thermic). After stirring for an additional 2.5 hr, 0.1 mol of methylene iodide was added. After another 5.0 hr of stirring, a further 0.05 mol of methylene iodide was added. The black reaction mixture was stirred overnight and then diluted with 150 ml of ether. An aqueous saturated NH_4Cl solution was added carefully dropwise until the ether layer discharged a black precipitate. The precipitate was extracted with ether; the combined etheral extracts were washed with saturated NH_4Cl solution, twice with saturated K_2CO_3 solution, and finally with a saturated NaCl solution. Sodium sulfate was used to dry the ether solution. The solvent was evaporated through a 50-cm column and the residue was distilled *in vacuo*. Bp: **2a**, 71–75° (12 mm); **2c**, 88–93° (12 mm); **2d**, 82–88° (12 mm). Yields: 40–45% (**2a–c**); 5–10% (**2d**) (+ 70% 1-methylcycloproylcarbinol). Purity (glpc): 95–98% (**2a–c**); 85–90% (**2d**).

Anal. Calcd for **2a**: C, 69.19; H, 10.33. Found for **2a**: C, 69.31; H, 10.32. Calcd for **2c,d**: C, 71.69; H, 10.94. Found for **2c**: C, 71.43; H, 11.01. Found for **2d**: C, 71.36; H, 11.08.

The nmr spectra of the formals show characteristic[6] sharp peaks at 4.6 (OCH_2O) and 3.3 ppm (carbinyl protons) in addition to the characteristic cyclopropane ring proton multiplets (**2a**, 0–1.4; **2c**, 0–1; **2d**, 0.2–0.5 ppm) and the methyl group absorptions (**2c**, 1.0; **2d**, 1.1 ppm). Mass spectra of **2a–d** display the characteristic pattern of dialkoxymethanes:[7] a weak $M^+ - 1$ signal (no parent peak), very strong signals corresponding to m/e for the "cyclopropylcarbinyl" cations (R^+), and moderately strong signals which correspond to m/e for RO^+ and $ROCH_2^+$. The ir spectra exhibit a stong doublet in the 1020–1120 cm^{-1} range which is known as characteristic of COCOC groups.[8]

Optimal Conditions for Cyclopropylcarbinol Formation.—A vigorously stirred mixture of 19.8 g of commercial Zn-Cu couple (Ventron/Alfa Inorganics), 0.2 g of iodine, 0.23 mol of methylene iodide, and 150 ml of dry ether was heated by an infrared heater until the reaction started and then stirred for 45 min more at 40°. Then allyl alcohol (0.1 mol in 25 ml of dry ether) was added dropwise (10 min), and the mixture was stirred for 75 min more at the same temperature. The work-up was as described above. The crude product was fractionated through a column and the fraction with bp 100–130° was purified by glc (25′ Carbowax 20M column at 112°).

Attempted Formal Hydrolysis.—Treatment of **2a** with 0.1 *N* oxalic acid for 45 min at 100° gave practically only the starting material. Stronger conditions were not attempted, due to the well-known[5] sensitivity of cyclopropylcarbinol toward acidic conditions.

Registry No.—**2a**, 20797-82-4; **2c**, 20797-83-5; **2d**, 20797-84-6.

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On the Mechanism of the Modified Hunsdiecker

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The modified Hunsdiecker reaction discovered by Cristol and Firth[1] greatly facilitated the synthesis of organic halides *via* decarboxylation. We wish to report the preparation of one of the proposed intermediates, the proof of its validity as an intermediate, and the proof that mercuric halides do not participate in the reaction as catalysts. The proposed reaction sequence for the modified Hunsdiecker is shown below in eq 1–3.[2]

$$HgO + 2Br_2 \longrightarrow HgBr_2 + [Br_2O] \qquad (1)$$

$$[Br_2O] + RCOOH \longrightarrow [RCOOBr] + HOBr \qquad (2)$$

$$[RCOOBr] \longrightarrow RBr + CO_2 \qquad (3)$$

Brackets are used to denote intermediates.

We have obtained Br_2O free of $HgBr_2$ and HgO by fractional sublimation in vacuum at Dry Ice–acetone temperatures. There is a 3% impurity of Br_2 as measured by ultraviolet spectroscopy. Ultraviolet absorption of Br_2O in carbon tetrachloride solutions shows two peaks at 3200 Å, and 6550 Å with ϵ of 240 and 12.3, respectively, which is in agreement with earlier work on Br_2O.[3] Further work is underway to ascertain the nature of bromine oxide from the HgO and Br_2 reactions as the data on Br_2O is tenuous. Dropwise addition of a CCl_4 solution of Br_2O to a solution of pentanoic acid in CCl_4 in the dark produced 30% yields of *n*-butyl bromide. Yields were based on the acid concentration. While these yields are modest compared to the normal modified Hunsdiecker, one must bear in mind that the Br_2O is not being generated *in situ* as is the case when one normally runs the modified Hunsdiecker. Furthermore, Br_2O decomposes slowly at temperatures above −50°, and, while the dropwise addition is occurring, some decomposition must occur. Also under the modified Hunsdiecker conditions, an excess of Br_2O and HgO is usually used.

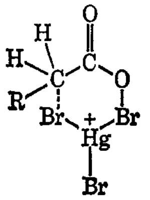
Table I shows the effect of $HgBr_2$ concentration versus per cent yield of alkyl halide. All of these reactions were run simultaneously under the same conditions of temperature and concentration. A CCl_4 solution of Br_2O was divided equally among the samples and added at the same rate. Obviously, there is no catalytic effect from the $HgBr_2$.

TABLE I

Sample no.	Mol of $HgBr_2 \times 10^{-5}$	Yield of alkyl halide, %
1	0.00	30.4
2	0.65	30.4
3	0.97	31.6
4	1.22	30.9
5	2.09	29.6
6	3.40	29.7

The amount $HgBr_2$ exceeded the solubility in CCl_4 after sample 4. This data was included to ensure that surface catalysis was not occurring.

Another possibility of $HgBr_2$ assistance could have been in the decomposition of the acyl hypobromide as shown below.



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[1] S. J. Cristol and W. C. Firth, *J. Org. Chem.*, **26**, 280 (1961).

[2] P. W. Jennings, Masters Thesis, University of Colorado, 1961.

To test this intermediate, we fortified the reaction with $HgCl_2$. There was no evidence found to indicate any *n*-alkyl chloride formed.

Experimental Section

Preparation of Br_2O.—A solution of Br_2O in CCl_4 was prepared by mechanically stirring 6.8 ml (19.9 g, 0.125 mol) of Br_2, 60 g (0.278 mol) of red HgO, and 300 ml of CCl_4 in a 500-ml round-bottom flask fitted with a reflux condenser. The solution was maintained at 45° and light was excluded. After 90 min, the solution was cooled to −20° by a Dry Ice–methanol bath and 80 g (0.359 mol) of fresh HgO was added. Stirring was continued for 30 min followed by filtration to remove the $HgBr_2$ and unreacted HgO.

The filtrate was then connected to a vacuum line and the contents transferred slowly at −25°. The CCl_4 and Br_2 transfers first leaving a brownish green solid which when transferred and collected gives the uv spectrum reported for Br_2O.[3]

Preparation of the Alkyl Halide.—In a typical experiment, the Br_2O in CCl_4 solution is added, via a pressure equalized dropping funnel, to 250-ml flask containing 4.4 g (0.043 mol) of *n*-pentanoic acid which is dissolved in 50 ml of CCl_4. The solution was refluxed in the dark during the addition of Br_2O which took approximately 75 min. The solution was then allowed to reflux for an additional 15 min. Products were analyzed by isolation and vapor phase chromatography.

Registry No.—Br_2O, 21308-80-5.

[3] (a) W. Brenschede, and H. J. Schumaker, *Z. Physikol. Chem.*, **29B**, 356 (1935); (b) W. Brenschede, and H. J. Schumaker, *Z. Anorg. Chem.*, **226**, 370 (1936).

Photoisomerization of *cis*-Cyclooctene to *trans*-Cyclooctene[1]

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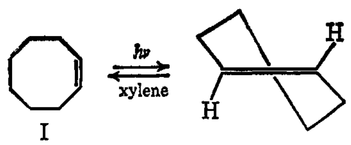
The need for modest quantities of *trans*-cyclooctene in connection with exploratory work in these laboratories coupled with the length of conventional syntheses[2,3] prompted us to explore a short direct route to this compound. The known benzene, toluene, and xylene sensitized isomerization of olefins[4] suggested the photosensitized isomerization of *cis*-cyclooctene as a potential route to the *trans* isomer. Since benzene is known to afford high yields of adduct when irradiated in the presence of cyclooctene,[5] xylene was chosen as sensitizer.



I

II

Irradiation of a solution of xylene and cyclooctene in purified cyclohexane followed by silver nitrate extraction and decomposition of the silver nitrate complex with concentrated ammonium hydroxide gave a two-component mixture. Preparative vpc isolation of the compounds followed by direct comparison with authentic materials showed the major product to be *trans*-cyclooctene (II) and the minor component to be 1,5-cyclooctadiene (III). That the 1,5-cyclooctadiene was not a photochemical product in this system was evident from the decrease in the percentage of III in the recycled irradiation mixtures (Table I). The dramatic decrease in III upon repeated photolysis suggests that it is a minor impurity in commercial cyclooctene which coextracts with II.

TABLE I

YIELD OF *trans*-CYCLOOCTENE AND 1,5-CYCLOOCTADIENE AS A FUNCTION RECYCLING PHOTOLYSIS MIXTURE

Number of cycles	Total yield, g	% II	% III
1	2.2	82	18
2	2.1	90	10
3	2.4	95	5
4	2.1	97	3

This method has proven useful in conveniently preparing up to 2.5 g of *trans*-cyclooctene per irradiation cycle. Although initial irradiations yield mixtures of II and III, the high reactivity of II still renders the material synthetically useful. Continued irradiation of samples with an intervening distillation to remove higher boiling material affords II in good purity (>97%). The method, although limited in the amount of material obtained, requires only a small amount of manipulative operations and thus should be useful in preparation of modest amounts of II for exploratory and mechanistic work.

Experimental Section

Cyclooctene (600 ml) in 900 ml of olefin-free cyclohexane was extracted four times with 100 ml of 30% aqueous silver nitrate. After the extract was washed with water, dried over Drierite, and distilled through a 3-in. column, 150 ml of xylene was added to form the irradiation mixture. The material was irradiated in 500-ml portions for 36 hr under nitrogen using a 450-W Hanovia medium pressure source and a Corex filter sleeve. The use of a Vycor filter gave faster conversions initially but led to buildup of polymer on the immersion well. The combined irradiation solutions were extracted four times with 80 ml of 20% aqueous silver nitrate; the silver nitrate solution was washed with pentane twice, 70 ml) and decomposed by dropwise addition into 150 ml of concentrated ammonium hydroxide at 0°. The oily aqueous solution was extracted with pentane (thrice, 75 ml), the pentane layer dried, and the pentane distilled through a 6-in. Vigreux column. Short-path distillation of the remaining light yellow liquid afforded 2.2 g (0.02 mol) of colorless liquid, bp 75–6° (75 mm). Vpc inspection (20% β,β-oxydipropionitrile on 60–80 Chrom P, 10 ft × 0.25 in., 70°) showed three components with retention times of 10, 12, and 28 min. These products were identified as *cis*-cyclooctene, *trans*-cyclooctene, and 1,5-cyclooctadiene. The percentage of *cis*-cyclooctene in seven individual runs varied from 1 to 3% of the *trans* isomer.

For recycling, the light yellow photolysis solution was distilled at atmospheric pressure through a short column to yield 1400 ml

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[1] A grant from the Eli Lilly Co., Indianapolis, Ind., is gratefully acknowledged.

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[3] A recent improvement over these methods has been reported: J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Commun.*, 1593 (1968).

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