with water, and dried. Recrystallization from ethyl acetate and benzene gave 9.0 g. (75%) of 1-(4-hydroxybenzyl)-2-naphthol (VII), m.p. 198–200°.

*Anal.* Calcd. for $C_{17}H_{14}O_2$: C, 81.57; H, 5.63. Found: C, 81.24; H, 5.67.

**Reaction of 1-Methoxymethyl-2-naphthol (I) with Cyanide Ion.**—A mixture of 5.8 g. of 1-methoxymethyl-2-naphthol, 2.6 g. of sodium methoxide, and 3.1 g. of sodium cyanide was dissolved in 100 ml. of dry methanol and heated under reflux for 12 hr.[10] The solution was cooled and poured into cold dilute hydrochloric acid (hood). The resulting solid was separated by suction filtration and washed repeatedly with cold water. Recrystallization of the dried product from ethyl acetate–benzene gave 4.3 g. (78%) of 1-cyanomethyl-2-naphthol (VIII), m.p. 184–185° (lit.[8] m.p. 177°). This substance exhibits strong infrared absorption at 4.45 $\mu$.

*Anal.* Calcd. for $C_{12}H_9NO$: C, 78.66; H, 4.95. Found: C, 78.41; H, 4.99.

**Reaction of *o*-Hydroxymethylphenol (IX) with Diethyl Malonate.**—To a solution prepared by dissolving 9.3 g. of sodium in 200 ml. of absolute ethanol were added 16.5 g. of *o*-hydroxymethylphenol and 53.0 g. of diethyl malonate. The solution was heated under reflux for 3 hr., cooled, and poured, with stirring, into cold dilute hydrochloric acid. The resulting mixture was extracted with three portions of ether and the combined extracts were processed in the usual way. Removal of ether at an aspirator and distillation of the residue afforded 16.0 g. (46%) of diethyl *o*-hydroxybenzylmalonate, b.p. 131–140°. The substance was identified by base hydrolysis to the corresponding diacid which, after crystallization from water, weighed 8.5 g. (31%), m.p. 139° dec.

*Anal.* Calcd. for $C_{10}H_{10}O_5$: C, 57.14; H, 4.79. Found: C, 57.13; H, 4.88.

**Self-Condensation of 1-Methoxymethyl-2-naphthol (I).**—1-Methoxymethyl-2-naphthol (6.0 g.) was dissolved in a solution of 2.0 g. of potassium hydroxide in 35 ml. of methanol and heated under reflux for 4 hr. The solution was concentrated essentially to dryness under reduced pressure and the residue was dissolved in water. Acidification gave a solid which was then dissolved in ethyl acetate and treated with activated charcoal. Addition of petroleum ether and cooling afforded 1.5 g. (31%) of 1-(2-hydroxy-1-naphthylmethyl)-2-naphthol (XI), m.p. 193–196°. A mixture melting point with authentic material was undepressed.

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## Reduction of Organomercury Compounds with Chromium(II)

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The synthetic utility of chromous ion in organic chemistry has been reinvestigated in recent years.[1] Applications of this versatile reducing agent were described early in this century[2] and date back to Berthelot.[3] We report here a rapid quantitative reduction of organomercuric salts by chromous ion. A general method for the formation of symmetrical disubstituted mercury compounds has been devised. By suitable modifications of the method it should be possible to (1) produce mixed disubstituted mercury compounds; (2) provide new approaches to organochromium compounds; and (3) produce symmetrical disubstituted mercury compounds directly from alkyl halides.

All of the reactions described in this note were carried out on a 0.105 molar scale. Reference will be made only to the relative equivalents of each reactant. The disubstituted organomercury compounds produced were shown to be stable to the reaction conditions.

Injection of 1 equiv. of aqueous chromous ion into a solution of 1 equiv. of benzylmercuric perchlorate in 100 ml. of dimethylformamide produced immediately upon contact a fine dispersion of free mercury and a green solution. The mercury was isolated by centrifugation and analyzed using standard analytical techniques. Dibenzylmercury was isolated quantitatively by flooding the reaction mixture with water.[4] The stoichiometry of the reaction is given in eq. 1.

$$2PhCH_2Hg^+ + 2Cr^{+2} \longrightarrow (PhCH_2)_2Hg + Hg + 2Cr^{+3} \qquad (1)$$

The most reasonable mechanism for the reaction is outlined in equations 1a–d.[5,6]

$$PhCH_2Hg^+ + Cr^{+2} \longrightarrow PhCH_2Hg\cdot + Cr^{+3} \qquad (1a)$$

$$PhCH_2Hg\cdot \longrightarrow PhCH_2\cdot + Hg \qquad (1b)$$

$$PhCH_2\cdot + Cr^{+2} \longrightarrow PhCH_2Cr^{+2} \qquad (1c)$$

$$PhCH_2Cr^{+2} + PhCH_2Hg^+ \longrightarrow (PhCH_2)_2Hg + Cr^{+3} \qquad (1d)$$

Step 1a must have a favorable potential as the oxidation potential of chromous ion is 0.41 v.[7] Steps 1b and 1a may occur simultaneously as the second bond dissociation of dialkylmercury compounds is thought to be very low. The bond dissociation energy of the methylmercury radical is approximately 7 kcal./mole.[8] The average bond dissociation energy of dialkylmercury compounds decreases with increasing stability of the alkyl radical.[9] The facile formation of nitrosochromic ion from the reaction of chromous ion with nitric oxide,[10] and more directly, the hydroperoxide experiments of Kochi[11] illustrate the effectiveness of chromous ion as a free-radical trap. Step 1c is rapid and quantitative with benzyl radicals. Step 1d has been shown

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[1] (a) P. L. Julian, W. Cole, A. Magnani, and E. W. Meyer, *J. Am. Chem. Soc.*, **67**, 1728 (1945); (b) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *ibid.*, **72**, 4077 (1950); (c) W. Cole and P. L. Julian, *J. Org. Chem.*, **19**, 131 (1954); (d) P. L. Julian, W. Cole, E. W. Meyer, and B. M. Regan, *J. Am. Chem. Soc.*, **77**, 4601 (1955); (e) F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959); (f) C. W. L. Bevan, T. Halsall, M. N. Nwaji, and D. A. H. Taylor, *J. Chem. Soc.*, 768 (1962); (g) K. O. Kopple, *J. Am. Chem. Soc.*, **84**, 1586 (1962); (h) D. H. R. Barton and J. T. Pinhey, *Proc. Chem. Soc.*, 279 (1960); 280 (1962); (i) G. Büchi and H. J. E. Loewenthal, *ibid.*, 280 (1962); (j) C. E. Castro and W. C. Kroy, Jr., *J. Am. Chem. Soc.*, **85**, 2769 (1963); (k) L. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964).

[2] (a) W. Traube and W. Passman, *Ber.*, **49**, 1692 (1916); (b) J. B. Conant and H. B. Cutler, *J. Am. Chem. Soc.*, **48**, 1023 (1926); (c) R. Graf, *J. prakt. Chem.*, **140**, 34 (1934); **146**, 90 (1936).

[3] M. Berthelot, *Ann. Chim.*, **49**, 401 (1866).

[4] Disubstituted mercury compounds are stable to both $Cr^{+2}$ and $Cr^{+3}$ under the reaction conditions and the reduction of these compounds must involve a higher potential than available from $Cr^{+2}$.

[5] An alternate mechanism utilizing Cr(IV) as an intermediate is less likely. Two electron changes in the reaction of $Cr^{+2}$ with various metal

$$R\text{–}Hg^+ + Cr^{+2} \longrightarrow R\text{–}Cr^{+3} + Hg$$
$$R\text{–}Cr^{+3} + Cr^{+2} \longrightarrow R\text{–}Cr^{+2} + Cr^{+3}$$

salts have been discounted on the basis of stability of products with respect to the alternate one-electron change mechanism. See ref. 6.

[6] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[7] G. Grube and G. Breitinger, *Z. Electrochem.*, **33**, 112 (1927).

[8] (a) C. M. Laurie and L. H. Long, *Trans. Faraday Soc.*, **53**, 1431 (1957); (b) S. J. U. Price and A. F. Trotman-Dickenson, *ibid.*, **53**, 939 (1957); B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc.* (London), **A218**, 264 (1953).

[9] B. G. Gowenlock, R. M. Haynes, and J. R. Majer, *Trans. Faraday Soc.*, **58**, 1905 (1962).

[10] M. Ardon and J. Herman, *J. Chem. Soc.*, 507 (1962).

[11] (a) J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1965); (b) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).

to occur readily by the following experiment. Benzylchromium ion was produced by the addition of a chromous sulfate solution to benzyl bromide in dimethylformamide. The characteristic blue color of chromous ion was immediately replaced by the yellow to brown color of benzylchromium ion. Subsequent immediate injection of benzylmercuric perchlorate in dimethylformamide generated a green solution. The isolated yield of dibenzylmercury from immediate work-up was 99%.

The generality of the reaction for the formation of disubstituted mercury compounds is indicated by reactions from benzyl, cyclohexyl, phenyl, and 4-phenylbutyl perchlorates in which the yields were 99, 91, 88, and 93%, respectively. It is not necessary to utilize perchlorate salts as the reaction proceeds as readily with the more covalent halides. The reaction is heterogeneous, but the yields are comparable.

As further confirmation of the proposed mechanism and in an attempt to devise an alternate method for the formation of organochromium salts, an inversion of the mode of addition was carried out. Slow addition of benzylmercuric perchlorate in dimethylformamide to 3 equiv. of chromous ion over a 6-hr. period diminished the yield of dibenzylmercury with a corresponding increase in the yield of free mercury. Approximately 72% of the mercury utilized was obtained as free mercury. Similarly, phenylmercuric perchlorate when added over a 12-hr. period yielded 62% of the mercury utilized as free mercury. Under the conditions of the experiment, reaction 1d becomes less favorable than reaction 1a compared with the alternate mode of addition.

Solutions of benzylchromium react instantly with mercuric bromide to give dibenzylmercury when 0.5 mole of mercuric bromide/mole of benzylchromium is utilized. It has been reported that benzylchromium[12] and phenylchromium[13] react with mercuric bromide to yield the substituted mercuric salt. Under the conditions reported either 1 molar equiv. or excess mercuric bromide was utilized. Under our experimental conditions the organochromium compound must react with the organomercuric salt produced. As reported above this reaction is facile. Mixed disubstituted mercury compounds should be produced when an organochromium ion ($R-Cr^{+2}$) and an organomercury ion ($R-Hg^{+}$) are mixed. At present the application of this method is severely limited by the small number of chromium compounds available.

### Experimental Section

**Chromous Sulfate.**—Chromous sulfate was prepared according to the procedure of Castro.[14] The reagent was approximately 0.70 *M* and was stored under nitrogen. Samples were removed with a syringe.

**Reduction of Mercuric Perchlorates.**—The organomercuric perchlorates were prepared by addition of 1 equiv. of 70% perchloric acid to the organomercuric acetate dissolved in degassed dimethylformamide. The resultant solution was maintained under nitrogen. The chromous sulfate was injected into the system through a serum cap. Finely divided mercury was immediately produced and a green solution resulted. The reaction mixture was centrifuged and the liquid layer was removed. The solid residue was washed consecutively with dimethylformamide, water, acetone, and ether. The mercury was dried under vacuum and dissolved in nitric acid. The acidic solution was diluted with distilled water and an aliquot was analyzed by addition of excess sodium thiocyanate and back titration with silver nitrate. The disubstituted organomercury compound was obtained by dilution of the dimethylformamide solution with water and isolation of the resulting solid by filtration. Recrystallization of the mercury compound was accomplished with either benzene or ethanol.

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[13] W. Herwig and H. H. Zeiss, *ibid.*, **79**, 6561 (1957).

[14] C. Castro, *ibid.*, **83**, 3262 (1961).

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## Oxidations with Oxygen Difluoride. III

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Oxygen difluoride was found to react readily with selected olefins at low temperatures.[1] The postulated mechanism involved the direct addition of the fragments F and OF, followed by subsequent decomposition of the unstable fluoroxyalkane. The known fluoroxyalkanes contain no hydrogen[2,3] and, in fact, it was found that the addition of a hydrogen-containing compound resulted in decomposition of the fluoroxy compound.[3] Therefore, the addition of oxygen difluoride to several perfluoro olefins was attempted.

The olefins examined included perfluoroethylene, perfluoropropene, perfluorocyclobutene, and perfluorobutene-2. These olefins were found to be much less reactive than the corresponding alkyl olefins and required either thermal or ultraviolet activation. Each olefin is discussed separately below.

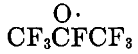
**Perfluoropropene** was completely unreactive to $OF_2$ at room temperature in the absence of light. After 12 hr. of irradiation in a 500-cc. spherical Pyrex reactor, both reactants were totally consumed, producing the products outlined in Table I. It is apparent that no fluoroxy alkanes were isolated; however, comparable amounts of $CF_3COF$ and $CF_4$ were found as well as $CF_3CF_3$ and $COF_2$. These fragments are believed to result from the decomposition of the two positional alkoxy radicals,  $CF_3\overset{O\cdot}{C}FCF_3$ and $CF_3CF_2CF_2O\cdot$, in the presence of fluorine radicals or a fluorine donor. They would be expected to decompose homolytically with cleavage of a carbon–carbon bond.[4] The mode

TABLE I

PERFLUOROPROPENE–$OF_2$

| Product | mmoles |
|---|---|
| $CF_4$ | 0.96 |
| $CF_3COF$ | 0.93 |
| $COF_2$ | 0.23 |
| $CF_3CF_3$ | 0.14 |
| $CF_3CF_2CF_3$ | 2.68 |
|  $CF_3\underset{\diagdown O \diagup}{CFCF_2}$ | 2.56 |

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[2] K. B. Kellog and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

[3] J. H. Prager and P. G. Thompson, *ibid.*, **87**, 230 (1965).

[4] The relative bond strengths being: C–F, −102 kcal./mole; C–C, −80 kcal./mole: E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 37.