The preparation of the tetra(N,N-diethylamide) (**3**) from the tetraacyl chloride is straightforward.

### Experimental Section

Sulfur dichloride was obtained from the Hooker Chemical Co. and was distilled from 1% phosphorus trichloride into a refrigerated receiver before use. The fraction distilling at 59° was used in these experiments.

Carbon suboxide was prepared by a method similar to that of Hurd and Pilgrim[4] wherein diacetyl tartaric anhydride[5] was pyrolyzed at 650–700° in a Vycor tube. The product, collected in a Dry Ice trap, was distilled into a clean glass vial and stored at −25°. The carbon suboxide was stable for several months under these conditions, but the amount desired for an experiment was distilled (bp 5–7°) prior to use.

**1,3-Dithiacyclobutane-2,2,4,4-tetraacyl Chloride.**—Into 100 ml of ether cooled to −5° was distilled 4.2 g of carbon suboxide. To this was added 6.2 g of sulfur dichloride and the reaction flask was stoppered and stored at −20° for 24 hr. After this time, the flask contained 3.1 g (30%) of pungent, moisture-sensitive, pale orange crystals of **1**: mp 79–82°; mass spectrum (50 eV), *m/e* (relative intensity, atoms chlorine) 340 (1,4), 277 (100,3), 249 (37,3), 207 (16,1), 179 (31,1), 170 (20,2), 135 (32,1), 107 (63,1), 63 (72,1); ir (Nujol), 1790 (C=O), 1740 (C=O), 1075, 1000, 882, 825, 725 (neat), 610, 580, 520, and 482 cm$^{-1}$.

*Anal.* Calcd for $C_6Cl_4O_4S_2$: C, 21.07; H, 0.00; Cl, 41.46; S, 18.75. Found: C, 21.50; H, 0.30; Cl, 41.54; S, 18.09.

The mother liquor was concentrated under vacuum to a deep orange paste that reacted vigorously with ethanol and gave, upon concentration and recrystallization, 1.5 g of the tetraethyl ester 2 (see below). In subsequent preparations, sublimation of the deep orange paste at 50° (0.1 mm) gave additional amounts of the acyl chloride 1.

**Tetraethyl 1,3-Dithiacyclobutane-2,2,4,4-tetracarboxylate.**—Admixture of 0.25 g of the acid chloride 1 with 3 ml of ethanol resulted in a vigorous reaction and formation of a yellow solution. Upon removal of excess ethanol, 0.28 g (100%) of a crystalline material formed that was free of chlorine but contained sulfur. The crystals were dissolved in hexane, decolorized with charcoal, and recrystallized to give white prisms: mp 59.5–60°; ir (halocarbon, Nujol), 1740 (ester C=O), 1220, 1095, 1025, 858, 838, 810, 745, 710, and 652 cm$^{-1}$; nmr ($CDCl_3$), 4.30 (q, 2.0, $J$ = 7 Hz, $CH_3CH_2$—O—) and 1.28 ppm (t, 3.0, $J$ = 7 Hz, $CH_3$—$CH_2$—O—). This material was homogeneous upon tlc in three solvent systems (acetone, benzene, 40:60 ether–Skellysolve B).

*Anal.* Calcd for $C_{14}H_{20}O_8S_2$: C, 44.20; H, 5.30; S, 16.86; mol wt, 380.4. Found: C, 44.26; H, 5.68; S, 16.56; mol wt (osmometry, $CHCl_3$), 386.

**1,3-Dithiacyclobutane-2,2,4,4-tetra-(N,N-diethyl carboxamide).**—A solution of 0.5 g of the acid chloride 1 in 50 ml ether was added with stirring to a solution of 1 g of diethylamine in 50 ml of ether. A solid precipitated, and, after 15 min, the mixture was filtered and the filtrate was treated with charcoal, refiltered, and concentrated under vacuum to an orange crystalline paste. This was triturated with hexane and the residue was recrystallized from hexane–acetone (6:1) to give 0.25 g of glistening white prisms: mp 194.5–195° (turns purple at melting point); ir (halocarbon, Nujol), 1640 (amide C=O), 1270, 1220, 1145, 1082, 1070, 810, 640, and 610 cm$^{-1}$.

*Anal.* Calcd for $C_{22}H_{40}N_4O_4S_2$: C, 54.08; H, 8.25; N, 11.46; S, 13.10. Found: C, 54.37; H, 8.37; N, 11.46; S, 13.08.

In another run, 0.154 g of the orange prisms were dissolved in 5 ml of ether and diethylamine was cautiously added until the solution was basic. Diethylammonium chloride, mp 219–221°, was formed in 94% (0.186 g) yield.

**Desulfuration of the Ester.**—One teaspoonful of W. R. Grace active Raney nickel was rinsed with ethanol and suspended in 50 ml of absolute ethanol. To this was added 0.3 g of the tetraethyl ester 2, and the mixture was stirred with a spatula at room temperature for 5 min. A tlc plate (benzene) showed that none of the starting material remained; so the mixture was filtered and concentrated. The reaction product was found to have the same retention time as diethyl malonate upon gas chromatography on a nonpolar (OV-1) and polar (OV-17) column. Thin layer chromatography (Skellysolve B) showed the product to be a single component with the same $R_f$ value as diethyl malonate. In addition, the reaction product had the odor of diethyl malonate. Addition of aqueous sulfuric acid to the Raney nickel resulted in the vigorous liberation of a gas with the odor of hydrogen sulfide.

**Registry No.**—Carbon suboxide, 504-64-3; sulfur dichloride, 10545-99-0; **1**, 17255-70-8; **2**, 17239-56-4; **3**, 17255-71-9.

**Acknowledgment.**—The author thanks Mr. Arnold Bloomquist, for technical assistance; Huffman Laboratories, Wheatridge, Colo., for the elemental analyses; and Mr. Adrian Swanson of the University of Minnesota, for mass spectral determinations.

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[4] C. D. Hurd and F. D. Pilgrim, *J. Amer. Chem. Soc.*, **55**, 757 (1933).

[5] Wohl and Oesterlin, *Ber.*, **34**, 1144 (1901).

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## Free-Radical Addition of Hydrogen Bromide to 1,5-Cyclooctadiene

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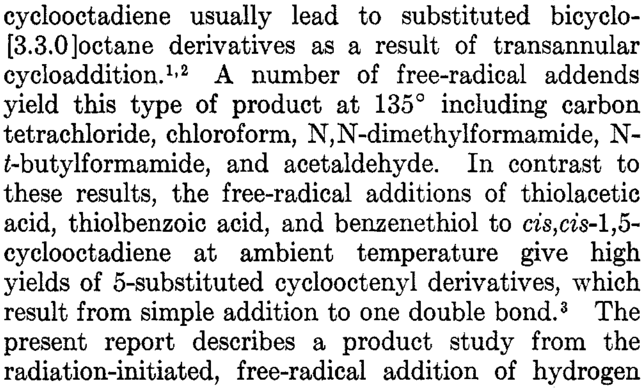
*Received April 15, 1968*

Free-radical addition reactions with *cis,cis*-1,5-cyclooctadiene usually lead to substituted bicyclo[3.3.0]octane derivatives as a result of transannular cycloaddition.[1,2] A number of free-radical addends yield this type of product at 135° including carbon tetrachloride, chloroform, N,N-dimethylformamide, N-*t*-butylformamide, and acetaldehyde. In contrast to these results, the free-radical additions of thiolacetic acid, thiolbenzoic acid, and benzenethiol to *cis,cis*-1,5-cyclooctadiene at ambient temperature give high yields of 5-substituted cyclooctenyl derivatives, which result from simple addition to one double bond.[3] The present report describes a product study from the radiation-initiated, free-radical addition of hydrogen bromide to *cis,cis*-1,5-cyclooctadiene which revealed an unexpected and striking decrease in reactivity for addition to cyclooctenyl double bonds.

**Addition of Hydrogen Bromide to 1,5-Cyclooctadiene.**—The reaction conditions and product yields are summarized in Table I. It was found that the addition of about 1 mol of hydrogen bromide/mol of cyclooctadiene at −10 to −15° gives an 88% distilled yield of 5-bromocyclooctene (I) at 100% conversion of diene. The $G$ value for product formation is high; $G$ for 5-bromocyclooctene is $6.8 \times 10^4$, which is consistent with a long kinetic length. No 2-bromobicyclo[3.3.0]octane was detected, and very little dibromocyclooctane (II) was found. The 5-bromocyclooctene



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[1] R. Dowbenko, *J. Amer. Chem. Soc.*, **86**, 946 (1964); *Tetrahedron*, **20**, 1843 (1964).

[2] L. Friedman, *J. Amer. Chem. Soc.*, **86**, 1885 (1964).

[3] J. M. Locke and E. W. Duck, *Chem. Commun.*, 151 (1965).

TABLE I

HYDROGEN BROMIDE ADDITION TO *cis,cis*-1,5-CYCLOOCTADIENE (0.12 mol) IN *n*-PENTANE[a]

| Temp, °C | Time, hr | Conversion of diolefin, % | Yield of 5-bromocyclooctene[b] | Yield of dibromocyclooctane[b] | $G_{\text{5-bromocyclooctene}}$[c] | $G_{\text{dibromocyclooctane}}$[c] |
|---|---|---|---|---|---|---|
| −15 | 0.5 | 83 | 84 | | $9.1 \times 10^4$ | |
| −10 | 0.75 | 100 | 88 | | $6.8 \times 10^4$ | |
| −18 | 1.0 | 100 | 67 | 17 | $3.9 \times 10^4$ | $1.07 \times 10^4$ |
| −18 | 1.5 | 100 | 66 | 22 | $2.7 \times 10^4$ | $9 \times 10^3$ |

[a] Dose rate, 40,600 rad/hr; HBr flow rate, 0.21 mol/hr. [b] Distilled yield based on reacted cyclooctadiene. [c] Molecules of product formed per 100 eV absorbed.

was shown to arise principally from free-radical addition. A control experiment performed in the absence of radiation initiation gave a 20% yield of 5-bromocyclooctene, probably as a result of slow ionic addition. The high selectivity to the product of monoaddition to one double bond is in agreement with the results reported for thiol addition.[3] The high selectivity for monoaddition is in marked contrast to the addition of hydrogen bromide to α,ω diolefins which normally give appreciable yields of α,ω-dibromides at moderate conversion of diolefin. If further hydrogen bromide is added to 5-bromocyclooctene, it is converted only slowly into dibromocyclooctanes (II). For example, after 1.5 hr, when *ca.* 2.5 mol of hydrogen bromide/mol of cyclooctadiene has passed into the reactor, the yield of dibromocyclooctane is only 22%; the remainder is 5-bromocyclooctene and unreacted hydrogen bromide. These data demonstrate that the absolute rate of addition of hydrogen bromide to the cyclooctenyl double bond of 5-bromocyclooctene is much slower than addition to a double bond in 1,5-cyclooctadiene.

**Competitive Addition of Hydrogen Bromide to 1,5-Cyclooctadiene and Cyclic Olefins.**—The competitive addition of hydrogen bromide to 1,5-cyclooctadiene and a number of cyclic olefins was studied in order to confirm the low reactivity of the double bond in 5-bromocyclooctene. *cis*-Cyclooctene was used as a model compound for the cyclooctenyl double bond in 5-bromocyclooctene. In general the reactivity of each unsaturate was compared with that of 1-hexene. The technique consisted of treating an accurately prepared mixture of 1-hexene and the unsaturate in *n*-pentane solution with sufficient hydrogen bromide to give 15–20% total conversion of unsaturates. The radical addition was initiated by ionizing radiation at low temperatures, −17 ± 3°. Low reaction temperatures minimized hydrogen bromide catalyzed double-bond migration.[4] The relative reactivity of the unsaturates, $\bar{P}$, was calculated from the molar ratio of alkyl bromides in the product times the molar ratios of unsaturates, the latter averaged over the course of the reaction. In experiments with 1-hexene–*cis*-cyclooctene mixtures, the difference in reactivity was large, resulting in high conversions of 1-hexene. In these experiments, $\bar{P}$ was more accurately calculated from the relative amounts of unsaturate reacted.[5] In one experiment a multicompetitive technique was used wherein hydrogen bromide was added to a mixture of five unsaturates: 1-hexene, cyclopentene, cyclohexene, cycloheptene, and cyclooctene. This technique ensured a direct measurement of relative reactivities with identical reaction conditions. The results are summarized in Table II. These results demonstrate that the rate of addition of hydrogen bromide to cyclooctene is very slow relative to 1-hexene, 1,5-cyclooctadiene (first double bond), and smaller ring cyclic olefins. Thus it is confirmed that the unusually high selectivity to the monoaddition product from addition of hydrogen bromide to 1,5-cyclooctadiene results from the lower reactivity of the cyclooctenyl double bond of the monoaddition product, 5-bromocyclooctene.

TABLE II

RELATIVE REACTIVITY OF UNSATURATES TO ADDITION OF HBr AT −17 ± 3°

| Unsaturate | Relative reactivity, $\bar{P}$ (per double bond) A[a] | B[b] |
|---|---|---|
| Cyclopentene | 2.7 | 3.0 |
| Cyclohexene | 2.9 | 3.5 |
| Cycloheptene | 1.4 | 1.3 |
| Cyclooctene | 0.018 | Low |
| 1,5-Cyclooctadiene | 0.77 | |
| 1-Hexene | 1 | 1 |

[a] Competitive experiments with 1-hexene, *n*-pentane 75 vol %, 41,000 rad/hr, 0.21 mol of HBr/hr, 10 min. [b] Competitive run with five unsaturates, *n*-pentane 65 vol %, 41,000 rad/hr, 0.21 mol of HBr/hr, 5 min.

The reduced reactivity of the cyclooctenyl double bond in free-radical addition is an unexpected result. Previously, Gresser, Rajbenbach, and Szwarc[6] reported that the order of reactivity of cyclic olefins toward addition of methyl radical at 65° is cyclooctene > cyclopentene > cycloheptene > cyclohexene. The present results demonstrate that the order of reactivity toward hydrogen bromide is nearly the reverse, with cyclooctene much less reactive than cyclohexene. The origin of the reduced reactivity of cyclooctene toward hydrogen bromide cannot be assessed from these data. A subsequent publication will summarize a detailed study of free-radical addition reactions with cyclic olefins which elucidates the reason for this reduced reactivity.

## Experimental Section

Infrared spectra were measured using a Perkin-Elmer Model 21 double-beam recording spectrophotometer with sodium chloride optics. The control settings were resolution, 927; response, 1; gain, 6.5; speed, 5; and suppression, 2. Infrared spectra of samples were recorded as thin films squeezed between salt plates or as solutions in Spectro Grade solvents in 0.05-mm sodium chloride microcavity cells (Type D, Barnes Eng. Co.) using a 4X beam condenser. Nmr spectra were measured on a Varian A-60 spectrometer. Gas–liquid partition chromatograms were obtained with an Aerograph Model 350B dual-column unit. The relative peak areas were assumed to represent relative per cent by weight. The absolute accuracy of the analyses is esti-

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(4) L. H. Gale, *J. Amer. Chem. Soc.*, **88**, 4661 (1966).

(5) J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc., B*, 1191 (1966).

(6) J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 3005 (1961).

mated to be within 10% with better accuracy for the relative values. Mass spectra were obtained using a CEC 21-103 mass spectrometer with an ionizing voltage of 70 V.

**Reagents.**—Hydrogen bromide (from The Matheson Co., Inc., Research Grade) was used directly; the minimum purity was 99.8%. *n*-Pentane (Phillips Pure Grade) was used directly. 1-Hexene (Phillips Pure Grade) was used directly with no purification. Analysis by glpc showed that this material was 99.6% pure, the impurity being *cis*- and *trans*-2-hexene (0.38). Cyclopentene (Phillips Research Grade) was used directly and has a minimum purity of 99.95%. *cis,cis*-1,5-Cyclooctadiene (Phillips Pure Grade), cycloheptene (Columbia Organic Chemicals), and cyclooctene (Cities Services Research and Development Co.) were purified by shaking successively with 10% aqueous sodium hydroxide, ferrous sulfate solution, and water. The olefins were dried with 3A molecular sieve and distilled through an 8-in. Vigreux column. The boiling points and glpc purities of these olefins were 1,5-cyclooctadiene, 48–50° (15 mm), 99.0%; cyclohexene, 82.8–83.5°, 99.0%; cycloheptene, 114–116°, 93.5%, and cyclooctene, 44–45° (20 mm), 99.0%. The cycloheptene was further purified by preparative glpc on a Ucon P/firebrick column (9.5-mm o.d. × 6 m long) yielding material with a purity of 98.1%.

**Addition of Hydrogen Bromide to 1,5-Cyclooctadiene.**—The apparatus consisted of a 150-ml cylindrical glass reactor fitted with a gas inlet tube (coarse fritted glass tip) and a thermocouple well. Hydrogen bromide was introduced through a calibrated glass rotometer and Teflon tubing. Unreacted hydrogen bromide exited from the reactor through another glass rotometer. The contents of the reactor were stirred by a magnetically driven Teflon-covered stirring bar. The reactor was surrounded with a copper coil containing recirculating isopropyl alcohol coolant. The entire reactor was placed in the irradiation zone of a 7500-Ci Co$^{60}$ facility. The dose rate was determined for the geometry of this experimental configuration using ferrous dosimetry.

In a typical experiment, 1,5-cyclooctadiene (13.2 g, 0.12 mol) and *n*-pentane (45 ml) were placed in the reactor and cooled to the desired temperature while purging with nitrogen. Hydrogen bromide was then introduced and the irradiation was started. At the completion of the experiment (1.5 hr) the contents of the reactor were purged with nitrogen. The product was washed with water, dried (3A molecular sieve), concentrated, and distilled, giving 15.1 g (67%) of 5-bromocyclooctene: bp 84–85° (10 mm); ir (neat) 1660 (C═C) and 720 cm$^{-1}$ (*cis*-HC═CH-); nmr (neat) $\delta$ 5.65 (m, 2, -CH═CH-), 4.25 (m, 1, -CHBr-), 2.2 (m, 8, -CH$_2$—CHBr- and -CH$_2$—CH═CH-), and 1.6 ppm (m, 2, -CH$_2$-).

*Anal.* Calcd for $C_8H_{13}Br$: C, 50.8; H, 6.9; Br, 42.3. Found: C, 50.9; H, 6.9; Br, 41.8.

Further distillation yielded 7.3 g (22%) of dibromocyclooctanes: bp 96–98 (1 mm); ir complex, no bands at 1660 and 720 cm$^{-1}$; nmr (neat) $\delta$ 4.4 (m, 2, -CHBr-), 2.2 (m, 8, -CH$_2$—CHBr-), and 1.7 ppm (m, 4, -CH$_2$-).

*Anal.* Calcd for $C_8H_{14}Br_2$: C, 35.6; H, 5.2; Br, 59.2. Found: C, 35.9; H, 5.3; Br, 59.3.

**Competitive Addition of Hydrogen Bromide.**—The apparatus and procedure were the same as described earlier with the exception that a limited quantity of hydrogen bromide reacted. The products from the competitive additions of hydrogen bromide to 1-hexene and cyclopentene, cyclohexene, cycloheptene, cyclooctene, and all four cyclic olefins together were analyzed by glpc on a Ucon 50 HB 2000/Chromosorb W column (6-mm o.d. × 3.0 m long) programmed from 40 to 150° (180° for samples with cyclooctene) at 6°/min with a helium flow rate of 75 cc/min. The products from the competitive addition of hydrogen bromide to 1-hexene and 1,5-cyclooctadiene were analyzed by glpc on a QF-1/firebrick column (6-mm o.d. × 1.5 m long) programmed from 40 to 180° at 6°/min with a helium flow rate of 75 cc/min. All glpc analyses were performed in duplicate or triplicate. *n*-Hexyl bromide, cyclopentyl bromide, and cyclohexyl bromide were identified by comparison of the ir spectra of glpc trapped samples with those of authentic materials (Eastman Organic Chemicals, Columbia Organic Chemicals, and Eastman Organic Chemicals, respectively). Cycloheptyl bromide was identified similarly by comparison with the authentic spectrum in the Sadtler Catalog of infrared spectra.[7] Cyclooctyl bromide was identified by mass spectrometry and exhibited the following ir spectrum (CCl$_4$, CS$_2$): 2850 s, 1470 s, 1445 s, 1345 w, 1320 vw, 1285 w, 1255 w, 1225 m, 1175 m, 1170 m, 1110 w, 1085 w, 1042 m, 955 w, 930 vw, 907 w, 852 w, 805 w, 785 w, 765 w, and 713 m cm$^{-1}$.

**Registry No.**—Hydrogen bromide, 10035-10-6; *cis,-cis*-1,5-cyclooctadiene, 111-78-4; I, 17223-82-4; 1,4-dibromocyclooctane, 17255-72-0; 1,5-dibromocyclooctane, 17255-73-1.

# Peroxide-Induced Reductions of 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone with Secondary Alcohols[1]

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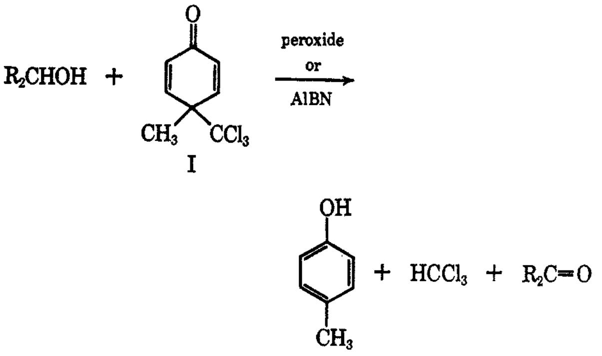
*Received April 15, 1968*

We have found that 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (I) is reduced by secondary alcohols



(1)

to *p*-cresol and chloroform with concurrent oxidation of the alcohol in a free-radical chain reaction. Table I lists the products obtained from some *t*-butyl peroxide induced reactions of I with 2-butanol.

TABLE I

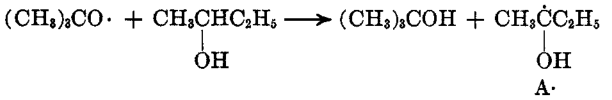
REACTIONS OF I WITH 2-BUTANOL AND *t*-BUTYL PEROXIDE[a]

| Reactants, mmol | | | Recovered | Products, mmol | | |
|---|---|---|---|---|---|---|
| I | 2-Butanol | *t*-Butyl peroxide | I | *p*-Cresol | 2-Butanone | HCCl$_3$ |
| 2.37 | 6.80 | 1.16 | 0 | 2.11 | 2.87 | 1.46 |
| 2.32 | 67.4 | .16 | 0.73 | 1.40 | 1.63 | 1.07 |
| 0.72 | 21.8 | .076 | 0.32 | 0.34 | 0.43 | 0.29 |

[a] For 9 hr at 125°.

A mechanism that would account for these products and their distribution includes the chain sequence in

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (2)$$



$$(CH_3)_3CO\cdot + \underset{\displaystyle OH}{CH_3\underset{|}{C}HC_2H_5} \longrightarrow (CH_3)_3COH + \underset{\displaystyle \underset{\displaystyle A\cdot}{OH}}{CH_3\underset{|}{\dot{C}}C_2H_5} \qquad (3)$$

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[7] Sadtler Catalog, Sadtler Research Laboratories, Philadelphia, Pa., 1959.

[1] This work was supported by a grant from the National Institutes of Health (AM-08517-02).

[2] Taken from the thesis submitted by K. L. J. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1968.