] However, *t*-butoxysulfonium chlorides have been postulated as unstable intermediates in the oxidation of sulfides to sulfoxides with *t*-butyl hypochlorite.[5]

The obvious convenience of a method for the preparation of alkoxysulfonium salts directly from sulfides prompted an investigation of the alkyl hypochlorite and related oxidations of sulfides in an attempt to isolate and characterize the intermediate salt.[6]

A variety of sulfides was oxidized with equimolar amounts of either *t*-butyl or isopropyl hypochlorite in methylene chloride at −78°. The initial alkoxysul-

---

(1) (a) Part VI in the series, Chemistry of Sulfoxides. (b) Part V: C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 5404 (1965).

(2) (a) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-5944); (b) Alfred P. Sloan Research Fellow, 1965–1968.

(3) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939); S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958); S. Kabuss, *Angew. Chem., Intern. Ed. Engl.*, **5**, 675 (1966).

(4) H. Meerwein, K. Zenner, and R. Gipp, *Ann.*, **688**, 67 (1965).

(5) P. Skell and M. F. Epstein, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Abstracts, p 26N.

(6) In a recent communication, K. Torssell [*Tetrahedron Letters*, 4445 (1966)] has indicated that "In connection with work on positive halogen compounds new routes to alkoxydimethylsulfonium salts were developed." No additional details were given.