

Examination of the PMR-spectrum of dihydroketomanoyl oxide confirms the mass-spectrometric results. The intensity of the signal at 206 c/s (from internal benzene standard in dilute  $\text{CCl}_4$  solution; 40 Mc/s) indicates the presence of four hydrogen atoms on the carbon atoms adjacent to the keto group.

Ketomanoyl oxide, in methanol solution, showed a comparatively <sup>7,8</sup> large positive Cotton effect ( $[\alpha]_{500} + 400^\circ$ ;  $[\alpha]_{313} + 3300^\circ$ ;  $[\alpha]_{275} - 3700^\circ$ ;  $[\alpha]_{275} - 3600^\circ$ ), which, as in the case of 3-oxo terpenoid-type compounds, was not lowered on addition of hydrochloric acid <sup>9</sup>. The inability to form a hemiketal is probably caused by 1,3-interaction of the axial methyl substituents.

Deuterium exchange <sup>10</sup> was effected by boiling dihydroketomanoyl oxide <sup>4</sup>, m.p. 91–92° (50 mg), with a solution obtained from sodium (7 mg), O-deuteromethanol (1.5 ml) and deuterium oxide (0.5 ml) under oxygen-free nitrogen for 10 min. followed by removal of the solvents. The procedure was repeated three times with fresh solvents. Addition of deuterium oxide (3 ml) to the residue and extraction with dry ether gave, after drying, removal of the solvent and sublimation of the residue, tetradeuterodihydroketomanoyl oxide, m.p. 89–92°.

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## Inductive Effects on the Donor Strengths of Some Oxo Compounds

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In a recent paper <sup>1</sup> it was reported that esters and ketones have almost equal donor strengths in reactions with  $\text{SbCl}_5$ . Passing from ketones to esters two main effects can be predicted. Thus the inductive effect would lead to a reduction of the donor strength owing to withdrawal of electrons from the carbonyl oxygen atom. This would be opposed, however, by delocalization of one of the lone pair of electrons of the ether oxygen atom. For the carbonyl oxygen atom the two effects seem to be of the same magnitude and on balance no appreciable difference is obtained. This is also reflected in the C=O bond lengths, which are almost equal in ketones and esters. On the other hand, in the presence of halogens, the inductive effect is dominant and the C=O bond lengths are shorter <sup>2</sup>. It has been shown moreover that halogen substitution has the same effect on the donor strengths of compounds containing S=O, Se=O and P=O bonds <sup>1</sup>. In this paper we report the effect of alkoxy substitution on the donor strengths of these compounds in order to determine the balance between the inductive and delocalization effects. The following esters have been studied:  $(\text{CH}_3\text{O})_2\text{SeO}$ ,  $(\text{CH}_3\text{O})_2\text{SO}$ ,  $(\text{CH}_3\text{O})(\text{CH}_3)\text{SO}_2$  and  $(\text{CH}_3\text{O})_3\text{PO}$ .

*Experimental.* Dimethylselenite,  $(\text{CH}_3\text{O})_2\text{SeO}$ , was prepared according to Michaelis and Landmann <sup>3</sup>. B.p. + 62–65°/11 mm.

Dimethyl sulfite,  $(\text{CH}_3\text{O})_2\text{SO}$ , was prepared according to Woss <sup>4</sup>. B.p. + 125°.

