labile to be further purified. Its benzaldehyde content was determined by dissolving a weighed sample in 95% alcohol, treated with DNPH, and determining the benzaldehyde DNPH gravimetrically.

*Anal.* Calcd for $C_{12}H_{12}ClN_3O_2$: $C_6H_5CH$, 33.9; Cl, 13.55. Found: $C_6H_5CH$, 32.7; Cl, 13.7.

**2,3-Dihydro-1H-imidazo[1,5-*b*]pyrazole-4,6(3aH,5H)-dione Hydrochloride (4).**—Compound **3** (32.7 g, 0.123 mol) was dissolved in methanol, filtered, and mixed with excess ether. The precipitated product was filtered, washed with ether, and dried to give 19.0 g (87%) of **4**. An analytical sample was prepared by recrystallization from 2-propanol containing a little hydrochloric acid. The compound did not exhibit a sharp melting point but decomposed gradually at about 170°.

*Anal.* Calcd for $C_5H_8ClN_3O_2$: C, 33.81; H, 4.45; Cl, 19.97. Found: C, 33.93; H, 4.74; Cl, 19.96.

Recrystallization of **4** from 90% 2-propanol converted it into the free base **5**: mp 205-207°; no uv maximum above 220 mμ; nmr ($DCl-D_2O$) δ 2.61 (m, 2, $CH_2CH_2CH$), 3.72 (m, 2, $CH_2CH_2CH$), 4.65 (m, 1, $CH_2CH_2CH$).

*Anal.* Calcd for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.54; H, 5.01; N, 29.77.

**Registry No.**—**1**, 20707-87-3; **2**, 20707-88-4; **3**, 20728-44-3; **4**, 20707-89-5; **5**, 20707-90-8; 5-(2-chloroethyl)-1-[(5-nitrofurfuryliden)amino]hydantoin, 20707-91-9; 1-{2-[1-(5-nitrofurfurylidenamino)-2,4-dioxo-5-imidazolidinyl]ethyl}pyridinium chloride, 20707-92-0.

# A New Synthesis of Dicyclopropylcarbinoxymethanes—By-Products in the Simmons-Smith Reaction with Allyl Alcohols

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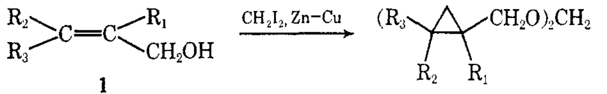
The effective and useful cyclopropanation reaction discovered by Simmons and Smith[1] can be applied with particular effectiveness to β,γ-unsaturated alcohols.[2] The neighboring hydroxyl group directs the stereochemical course and facilitates the reaction.[2] We were surprised when application of this synthesis to allyl alcohol (**1a** and **1b**) gave poor yields of cyclopropylcarbinol. Closer investigation of the reaction product showed that substantial amounts of the formal, dicyclopropylcarbinoxymethane, **2a** and **2b**, had formed. To our knowledge, observation of such a product in the Simmons-Smith reaction is unprecedented.[2,3]

In fact, it has been possible to develop this "side reaction" into a useful one-step synthesis of some dicyclopropylcarbinoxymethanes. Dialkoxymethanes (formals) are usually prepared by the treatment of formaldehyde with an alcohol (or, sometimes, an orthoformate ester) in the presence of an acid catalyst.[4] Occasionally, the reaction of alkoxides and a dihalomethane or α-halomethyl ether is employed.[4] Our synthesis may be advantageous in cases where the corresponding cyclopropylcarbinols are not readily available or where they are unstable toward acidic conditions.[5]



**1**

**2a–2c**, 40–45%
**2d**, 5–10%

**a**, $R_1 = R_2 = R_3 = H$
**b**, $R_1 = R_2 = D; R_3 = H$
**c**, $R_1 = H; R_2, R_3 = CH_3, H$
**d**, $R_1 = CH_3; R_2 = R_3 = H$

During the course of the Simmons-Smith reaction on allyl alcohol, the $(RO)_2CH_2/ROH$ (R = cyclopropylcarbinyl) ratio increases with time, demonstrating that an initially formed cyclopropylcarbinyl intermediate reacts subsequently with a methylene donor. If the allyl alcohol/$CH_2I_2$ ratio was kept constant, reduction in the amount of Zn-Cu couple used decreased the $(RO)_2CH_2/ROH$ product ratio. For this reason we believe that the bis(iodomethyl) zinc-zinc iodide complex[1] rather than methylene iodide is the species responsible for formal production. For example, it is conceivable that a species such as $(CH_2{=}CHCH_2OCH_2)_2Zn \cdot ZnI_2$, obtained by exchange,[2f] might decompose preferentially to the mixed formal, $C_3H_5CH_2OCH_2OCH_2CH{=}CH_2$, a precursor of **2a**. We have not investigated the mechanism of formal formation.

Methallyl alcohol (**1d**) gave significantly lower yields of formal than did the other allyl alcohols (**1a–1c**), evidently for steric reasons, known to be a factor in the Simmons-Smith reaction.[1,2] For this reason, formal by-products may not be significant when more highly substituted allyl alcohols are employed. The reported[2b] low yield (26%) of cyclopropylethanol obtained by the Simmons-Smith reaction on 1-buten-4-ol may be due to formal formation; if so, this procedure might be used for the synthesis of such compounds.

Unfortunately, it was difficult to prevent dialkoxylmethane formation in the cases of **1a–1c**. After a short reaction period, much starting allyl alcohol remained, while long reaction times favored formal production. The best conditions, we found, gave only 15-20% yields of cyclopropylcarbinol after the necessary purification by glpc. In addition, we were not successful in finding conditions for the hydrolysis of **2a**. Mild oxalic acid treatment produced no reaction, and more strenuous conditions are known to give rise to rearrangement of cyclopropylcarbinol.[5]

## Experimental Section

**General Procedure.**—The following conditions are optimal for formal synthesis. Methylene iodide (0.2 mol) was added to a vigorously stirred mixture of 29.4 g of commercial Zn-Cu couple (Ventron/Alfa Inorganics), 0.2 g of iodine, and 125 ml of dry ether, maintained at 40°. After 0.5 hr, 0.1 mol of the appropriate allyl alcohol was added dropwise within 15 min (strongly exo-

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[1] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964); E. P. Blanchard and H. E. Simmmons, *ibid.*, **86**, 1337 (1964).

[2] (a) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963); (b) Y. Armand, R. Perraud, J.-L. Pierre, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 1893 (1965); (c) W. G. Dauben and A. C. Ashcraft, *J. Amer. Chem. Soc.*, **85**, 3673 (1963); (d) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963); (e) J. H.-H. Chan and B. Rickborn, *ibid.*, **90**, 6406 (1968); (f) G. Wittig and M. Jautelat, *Ann.*, **702**, 24 (1967).

[3] Confirmed by H. Simmons, private communication.

[4] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, p 261-267; "Rodd's Chemistry of Carbon Compounds," Vol. I, S. Coffey, Ed., Elsevier Publishing Co., New York, N. Y., 1965, Part C, p 28.

[5] M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

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.

**Acknowledgment.**—This research was supported by grants from the National Institutes of Health (AI-07766), the National Science Foundation, and the Petroleum Research Fund administered by the American Chemical Society.

[6] T. Sato, Y. Saito, M. Kainosho, and K. Hata, *Bull. Chem. Soc. Jap.*, **40**, 391 (1967).

[7] P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen, and S.-O. Lawesson, *J. Amer. Chem. Soc.*, **87**, 4559 (1965).

[8] K. Nukada, *Nippon Kagaku Zasshi*, **80**, 1112 (1959); *Chem. Abstr.*, **54**, 1071*b* (1960).

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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 $\epsilon$ 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.

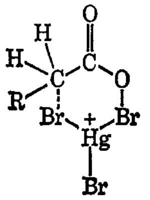
Table I shows the effect of $HgBr_2$ concentration versus per cent yield of alkyl halide. All of these reactions were run simultaneously under the same conditions of temperature and concentration. A $CCl_4$ solution of $Br_2O$ was divided equally among the samples and added at the same rate. Obviously, 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.