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PRELIMINARY COMMUNICATION

NEW REACTIONS OF PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS: PREPARATION OF PERHALOGENATED OXIRANES

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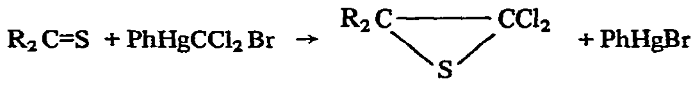
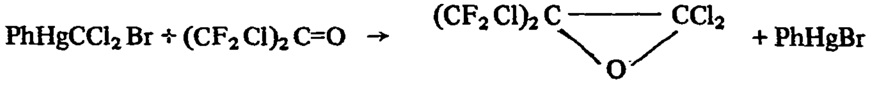
Our recent investigations have shown that phenyl(bromodichloromethyl)mercury-derived dichlorocarbene undergoes addition to the C=S bond[1]:


(1)

(R = Cl and Ph)

This finding has prompted further interest in the addition of dihalocarbenes to double bonds between carbon and Group VI elements. In the present communication we report concerning dihalocarbene additions to the C=O bond.

The oxygen analogs of the substrates used in reaction (1), phosgene and benzophenone, did not react with CCl_2 produced by thermolysis of phenyl(bromodichloromethyl)mercury in benzene at 60–80°. In both cases phenylmercuric bromide was formed in good yield, but the sole CCl_2-derived product was tetrachloroethylene. Similar results were obtained with a dialkyl ketone, $n\text{-}C_3H_7COC_2H_5$, and with the perhalogenated acetones $(CCl_3)_2C=O$ and $(CFCl_2)_2C=O$. However, with the more highly fluorinated acetone derivatives, $(CF_2Cl)_2C=O$, $(CF_3)_2C=O$ and $(CF_2Cl)(CFCl_2)C=O$, dichlorocarbene addition to the C=O bond was observed. With these ketones, addition of CClBr and CBr_2 to the C=O linkage also could be achieved. As an example we describe the preparation of 2,2-dichloro-3,3-bis(chlorodifluoromethyl)oxirane (eq.2).


(2)

A mixture of 10.0 mmoles of $PhHgCCl_2Br$ and 20.0 mmoles of $(CF_2Cl)_2C=O$ in 50 ml of benzene under nitrogen in a flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was stirred and heated at 60° for 72 h. At the end of this time, phenylmercuric bromide (10 mmoles) was filtered, and the

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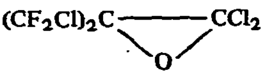
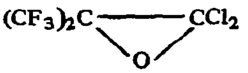
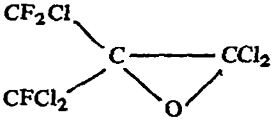
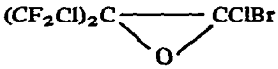
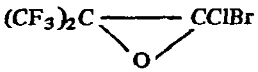
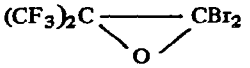
TABLE 1

OXIRANES PREPARED BY THE MERCURIAL ROUTE

Oxirane	Yield (%)	b.p. (°C/mm)	n_D^{25}
	74	98–102/125	1.4048
	36	67–70/760	1.3300
	33	130–132/125	1.4415
	48	114–116/126	1.4298
	26	73–75/760	1.3550
	25	99–101/760	1.3820

filtrate was distilled. After removal of solvent, unconverted ketone and a minor amount of tetrachloroethylene, 2.2 g (7.4 mmoles; 74% yield) of the product oxirane, b.p. 98–102°/125 mm, n_D^{25} 1.4048, was obtained. (Found: C, 17.17; Cl, 50.28. $C_4Cl_4F_4O$ calcd: C, 17.04; Cl, 50.32). The analytical sample was obtained by GLPC on a DC 200 silicone oil column at 60°. The mass spectrum of this oxirane did not show a parent ion peak at 80 eV or at 9.8 eV. The most intense fragments were CCl_2^+ (100), CF_2Cl^+ (75.5) and $COCl^+$ (30.0), and the heaviest fragment observed corresponded to M–Cl, $C_4F_4Cl_3O^+$ (13.0). IR (neat liquid): 1785w, 1380s, 1360m, 1330sh, 1240s, 1200s, 1175s, 1170s, 1138m, 1090s, 1075s, 1030s, 1000sh, 985s, 920sh, 910sh, 895sh, 885s, 875sh, 855s, 845s, 835sh, 800w, 750w, 720w, 690m and 665m cm^{-1}.

The other oxiranes prepared in this study thus far are shown in Table 1. Reactions reading to the 2,2-dihalo-3,3-bis(trifluoromethyl)oxiranes were carried out at autogenous pressure in a sealed tube at 60° since the starting ketone, $(CF_3)_2C{=}O$, is a gas at room temperature. The yields recorded are not necessarily the optimum yields for these reactions.

Similar additions of difluorocarbene [via pyrolysis of perfluoro(methyloxirane)] to the C=O bond of highly fluorinated ketones (*e.g.*, $(CF_3)_2C{=}O$ and $(C_2F_5)_2C{=}O$) have been described in a duPont patent[2], and the addition of $(CF_3)_2C$ (via bis(trifluoromethyl)-diazirine) to $F_2C{=}O$ gave 2,2-difluoro-3,3-bis(trifluoromethyl)oxirane[3].

From the successful examples cited in these references and found during the present study, it would seem that extensive fluorine substitution is a requirement for CX_2 addition to the C=O bond. The effect of such highly electronegative substituents (F, CF_3,

CF_2Cl) could possibly be to stabilize a three-center transition state of the type shown in Fig.1.

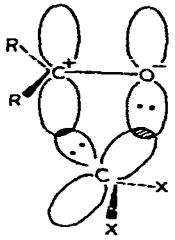
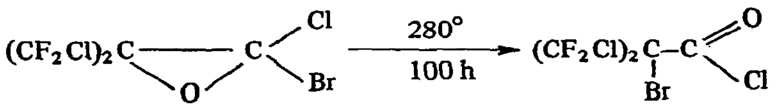


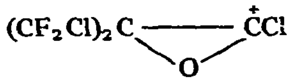
Fig.1. Suggested transition state for CX_2 addition to polyfluoroketones. The extreme form is shown: overlap between a filled oxygen *p* orbital and the vacant carbene *p* orbital and between the filled carbene sp^2 orbital and the vacant carbon *p* orbital.

Reactions of these oxiranes are under investigation. Of interest is the thermolysis of 2-bromo-2-chloro-3,3-bis(chlorodifluoromethyl)oxirane:



(3)

(60%)

a process which very possibly could proceed via the  ion.

ACKNOWLEDGEMENTS

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3 W. Mahler, *J. Amer. Chem. Soc.*, 90 (1968) 523.