collected. All fractions were weighed and analyzed by thin layer chromatography, pmr spectra, and ir spectra. All the above products except **3** were isolated and their structures characterized by pmr and ir spectra, melting points, and carbon–hydrogen analyses.

Outside the aromatic region, the pmr spectra show (a) for **1** a singlet (2 H) at τ 5.14, (b) for **2** ($v_{C=C}$ at 1600 cm^{-1}) a singlet (2 H) at τ 5.03, (c) for **3** two singlets (1 H each) at τ 5.43 and 4.61, (d) for **4** two singlets (1 H each) at τ 5.44 and 4.31, (e) for **5** a singlet (1 H) at τ 5.44 and a pair of doublets (1 H each, J_{gem} = 16.5 Hz) at τ 6.67 and 6.18.

Anal. Calcd for C$_{16}$H$_{10}$Cl$_4$ (**1**): C, 55.85; H, 2.93. Found: C, 55.58; H, 3.03. Calcd for C$_{16}$H$_{10}$Cl$_4$ (**3**): C, 55.85; H, 2.93. Found: C, 55.87; H, 3.09. Calcd for C$_{16}$H$_{10}$Cl$_4$ (**4**): C, 55.85; H, 2.93. Found: C, 55.83; H, 3.05. Calcd for C$_{16}$H$_{11}$Cl$_3$ (**5**): C, 62.07; H, 3.58. Found: C, 62.09; H, 3.65.

A similar reaction of anthracene with tetrachloroethylene in a sealed tube at 210° for 2 days gave large amounts of recovered anthracene (*ca.* 80% recovery). Anthracene was separated from the crude reaction mixture (*via* crystallization and the formation of the maleic anhydride adduct of anthracene), and a pmr spectrum of the resulting mixture showed the presence of **1** with only trace amounts of other products. Chromatography over alumina gave **1** in *ca.* 5% yield.

Preparation of 3 and 4.—Dry chlorine gas was bubbled into a stirred solution of 10.0 g (36.6 mmol) of **2** in 50 ml of nitromethane until saturation was achieved. The reaction vessel was stoppered and wrapped in aluminum foil to prevent photoinitiated reactions from taking place. The reaction progress was followed by the disappearance of the double-bond absorption (1600-cm^{-1} band) in the ir spectrum. After standing at room temperature for 1 day, a 50:50 mixture (by pmr spectroscopy) of the two epimers **3** and **4** resulted. The crude product, 7.5 g of oil, was crystallized from ethanol to give 2.0 g (16% yield) of each epimer. The low yield was due to the difficulty involved in separating the two epimers. The epimers could also be separated by chromatography over silica gel (**4** is eluted first with 5% benzene in Skellysolve B).

Photochlorination of 2 to Give 1.—Dry chlorine gas was bubbled through a solution of 1.0 g (3.36 mmol) of **2** in 20 ml of carbon tetrachloride until the solution turned deep green. The reaction vessel was stoppered and set in the presence of a sun lamp for 5 hr, after which time the double bond absorption at the 1600-cm^{-1} band in the ir spectrum had disappeared. The carbon tetrachloride was removed by rotary evaporation and the remaining oil crystallized from Skellysolve B to give 1.1 g (87% yield) of **1**, mp 204–205°.

Preparation of 5.—The reaction vessel containing 3.0 g (8.7 mmol) of a 50:50 mixture of **3** and **4** in 50 ml of ethanol was placed in a Parr bomb hydrogenation apparatus and flushed several times with hydrogen gas. The mixture was allowed to react for 2.5 days at 40-psi hydrogen gas pressure. The catalyst was removed by filtration, and the ethanol was removed by rotatary evaporation to give an oil which was crystallized from methanol to give 1.0 g (35%) of 5,8,8-trichlorodibenzobicyclo-[3.2.1]octadiene (**5**), mp 124–125°.

Treatment of 1 and 3 and 4, under Diels–Alder Reaction Conditions.—In 0.5-in. medium-walled glass tubes were sealed (a) 0.35 g of **1**, (b) 0.38 g of **1** and 0.51 g of anthracene, (c) 0.43 g of a mixture of **3** (90%) and **4** (10%) and 0.25 g of 9,10-dihydroanthracene, and (d) 0.31 g of **1** and 0.28 g of 9,10-dihydroanthracene. These tubes were heated at 230° in a silicon oil bath for 1 day. The tubes were opened, and pmr spectra were taken of the resulting dark colored mixtures.

(a) The pmr spectrum showed **1** and **4** present in the ratio of 2:1, respectively. A trace of **3** also was discernible in the pmr spectrum. Isolation by chromatography gave 0.19 g (54%) of recovered **1** and 0.10 g (29%) of **4**.

(b) The pmr spectrum indicated the presence of **1**, **4**, and **5** but in admixture with a number of unidentifiable compounds. This mixture was worked up by chromatography over silica gel. The fractions containing anthracene were combined and analyzed by glpc [5-ft column with 20% SE-30 on Chromosorb W (60–80 mesh) at 200°]. The peak that corresponded to 9-chloroanthracene (ratio of anthracene to 9-chloroanthracene was *ca.* 20:1) was collected and shown to be 9-chloroanthracene by ir and mixture melting point with an authentic sample of 9-chloroanthracene.[14]

(14) D. C. Nonhebel, *J. Chem. Soc.*, 1216 (1963).

(c) The pmr spectrum showed only anthracene and **5** present. These were separated by chromatography over silica gel to give 0.25 g (65%) of **5**.

(d) The pmr spectrum was similar to that of reaction b. No attempt was made to isolate the products.

Reduction of 1 with Tri-*n*-butyltin Hydride (Dilute Conditions). —To a solution of 0.5 g (1.45 mmol) of **1** in 50 ml of dry benzene at reflux was slowly added (under nitrogen) a solution of 0.411 g (1.42 mmol) of tri-*n*-butyltin hydride and 40 mg of benzoyl peroxide dissolved in 30 ml of dry benzene. Reflux was maintained for 14 hr. A pmr spectrum was taken which indicated the presence of **1** (10%), **6** (32%), **2** (*ca.* 1%), **7**[15] (15%), and **5** (42%). The solvent was removed and the oil placed on a chromatography column containing 25 g of Fischer absorption alumina. The column was eluted with 3% benzene–97% Skellysolve B. Partial separation was achieved by this method. First off the column was a mixture of **2** and **5** followed by **2** and then a second mixture of **1** and **6**. The fractions collected were analyzed by thin layer chromatography and pmr spectroscopy.

Reduction of 1 with Tri-*n*-butyltin Hydride (Concentrated Conditions).—A solution of 30 ml of dry benzene, 0.50 g (1.45 mmol) of **1**, 0.67 g (2.3 mmol) of *n*-BuSnH, and 40 mg of benzoyl peroxide were held at reflux (under nitrogen). After 11 hr at reflux the solution was concentrated, and a pmr spectrum indicated the presence of *n*-Bu$_3$SnCl and a mixture of **6**[1] (80%) and **7**[12] (20%).

Reduction of 6 with Tri-*n*-butyltin Hydride.—Similar treatment of **6** with *n*-Bu$_3$SnH either at high or low concentrations gave **7** as the only observable product.

(15) S. J. Cristol and N. L. House, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).

Halogenation with Copper(II) Halides. Synthesis of Copper(I) Bromide–Diolefin Complexes

WILLIAM C. BAIRD, JR., AND JOHN H. SURRIDGE

Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey 07036
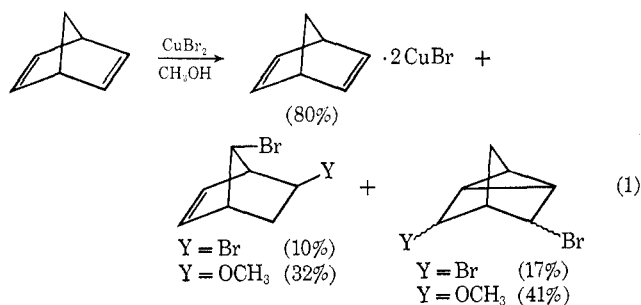
Copper(I) halide–olefin complexes have been prepared by treatment of an ethanolic solution of copper(II) halide and olefin with sulfur dioxide.[1] This technique, which is dependent upon the reduction of copper(II) to copper(I) by sulfur dioxide, has been utilized for the preparation of both copper(I) chloride– and bromide–olefin complexes. The synthesis of two copper(I) bromide–olefin complexes has been described in which the presence of a reducing agent was not required. The addition of norbornadiene[2] or *cis,trans*-cyclodeca-1,5-diene[1c] to a solution of copper(II) bromide dihydrate in ethanol led directly to the formation and precipitation of the corresponding copper(I) bromide complexes. While it was apparent that a redox reac-

(1) (a) H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963); (b) J. H. van den Hende and W. C. Baird, Jr., *J. Amer. Chem. Soc.*, **85**, 1009 (1963); (c) J. C. Trebellas, J. R. Olechowski, and H. B. Jonassen, *Inorg. Chem.*, **4**, 1818 (1965).
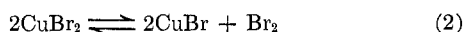
(2) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

tion between copper(II) bromide and olefin was occurring, the nature of the olefin oxidation product was not defined.

A reexamination of these complex forming reactions has revealed that the reaction involved copper(II) bromide bromination of these diolefins to yield dibromo- and bromoalkoxy alkenes. The copper(I) bromide released during the bromination subsequently coordinated with diolefin and separated as the stable copper(I) bromide–diolefin complex. Equation 1 illustrates the reaction utilizing norbornadiene; a similar result was obtained with *cis,cis*-cycloocta-1,5-diene.

reaction was driven to completion by the removal of the equilibrium concentration of bromine by the unsaturated substrate.

Since the reactions of norbornadiene and cyclooctadiene occurred rapidly at room temperature, it may be argued that in these cases the dissociation of the copper(II) salt (eq 2) is promoted by the removal of copper(I) bromide *via* stable complex formation with olefin. It has been observed, however, that simple monoolefins are also readily brominated *at room temperature* by methanolic copper(II) bromide. Even though the copper(I) halide complexes of these olefins are relatively labile under these conditions,[5] the consumption of both copper(I) bromide and bromine by olefin provides a driving force for the reactions. In any event it is apparent that methanol–copper(II) bromide solutions contain an active brominating agent whose generation is *not dependent upon thermal treatment* and that the

While the ability of copper(II) halides to halogenate carbonyl compounds and polynuclear aromatics had been previously demonstrated,[3] the halogenation of olefinic and acetylenic bonds by these salts has been described only relatively recently.[3,4] These particular reactions involved refluxing methanolic solutions of copper(II) bromide and unsaturates for 3–100 hr; yields of brominated products ranged from 8 to 100%. A kinetic analysis of the copper(II) bromide bromination of allyl alcohol indicated that the reaction proceeded through the thermally induced dissociation of copper-(II) bromide to molecular bromine (eq 2).[3] The

$$2CuBr_2 \rightleftharpoons 2CuBr + Br_2 \qquad (2)$$

influence of copper ion coordination on the reaction is significant.

It is known that the relative stabilities of metal ion oxidation states are sensitive to complexation.[6] While in water the equilibrium of eq 2 would be completely in favor of copper(II),[7] coordinating solvents, or ligands, that tend to stabilize copper(I) relative to copper(II), would shift the equilibrium of eq 2 toward molecular bromine. With transition metals possessing large numbers of d electrons, e.g. copper(I), stabilization is favored by those unsaturated ligands capable of π bonding with the metal ion.[6] Consequently, ligands possessing such structural features as C=C, C≡N, C=O, P, etc. would be particularly effective for complexing and stabilizing copper(I) and hence promoting the dissociation of copper(II) halides. Several examples of this complexation–dissociation have been described. Bromine has been isolated from solutions of copper(II) bromide in acetonitrile, a strong ligand for the stabilization of lower valent transition metal salts.[8,9] The free halogen and tribomide ion have been detected spectrophotometrically in solutions of copper(II) bromide in a variety of coordinating organic solvents.[10] Olefins have been converted nearly quantitatively to vicinal dibromoalkanes in a few minutes at 25° by copper (II) bromide in acetonitrile and other complexing solvents.[11] In addition, styrene and butene-2 have reduced solutions of copper(II) chloride in methanol and acetonitrile at 100°.[12]

The ability of coordinated copper(II) halides to function as selective halogenating agents for simple olefinic unsaturation would appear real. The scope of these reactions has been studied; the synthetic utility and mechanistic interpretations of this chemistry will be presented in future papers.

Experimental Section

Nmr spectra were recorded on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Ir spectra were measured on a Beckman IR-5A and a Beckman IR-20 spectrophotometer. Glpc was carried out on a Perkin–Elmer 154D fractometer. Preparative glpc was performed on a Varian Aerograph Autoprep Model A-700. All reagents were obtained from commercial sources and were used as received.

Reaction of Norbornadiene with Methanolic Copper(II) Bromide.—A solution of 890 mg (4 mmol) of anhydrous copper(II) bromide in 5 ml of methyl alcohol was added with stirring at room temperature to a solution of 920 mg (10 mmol) of norbornadiene in 10 ml of methanol. A white precipitate formed immediately. The precipitate was removed by filtration, and was washed with methanol. The complex was dried over calcium chloride in a norbornadiene atmosphere; the yield of norbornadiene di[copper(I) bromide] was 600 mg (79.5%).

Anal. Calcd for $C_7H_8Cu_2Br_2$: C, 22.18; H, 2.13; Br, 42.17. Found: C, 19.59; H, 2.12; Br, 44.88. The stability of the complex is such that accurate analysis is difficult.[2]

The reaction filtrate was analyzed by glpc on a 2 m × 0.25 in. diethylene glycol succinate column at 140° and 150-ml/min helium flow and was shown to contain the following compounds: 3-bromo-5-methoxynortricyclene (11.0 min from air, 41%); *exo,syn*-5-methoxy-7-bromonorbornene-2 (13.0 min, 32%); 3,5-

(3) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **30**, 587 (1965), and references cited therein.

(4) C. E. Castro, *ibid.*, **26**, 4183 (1961).

(5) For a discussion of the formation constants and heats of formation for various copper(I)–olefin complexes, see J. M. Harvilchuck, D. A. Aikens, and R. C. Murray, Jr. *Inorg. Chem.*, **8**, 539 (1969); see also ref 1b. Copper-(II)–olefin complexes have not been described.

(6) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul Ltd., London, 1960, Chapter 6.

(7) L. Pauling, "College Chemistry," W. H. Freeman and Co., San Francisco, Calif., 1951, p 554.

(8) R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965).

(9) J. C. Barnes and D. C. Hume, *Inorg. Chem.*, **2**, 444 (1963).

(10) W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta*, **46**, 1848 (1963).

(11) W. C. Baird, Jr. unpublished results.

(12) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963).

dibromonortricyclene (22.0 min, 17%); *exo,syn*-5,7-dibromo-norbornene-2 (28.5 min, 10%).[13] The products were identified by comparison of their glpc retention times with those of authentic samples obtained by the addition of bromine to norbornadiene in carbon tetrachloride and in methanol.[14] The composition of the product mixture in the latter solvent was identical with that reported above.

Reaction of Cyclooctadiene-1,5 with Methanolic Copper(II) Bromide.—A solution of 15.0 g (0.067 mol) of copper(II) bromide in 75 ml of methanol was added dropwise at room temperature to a stirred solution of 11.0 g (0.102 mol) of cyclooctadiene-1,5 in 30 ml of methanol over a period of 30 min. A white precipitate appeared after a few minutes. The complex was separated by filtration and was washed with methanol and pentane. The complex was dried over calcium chloride in a cyclooctadiene atmosphere to give 13.3 g (80.5%) of bis[cyclooctadiene–copper(I) bromide].

Anal. Calcd for $(C_8H_{12}CuBr)_2$: C, 38.18; H, 4.81; Br, 32.76. Found: C, 38.26; H, 5.14; Br, 33.70.

The complex is identical in structure with that of the corresponding copper(I) chloride complex.[1b]

The reaction filtrate was poured into 200 ml of water and extracted with *n*-pentane (three 150-ml portions). The pentane extracts were combined and dried over magnesium sulfate; the solvent was removed on a rotary evaporator to give 6.7 g of colorless oil. Analysis by glpc (1 m × 0.25 in. 5% polypropylene glycol, 150°, 110-ml/min helium flow) showed in addition to some unreacted cyclooctadiene the following mixture: 5-bromo-6-methoxycyclooctene (2.2 min, 4.6%); 5,6-dibromocyclooctene (4.4 min, 55.8%); two unidentified compounds at 7.6 min (7.2%) and 9.2 min (32.4%). A 5-g sample of the product was chromatographed over 75 g of acid-washed alumina. Elution with pentane provided a sample of 5,6-dibromocyclooctene of 95% purity (glpc).

Anal. Calcd for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.64. Found: C, 35.87; H, 4.48; Br, 59.54.

The nmr spectrum (CDCl₃) had the following pattern: δ 5.68 (m, 2, =CH), 4.67 (m, 2, BrCH), 1.83–3.00 (m, 8, CH₂). Hydrogenation of the olefinic dibromide over 10% palladium on charcoal in ethanol consumed 3 mol of hydrogen/mol of dibromide and yielded cyclooctane; this result indicated that no transannular addition reactions had occurred.

Continued elution of the column with 10% ether–pentane permitted the recovery of the two compounds of long retention time. The nmr spectrum (CDCl₃) indicated a mixture of polybrominated cyclooctanes; these materials were not characterized further. The addition of bromine to cyclooctadiene in methanol produced a product mixture similar to that previously described; the composition was 9.8% bromo ether, 31.4% dibromocyclooctene, and 59% polybrominated material.

Reaction of Cyclohexene with Methanolic Copper(II) Bromide.—A solution of 8.2 g (0.1 mol) of cyclohexene and 23.0 g (0.1 mol) of copper(II) bromide was stirred at room temperature for 1 hr. The copper(I) bromide (12.9 g, 90%) was separated by filtration, and the filtrate was poured into 100–150 ml of water. The product was extracted with pentane (three 100-ml portions), and the combined pentane extracts were washed with water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator to give 10.2 g of product. Glpc analysis (2 m × 0.25 in. 20% diethylene glycol succinate, 125°, 200-ml/min helium flow) showed the product to be a mixture of *trans*-1-bromo-2-methoxycyclohexane (4.5 min, 25%) and *trans*-1,2-dibromocyclohexane (9.0 min, 75%). Samples of the individual compounds (>95% pure by glpc) were obtained by preparative glpc (12 ft × ³/₈ in. 20% FFAP[15] column, 175°, 120-ml/min helium flow). The *trans*-dibromide was identical with an authentic sample. The bromomethoxycyclohexane ($n^{20}D$ 1.4874; lit. $n^{20}D$ 1.4884[16]), had the following nmr pattern: δ 2.74–4.50 (m, 2, CHO, CHBr), 3.33 (s, 3, CH₃O), 0.75–2.50 (m, 8, CH₂).

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78; Br, 41.39. Found: C, 43.95; H, 7.00; Br, 41.16.

Registry No.—5,6-Dibromocyclooctene, 24165-06-8.

(13) The isomeric nortricyclene derivatives were not resolved under these glpc conditions. The reported toxicity of these materials discouraged a detailed analysis of the reaction products.

(14) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956).

(15) Varian Aerograph, Walnut Creek, Calif.

(16) S. Winstein and R. B. Henderson, *J. Amer. Chem. Soc.*, **65**, 2196 (1943).
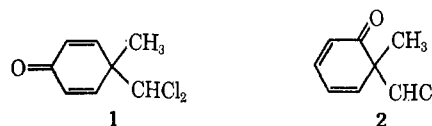
Some Transformations of 1-Methyl-1-dichloromethylcyclohexane Derivatives

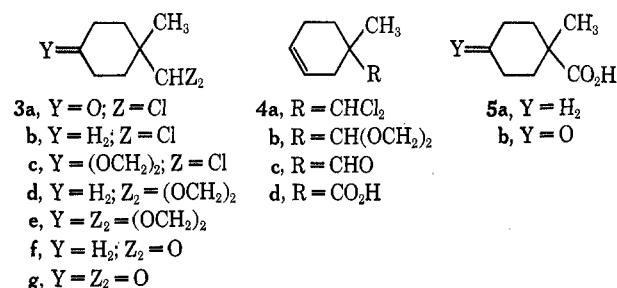ERNEST WENKERT, PETER BAKUZIS, AND FORTUNA HAVIV

Department of Chemistry, Indiana University, Bloomington, Indiana 47401

Recent studies on the chemistry of cyclohexadienones 1[1] and 2[2] yielded interesting tangential data which are presented herewith.

4-Dichloromethyl-4-methylcyclohexanone (3a), the product of hydrogenation of 1, was converted to the dichloride 3b by Wolff–Kishner reduction of its semicarbazone, to the olefin 4a by a Bamford–Stevens reduction of its tosylhydrazone, and to the ketal 3c by treatment with ethylene glycol and acid. Exposure of each of the products to sodium ethylene glycolate in ethylene glycol led to the ethylene acetals 3d, 4b, and 3e, respectively, whose acid hydrolyses gave aldehydes 3f,[3] 4c,[4] and 3g, respectively. Oxidation of these aldehydes yielded acids 5a,[3] 4d,[5] and 5b,[6] respectively.

3a, Y = O; Z = Cl
b, Y = H₂; Z = Cl
c, Y = (OCH₂)₂; Z = Cl
d, Y = H₂; Z₂ = (OCH₂)₂
e, Y = Z₂ = (OCH₂)₂
f, Y = H₂; Z₂ = O
g, Y = Z₂ = O

4a, R = CHCl₂
b, R = CH(OCH₂)₂
c, R = CHO
d, R = CO₂H

5a, Y = H₂
b, Y = O

The acetylation, a consequence of two consecutive chloride displacements or chlorocarbene formation, alcohol addition, and subsequent chloride displacement, represents a crucial step of an unusual method of construction of quaternary carboxyl functions. While the mechanism of the acetylation was not determined, the first step, proton abstraction, of one of the alternate paths, the carbene route, was shown to be operative. Under the reaction conditions the dichloride 3b underwent deuterium exchange, whereas its acetal 3b did not.

As a follow-up of a study of hydrogenation of dienone 2,[2] hydride reductions of 2 and its hydro derivatives were undertaken. The formation of a single alcohol (6) on reduction of the dienone with sodium borohydride in ethanol has been reported already.[2] Hydrogenation

(1) E. Wenkert, F. Haviv, and A. Zeitlin, *J. Amer. Chem. Soc.*, **91**, 2299 (1969).

(2) E. Wenkert, P. Bakuzis, R. J. Baumgarten, D. Doddrell, P. W. Jeffs, C. L. Leicht, R. A. Mueller, and A. Yoshikoshi, *ibid.*, **92**, 1617 (1970).

(3) W. Parker and R. A. Raphael, *J. Chem. Soc.*, 1723 (1955).

(4) H. Pines, R. J. Pavlik, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **73**, 5738 (1951).

(5) T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965), and references cited therein.

(6) M. Rubin and H. Wishinsky, *J. Amer. Chem. Soc.*, **68**, 338 (1946).