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 CCl<sub>4</sub> 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 7,8 large positive Cotton effect ( $[a]_{500} + 400^{\circ}$ ;  $[a]_{318} + 3300^{\circ}$ ;  $[a]_{275} - 3700^{\circ}$ ;  $[a]_{273} - 3600^{\circ}$ ), which, as in the case of 3-oxo terpenoid-type compounds, was not lowered on addition of hydrochloric acid 9. The inability to form a hemiketal is probably caused by 1,3-interaction of the axial methyl substituents.

Deuterium exchange 10 was effected by boiling dihydroketomanoyl oxide 4, 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 proceedure 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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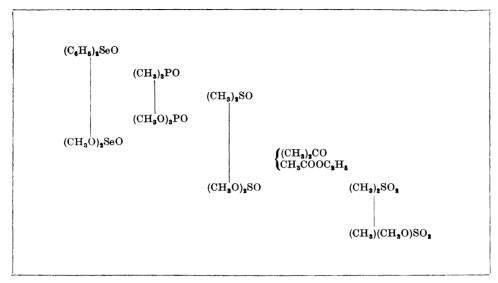
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n a recent paper it was reported that esters and ketones have almost equal donor strengths in reactions with SbCl<sub>5</sub>. Passing from ketones to esters two main effects can be predicted. Thus the inductive effect would lead to a reduction of 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 2. It has been shown moreover that halogen substitution has the same effect on the donor strengths of compounds  $\tilde{S}e = 0$  and containing S = 0, bonds 1. 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: (CH<sub>3</sub>O)<sub>2</sub>SeO,  $(CH_3O)_2SO$ ,  $(CH_3O)(CH_3)SO_2$ (CH<sub>3</sub>O)<sub>3</sub>PO.

Experimental. Dimethyl selenite, (CH<sub>2</sub>O)<sub>2</sub>SeO, was prepared according to Michaelis and Landmann <sup>3</sup> Rn ± 62 = 65°/11 mm

mann <sup>3</sup>. B.p. + 62-65°/11 mm. Dimethyl sulfite, (CH<sub>3</sub>O)<sub>2</sub>SO, was prepared according to Woss <sup>4</sup>. B.p. + 125°.

Table 1. Relative donor strengths (decreasing from top to bottom). The magnitudes of the displacements between the molecules do not correspond to quantitative measurements.



Methyl methansulfonate, (CH<sub>3</sub>O)(CH<sub>3</sub>)SO<sub>3</sub>, was prepared according to Karbatow 5. B.p.  $+200-202^{\circ}$ .

Trimethyl phosphate, (CH<sub>3</sub>O)<sub>3</sub>PO, was prepared according to Drushel 6. B.p. 85-87°/12

All experiments were made in ethylene chloride solutions as described in an earlier paper 1.

Results and discussion. The relative donor strengths with  $SbCl_5$  as acceptor molecule are given in Table 1. It is immediately clear that in all cases the substitution has produced quite a different result from that obtained for ketones. The inductive effect is obviously dominant. It is too early to conclude from the individual differences anything which would indicate particularly large inductive effects on the Se = O bond. Further structural and thermochemical work is needed.

In this connection, consideration of the consequence of adduct formation on the bonds in the oxo compounds shows that the inductive effect should be most pronounced. The weakening of the carbonyl bond in esters of carboxylic acids and the strengthening of the adjacent C-O bond can also be described primarily, as an inductive effect? further favoured by the delocalization effect. Thus by adduct formation the two effects reinforce giving a

particularly large net effect in esters of carboxylic acids. However, by substitution (passing from ketone to ester) they are opposed, so that the net effect is almost negligible. In resonance language the effect of delocalization is expressed by

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