Dichlorocarbene Chlorination of Alcohols in an Alkaline Micelle

Sir:

Dichlorocarbene is often used for the introduction of a dichloromethylene function into an organic compound.[1] Especially, dichlorocarbene additions to double bonds are very successfully applied to prepare dichlorocyclopropanes. Among many procedures in the literature for generating dichlorocarbene, one reported by Makasza, *et al.*,[2] using an emulsifying system seems to be most convienient and efficient. Even for dichlorocarbene insertions, the procedure (with a slight modification using benzene) was found to give excellent results as reported by us recently.[3,4]

Now we wish to report that dichlorocarbene reacts very readily with alcohols, leading to the corresponding chlorides. The reaction affords considerable preparative advantage[5] (*e.g.*, preparation of a chloride in excellent yield under basic conditions and/or at room temperature) and mechanistic interest.

A mixture of 1-adamantyl alcohol (1.52 g, 0.01 mol), 20 ml of 50% aqueous sodium hydroxide solution, and 0.04 g of triethylbenzylammonium chloride was stirred vigorously at 40° to emulsify, and then 16 ml of chloroform was added dropwise into the emulsion during 2 hr and the mixture was stirred for a further 2 hr. Usual workup gave 1.60 g of practically pure 1-adamantyl chloride (94% yield), *m/e* 170; ir and nmr spectra were identical with those reported.

Dichlorocarbene chlorination of various alcohols proceeded similarly and the results are shown in Table I.

Table I. Dichlorocarbene Chlorination of Alcohols

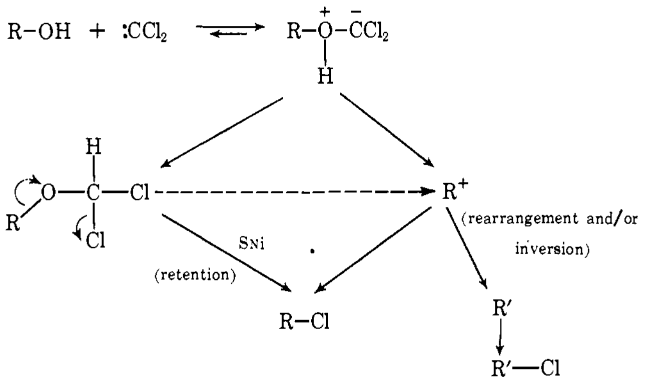
Starting alcohols	Product (yield, %)
1-Adamantyl alcohol	1-Adamantyl chloride (94) 1-Adamantyl formate (sa)[a]
Benzyl alcohol	Benzyl chloride (90) Benzyl formate (sa)
l-Menthyl alcohol	*l*-Menthyl chloride[b] *d*-Menthyl chloride[b]
2-*exo*-Norbornyl alcohol	2-*exo*-Norbornyl chloride (90)
2-*endo*-Norbornyl alcohol	2-*exo*-Norbornyl chloride (47) 2-*endo*-Norbornyl chloride (44)
(1-Adamantyl)methyl alcohol	(1-Adamantyl)methyl chloride (40) Homoadamantyl chloride (13) (1-Adamantyl)methyl formate (35)

[a] sa = small amount. [b] $\alpha_D = -23.6°$.

The reaction was always very exothermic and practically complete within a few minutes at room temperature.

Since the major chloride obtained was that resulting from retention of configuration of the starting alcohol (see Table I), the SNi mechanism may be operative. However, the rearrangement (from adamantylcarbinyl to homoadamantyl) and the inversion (from *endo*-2-norbornyl to *exo*-2-norbornyl or from *l*-methyl to *d*-methyl) observed suggest considerable leakage to a carbonium ion (as shown in Scheme I).

Scheme I



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(1) *E.g.*, see W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(2) M. Makasza and M. Wawrzyniewiez, *Tetrahedron Lett.*, 4659 (1969).

(3) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, **92**, 6670 (1970).

(4) Seyferth's procedure using trichloromethylmercuric reagents was also reported to give good results: D. Seyferth, *et al.*, *J. Org. Chem.*, **35**, 1989, 1993 (1970); *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

(5) The reaction of alcohols with dichlorocarbene in basic media afforded corresponding olefins, *e.g.*, P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959).

Unusual Metalloporphyrins. VI. Metal Shuttling between Imidazole Nitrogens in a Ruthenium Porphyrin Imidazole

Sir:

The great biological significance of the iron(II)-porphyrins has caused substantial interest in their properties, structures, and mechanisms. The fact that imidazole derivatives are such frequent axial ligands in these complexes makes the iron(II)-porphyrin-imidazole complexes a subject of concern to the coordination chemist. Among the problems involved in the study of such compounds are both the ease of oxidation and the paramagnetism frequently found in iron(II) compounds. The only reported ruthenium porphyrin had been ruthenium(III) carbonyltetraphenylporphine chloride.[1] It was anticipated, however, that a porphyrin of ruthenium in the +2 state would eliminate these obstacles to the facile study of the metal-imidazole bond in heme-type compounds.

Ruthenium(II) carbonylmesoporphyrin IX dimethyl ester (I) was prepared by refluxing 0.50 g of mesoporphyrin IX dimethyl ester with 2.00 g of ruthenium dodecacarbonyl in benzene under nitrogen for 48 hr. The product, purified by chromatography with acetone on neutral alumina, is crystallized from tetrahydrofuran-hexane to give I, a brick red, air-stable solid, mp 290° dec. *Anal.* Calcd for $RuC_{37}H_{40}O_5N_4$: C, 61.57; H, 5.59; N, 7.76; Ru, 14.00; mol wt, 721.8. Found: C, 61.28; H, 5.75; N, 7.60; Ru, 13.80; mol wt (in benzene), 722. The product has a visible spectrum which is typical of metalloporphyrins[2] with α and β bands at 548 (ϵ 3.43 × 10^4) and 518 nm (1.53 × 10^4), respectively, and a Soret band at 393 nm (2.85 × 10^5) in tetrahydrofuran. The presence of a C≡O ligand is confirmed by the ir spectrum which has a

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(1) E. B. Fleischer, *Chem. Commun.*, 475 (1969).

(2) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964, p 75.