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Interaction between Aldehyde and Tris(trimethylsiloxy)aluminum

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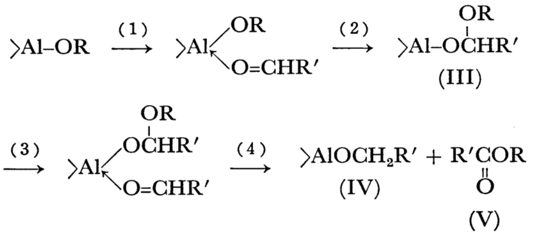
The syntheses and properties of aluminum silanolates and organoaluminum silanolates have been reported by several workers.[1-3] We have now compared their catalytic properties with those of metal alkyls and metal alcoholates in the polymerizations of aldehydes and cyclic ethers.[4,5] Tris(trimethylsiloxy)aluminum (I), $\text{Al(OSiMe}_3)_3$, was compared with aluminum *t*-butoxide (II) as a catalyst for the Tishchenko reaction,[6] which is closely related to the aldehyde polymerization.[7-9]

The Tishchenko reaction proceeds through a cycle of four steps:[7-9]



$$>\text{Al–OR} \xrightarrow{(1)} >\text{Al}\begin{smallmatrix}\nearrow\text{OR}\\ \searrow\text{O=CHR}'\end{smallmatrix} \xrightarrow{(2)} \underset{\text{(III)}}{>\text{Al–O}\overset{\text{OR}}{\overset{|}{\text{C}}}\text{HR}'}$$

$$\xrightarrow{(3)} >\text{Al}\begin{smallmatrix}\nearrow\text{O}\overset{\text{OR}}{\overset{|}{\text{C}}}\text{HR}'\\ \searrow\text{O=CHR}'\end{smallmatrix} \xrightarrow{(4)} \underset{\text{(IV)}}{>\text{AlOCH}_2\text{R}'} + \underset{\text{(V)}}{\text{R}'\underset{\underset{\text{O}}{\|}}{\text{C}}\text{OR}}$$

(1) The coordination of aldehyde with an aluminum alcoholate. (2) The transfer of the alkoxyl group to the carbonyl of aldehyde to form an aluminum alcoholate of hemiacetal (III). (3) The coordination of the second aldehyde molecule to the hemiacetal alcoholate. (4) Hydride transfer from the hemiacetal alcoholate onto the second aldehyde to produce an aluminum alcoholate (IV) and ester (V). After the first cycle, the so-called Tishchenko ester, $\text{R}'\text{CO}_2\text{CH}_2\text{R}'$ (VI), is continuously produced. We[5] disclosed previously that the reaction on *n*-butyraldehyde with I did not produce the silyl ester of *n*-butyric acid, which was expected from the above scheme, but did give the *n*-butyrate of the aldol of *n*-butyraldehyde as a by-product.[6] In this reaction aldol was first formed; it was then reacted with I to give its aluminum alcoholate, which in turn acted as an initiator of the Tishchenko reaction of *n*-butyraldehyde, producing *n*-butyl *n*-butyrate.

The present study was designed to examine the interaction of I with aldehyde along the lines of the above scheme of the Tishchenko reaction.

The coordination of *n*-butyraldehyde with I was demonstrated by the shift of the IR carbonyl band of aldehyde, $\Delta\nu_{\text{C=O}}$, caused by I (145 cm^{-1}); this shift was even greater than that caused by II (140 cm^{-1}). The corresponding values of $\Delta\nu_{\text{C=O}}$ for CCl_3CHO were 125 cm^{-1} and 114 cm^{-1} respectively. The coordination was also indicated by NMR; *i. e.*, the chemical shift of aldehyde hydrogen in the NMR of a mixture of benzaldehyde and I was found to depend upon their ratio. This observation corresponds to that in the NMR spectrum of the acetone-aluminum isopropoxide system.[10]

The siloxyl transfer from I to aldehyde was examined by means of study by the NMR spectrum. We have demonstrated previously that the hydrogen of the aluminum alcoholate of hemiacetal III shows a chemical shift different from that of the formyl hydrogen of the starting aldehyde.[11] In the NMR spectrum of a mixture of I and benzaldehyde in *n*-heptane at 20°C, no new signal was detected after 3 days. This observation may be taken as obviating the transfer of the siloxyl group to benzaldehyde. In chloral, however, the transfer of the siloxyl group to chloral does take place, as is indicated by the formation of $\text{CCl}_3\text{CO}_2\text{SiMe}_3$. The difference in reactivity between benzaldehyde and chloral toward the siloxyl transfer may be explained by the electron-withdrawing effect of the trichloromethyl group; *i. e.*, chloral is more electrophillic, and hence it is more reactive.

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1) T. Saegusa, T. Ueshima, T. Nakajima and J. Furukawa, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **68**, 2514 (1965).

2) T. Saegusa, T. Ueshima and K. Kato. This Bulletin, to be published.

3) T. Saegusa, S. Kitagawa and T. Ueshima, *ibid.*, **40**, 1960 (1967).

4) J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," John Wiley & Sons, New York (1963).

5) J. Furukawa, T. Saegusa and H. Fujii, *Makromol. Chem.*, **44/46**, 398 (1961).

6) T. Saegusa, K. Hirota, E. Hirasawa and H. Fujii, This Bulletin, **40**, 967 (1967).

7) V. J. Shiner and D. Whittaker, *J. Am. Chem. Soc.*, **85**, 2337 (1963).

8) T. Saegusa, T. Ueshima, K. Kauchi and S. Kitagawa, *J. Org. Chem.*, in press.

9) T. Saegusa, K. Hirota, E. Hirasawa and H. Fujii, This Bulletin, **40**, 967 (1967).

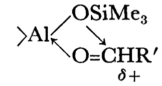
10) V. J. Shiner and D. Whittaker, *J. Am. Chem. Soc.*, **85**, 2337 (1963).

11) T. Saegusa, T. Ueshima, K. Kauchi and S. Kitagawa, *J. Org. Chem.*, **33**, 3657 (1968).

Table 1. Reaction between aldehydes and aluminum compounds

Aldehyde	Reaction condition	Products (%)			
		I		II	
C_6H_5CHO	a	No reaction		$C_6H_5COOCH_2C_6H_5$	98
		No reaction		$C_6H_5COOC(CH_3)_3$	1.2[d]
CCl_3CHO	b	$CCl_3COOCH_2CCl_3$ (VII)	70.6	(VII)	0
		$CCl_3COOSi(CH_3)_3$ (VIIII)	0.2[d]	$CCl_3COOC(CH_3)_3$ (IX)	0
				$>AlOCH(CCl_3)OC(CH_3)_3$[e]	41[d]
CCl_3CHO	c	VII	29.4		0.3
		VIII	0.2[d]		0.1[d]

a) Aldehyde 0.1 mol, aluminum compound 0.01 mol, *n*-heptane 10 m*l*, 20°C 3 days.
b) Aldehyde, aluminum compound, each 0.1 mol, *n*-heptane 40 m*l*, 30°C 13 days.
c) Aldehyde 0.1 mol, aluminum compound, 0.01 mol, benzene 50 m*l*, 80°C 10 hr.
d) Yield (%) based upon the initial aluminum.
e) The quantity was determined by the method described in the experimental section.



The hydride transfer from the alcoholate of silylhemiacetal to the coordinating aldehyde seems to occur quite easily. The formation of trimethylsilyl trichloroacetate from chloral and I implies the transfer of the hydrogen of the alcoholate of silylhemiacetal, $>AlO\underset{\overset{|}{CCl_3}}{C}HOSiMe_3$, to chloral in spite of the electron-withdrawing trichloromethyl group in the alcoholate. Therefore, the absence of the formation of n-$C_3H_7COOSiMe_3$ in the reaction of I with n-C_3H_7CHO may be ascribed to the lack of siloxyl transfer, but not to the lack of a hydride transfer reaction.

In the scheme from (1) to (4), the ester (V) consisting of the alkoxyl (or siloxyl) group which is originally attached to the catalyst was the key compound. The possibility of an ester exchange reaction between the catalyst alkoxyl group and the ester (VI) producing V has been eliminated by reference experiments; *i. e.*, a mixture of I or II and the VI ester under the same conditions did not give V. Furthermore, trimethylsilyl *n*-butyrate was found to be fairly stable; it does not decompose during the reaction.

In conclusion, the difference in catalyst behavior between I and II is due to the difference in transfer reactivity between siloxyl and alkoxyl groups. The lower reactivity of siloxyl transfer may be ascribed to a decreased nucleophilicity of the siloxyl group because of the electron-withdrawing effect of silicon through the $d\pi$-$p\pi$ bond. This assumption is supported by the lower basicity of trimethylsilanol compared with trimethylcarbinol.[12]

Experimental

Materials. I and II were prepared and purified by procedures described before.[6] The benzaldehyde and chloral were commerical reagents which had been purified by repeated fractional distillations. Trimethylsilyl trichloroacetate, $CCl_3CO_2SiMe_3$, was prepared from sodium trichloroacetate and chlorotrimethylsilane by a procedure described before.[6]

$CCl_3CO_2SiMe_3$ is quite vulnerable to moisture and is readily hydrolyzed. The product was identified as follows. The NMR spectrum of $CCl_3CO_2SiMe_3$ shows a sharp singlet at 0.40 ppm (δ) assignable to protons of Si–CH_3. The product, 0.5375 g, was decomposed with water, and hexamethyldisiloxane was extracted with ethyl ether and analyzed by vpc. The CCl_3CO_2H in the water layer was titrated with 1/10 N NaOH. $Me_3SiOSiMe_3$.

Found: 0.1834 g. Calcd: 0.1852 g. Acidity, Found: 2.298×10^{-3} mol. Calcd: 2.282×10^{-3} mol.

The 2,2,2-trichloroethyl trichloroacetate was prepared by the method described in the literature.[13]

Products Analyses. The products were identified by vpc using two columns (PEG 20000 and Silicone DC 550). Silicone DC 550 and dioctyl phthalate were used for the identification of $CCl_3CO_2SiMe_3$.

Reactions of Chloral. A representative procedure was as follows. A mixture of 0.01 mol of chloral, 0.01 mol of I, and 40 m*l* of *n*-heptane was kept in a sealed tube at 30°C for 13 days. In order to avoid the hygroscopic decompsotion of the products, the reaction mixture was directly analyzed by vpc. The products were $CCl_3CO_2CH_2CCl_3$ (70.6%) and $CCl_3COOSiMe_3$ (0.21%). In the case of the reaction with aluminum *t*-butoxide, no reaction product was detected by vpc analysis. When the reaction system was treated with excess acetic anhydride and was subjected to vacuum distillation, 41% of $AcOCH(CCl_3)OCMe_3$ was obtained.

Found: C, 36.71; H, 5.18; Cl, 40.46%. Calcd for $C_8H_{13}O_3Cl_3$: C, 36.46; H, 4.97; Cl, 40.36%.

The NMR and IR spectra were compatible with this structure. The formation of this compound clearly

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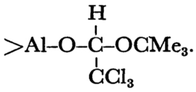
[12] R. West and R. H. Baney, *J. Am. Chem. Soc.*, **81**, 6145 (1959).

[13] R. Dworzak, *Monatsh*, **47**, 11 (1927).

indicates the presence of  $>\mathrm{Al{-}O{-}}\overset{\mathrm{H}}{\underset{\mathrm{CCl_3}}{\mathrm{C}}}\mathrm{{-}OCMe_3}$.

Reaction of Benzaldehyde. A procedure similar to the above was adopted. After the reaction, the products were identified and determined quantitatively by vpc analysis without any after-treatment. In the case of I, no reaction product was found. In the NMR spectrum of the I-benzaldehyde system after the reaction, no signal except for those assignable to the starting reagents was recognized.