BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1960—1964 (1967)

# Reactions of Aldehyde Caused by Tris(trimethylsiloxy)aluminum

Takeo SAEGUSA, Sadao KITAGAWA and Takashi UESHIMA

*Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto*

(Received March 4, 1967)

Reactions of *n*-butyraldehyde caused by tris(trimethylsiloxy)aluminum were examined and compared with those caused by aluminum *t*-butoxide. In the Tishchenko reaction of aldehyde caused by aluminum *t*-butoxide, the *t*-butoxy group was first transferred from aluminum to the carbonyl group of *n*-butyraldehyde to produce *t*-butyl *n*-butyrate. On the other hand, we observed no formation of trimethylsilyl *n*-butyrate by the transfer of the trimethylsiloxy group to *n*-butyraldehyde. However, esters of the *n*-butyric acid of *n*-butanol and the glycol derived from the aldol of *n*-butyraldehyde were found in the system with tris(trimethylsiloxy)aluminum: their formation was ascribed to the aluminum alkoxide species which was first formed between tris(trimethylsiloxy)aluminum and the aldol of *n*-butyraldehyde. The above assumption has been supported by the finding that aluminum *t*-butoxide caused the Tishchenko reaction of benzaldehyde, producing benzyl benzoate almost quantitatively, whereas tris(trimethylsiloxy)-aluminum did not cause any change because aldol condensation was impossible for benzaldehyde.

There have been established several synthetic reactions involving aluminum alkoxide and aldehyde, *e.g.,* the Meerwein-Ponndorf-Verley reduction, the Oppenauer oxidation, and the Tishchenko reaction. We found the polymerization of aldehyde by an aluminum alkoxide catalyst[1-3] and pointed out its close relationship with the above organic reactions.[2,3] From analogical inference, we then

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[1] J. Furukawa, T. Saegusa, H. Fujii, A. Kawasaki, H. Imai and Y. Fujii, *Makromol. Chem.,* **37**, 149 (1960).

[2] J. Furukawa, T. Saegusa and H. Fujii, *ibid.,* **44/46**, 398 (1961).

[3] J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," John Wiley & Sons, New York (1963), pp. 94—103.

examined the catalytic activity of tris(trimethylsiloxy)aluminum (I), $Al[OSi(CH_3)_3]_3$, for the polymerization of acetaldehyde. Although I caused the acetaldehyde polymerization, it differed from aluminum alkoxide in the stereoregularity of the product polymer of acetaldehyde.[4]

In the present studies we examined the behavior of I as the catalyst for the reactions of aldehyde and compared it with the behavior of aluminum *t*-butoxide, $Al[OC(CH_3)_3]_3$ (II).

## Experimental

All the reactions described below were carried out under a nitrogen atmosphere.

**Reagents.** *Aldehydes.* Commercial reagents of *n*-butyraldehyde and benzaldehyde were dried over anhydrous sodium sulfate and purified by repeated fractional distillation through a 30 cm Widmar column. By gas chromatography, the purities of the two aldehydes were found to be 99.90—99.99%.

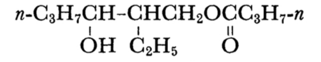
*Trimethylsilanol.* According to the procedure of Sommer *et al.*,[5] trimethylsilanol was prepared and purified by fractional distillation, bp 99.5—99.7°C.

*Tris(trimethylsiloxy)aluminum (I).* I was prepared by a new method using the reaction of triethylaluminum ($Al(C_2H_5)_3$) with trimethylsilanol. The method of preparing I described in the literature begins from $AlCl_3$ and $(CH_3)_3SiONa$.[6] Compared with this, the present procedure is much more convenient, since the isolation of the product is easier. To $Al(C_2H_5)_3$ in benzene, a benzene solution of trimethylsilanol was added, drop by drop, in three portions. After the first portion of trimethylsilanol had been added at 0°C with stirring and ice-cooling, the reaction mixture was once warmed at 25°C for 2 hr, and then cooled again to 0°C; the second portion was then added. The reaction mixture, after the addition of the third portion, was finally heated to reflux for 3 hr. The total amount of $(CH_3)_3SiOH$ was 5% in excess of the stoichiometric amount of $Al(C_2H_5)_3$. From the residue left after the freeze-drying of the benzene solution, I was isolated by sublimation at 155°C/1.2 mmHg. The yield was 85—90%. The product was identified by means of its melting point (mp 238°C[6]) and its NMR spectrum. The high purity of the product in the present studies was further assured by the gas chromatographical analysis of the total amount of trimethylsilanol and hexamethyldisiloxane in the acid hydrolysis mixture of the product.

*Solvents.* Benzene and *n*-heptane were purified by the usual procedures and finally distilled over Na-K alloy.

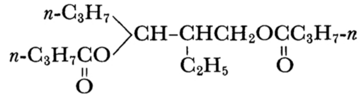
**Reaction of *n*-Butyraldehyde.** A mixture of an aluminum compound (I or II) and *n*-butyraldehyde in a solvent was stirred at an appropriate temperature for the indicated length of time. Then the reaction mixture was subjected to vacuum distillation at 0.1 mmHg and at temperatures up to 60°C, after which the distillate was analyzed by gas chromatography. Reference experiments showed that *n*-butyraldehyde, trimethylsilanol, *n*-butyl *n*-butyrate, *t*-butyl *n*-butyrate, and trimethylsilyl *n*-butyrate were isolated almost quantitatively from the reaction mixture by the vacuum distillation, if they were present. The residue of the vacuum distillation was hydrolyzed by dilute hydrochloric acid, and the acid hydrolysis mixture was extracted with ether. The ether extract was analyzed by gas chromatography.

2-Ethyl-1, 3-hexanediol-1-*n*-butyrate (III) and 2-ethyl-1, 3-hexanediol di-*n*-butyrate (IV) were isolated in the distillation of the ether extract of the less volatile part (bp 137°C/8 mmHg and 132—135°C/5 mmHg respectively); they were identified by elemental analysis and by means of their infrared and NMR spectra, and also by the quantitative analysis by gas chromatography of the 2-ethyl-1, 3-hexanediol in the alkaline hydrolysis mixture of the two substances.



$$n\text{-}C_3H_7\underset{\mid \atop OH}{CH}\text{-}\underset{\mid \atop C_2H_5}{CH}CH_2O\underset{\parallel \atop O}{C}C_3H_7\text{-}n$$

(III)



$$\left.\begin{array}{l} n\text{-}C_3H_7 \\ n\text{-}C_3H_7\underset{\parallel \atop O}{C}O \end{array}\right\rangle CH\text{-}\underset{\mid \atop C_2H_5}{CH}CH_2O\underset{\parallel \atop O}{C}C_3H_7\text{-}n$$

(IV)

**Reaction of Benzaldehyde.** A similar procedure was adopted.

**Product Analysis.** The reaction products were identified by gas chromatography with two columns, silicone DC550 and PEG 20000, and were quantitatively analyzed by means of the peak-area technique.

**Syntheses of Authentic Samples.** The following compounds were prepared as the authentic samples in gas chromatography.

*2-Ethyl-2-hexenal (V)* was prepared by the distillation, with the accompanying dehydration, of 2-ethyl-3-hydroxyhexanal (butyraldol)[7] and was purified by distillation, bp 172.5—173.0°C.[8]

*Trimethylsilyl n-Butyrate* was prepared as follows. A benzene solution of chlorotrimethylsilane was added to a suspension of sodium *n*-butyrate in benzene at 55—59°C. The molar ratio of $(CH_3)_3SiCl/C_3H_7CO_2Na$ was 2.0. The reaction mixture was then refluxed for 7 hr. The benzene layer was distilled to give trimethylsilyl *n*-butyrate, bp 142—143°C.

Found: C, 50.89; H, 10.01%. Calcd for $C_7H_{16}O_2Si$: C, 51.18; H, 9.82%. The yield was 21% (based upon the sodium *n*-butyrate).

The other esters of the authentic samples were prepared by the reaction of acid chloride and alcohol.

## Results and Discussion

The results of the reactions of *n*-butyraldehyde caused by I and by II are compared with each other in Table 1. It is shown that the natures and composition of the products of two the catalysts

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

[5] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 2282 (1946).

[6] H. Schmidbaur, *Angew. Chem.*, **77**, 206 (1965).

[7] M. V. Grignard and A. Vesterman, *Bull. Soc. Chim. France*, **37**, 425 (1925).

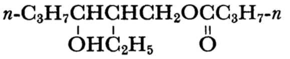
[8] C. Weizmann and S. F. Garrad, *J. Chem. Soc.*, **117**, 324 (1920).

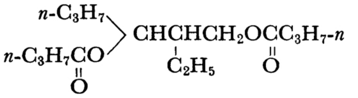
are quite similar in the reactions at 20°C, but that they differ from each other at 80°C. Two observations have been made to distinguish the two catalysts from each other. First, the admixing of *n*-butyraldehyde with II caused heat-evolution, whereas that with I did not. Secondly, *t*-butyl *n*-butyrate (VI) was formed in the reaction with the catalyst II, whereas trimethylsilyl *n*-butyrate was not formed with the catalyst I. In addition to the products indicated in Table 1, small amounts of trimethylsilanol (VII) and V were found in the reaction mixture with I.

TABLE 1. REACTION OF *n*-BUTYRALDEHYDE

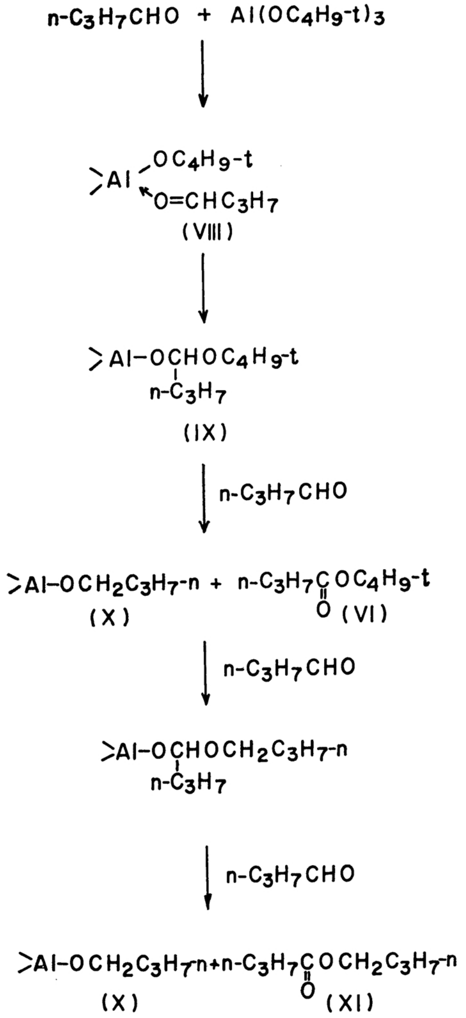
| Reaction condition | Catalyst | Unreacted aldehyde[a)] % | Product yield, %[a)] | | |
|---|---|---|---|---|---|
| | | | *n*-Butyl *n*-butyrate | III[b)] | IV[c)] |
| 20°C<br>6 days | I | 2.3 | 71.8 | 2.7 | 5.5 |
| | II | 0 | 81.5 | trace | 2.8 |
| 80°C<br>6 hr | I | 11.0 | 15.7 | 37.0 | 12.5 |
| | II | 0.2 | 62.7 | 6.5 | 6.5 |

a) Based on the initially charged *n*-butyraldehyde

b)

$n\text{-}C_3H_7\underset{OH}{C}H\underset{C_2H_5}{C}HCH_2O\underset{O}{C}C_3H_7\text{-}n$

c)

$\begin{matrix}n\text{-}C_3H_7\\ n\text{-}C_3H_7\underset{O}{C}O\end{matrix}\Big\rangle CH\underset{C_2H_5}{C}HCH_2O\underset{O}{C}C_3H_7\text{-}n$

The formation of VI (in a yield of about 10% (based on II)) can be reasonably explained by Scheme 1. Thus, the *t*-butoxy group is transferred in a complex (VIII) from aluminum to the coordinated *n*-butyraldehyde molecule[1-3)] to form an aluminum alkoxide of hemi-acetal (IX). Then

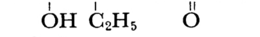


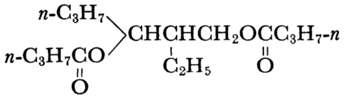
Scheme 1

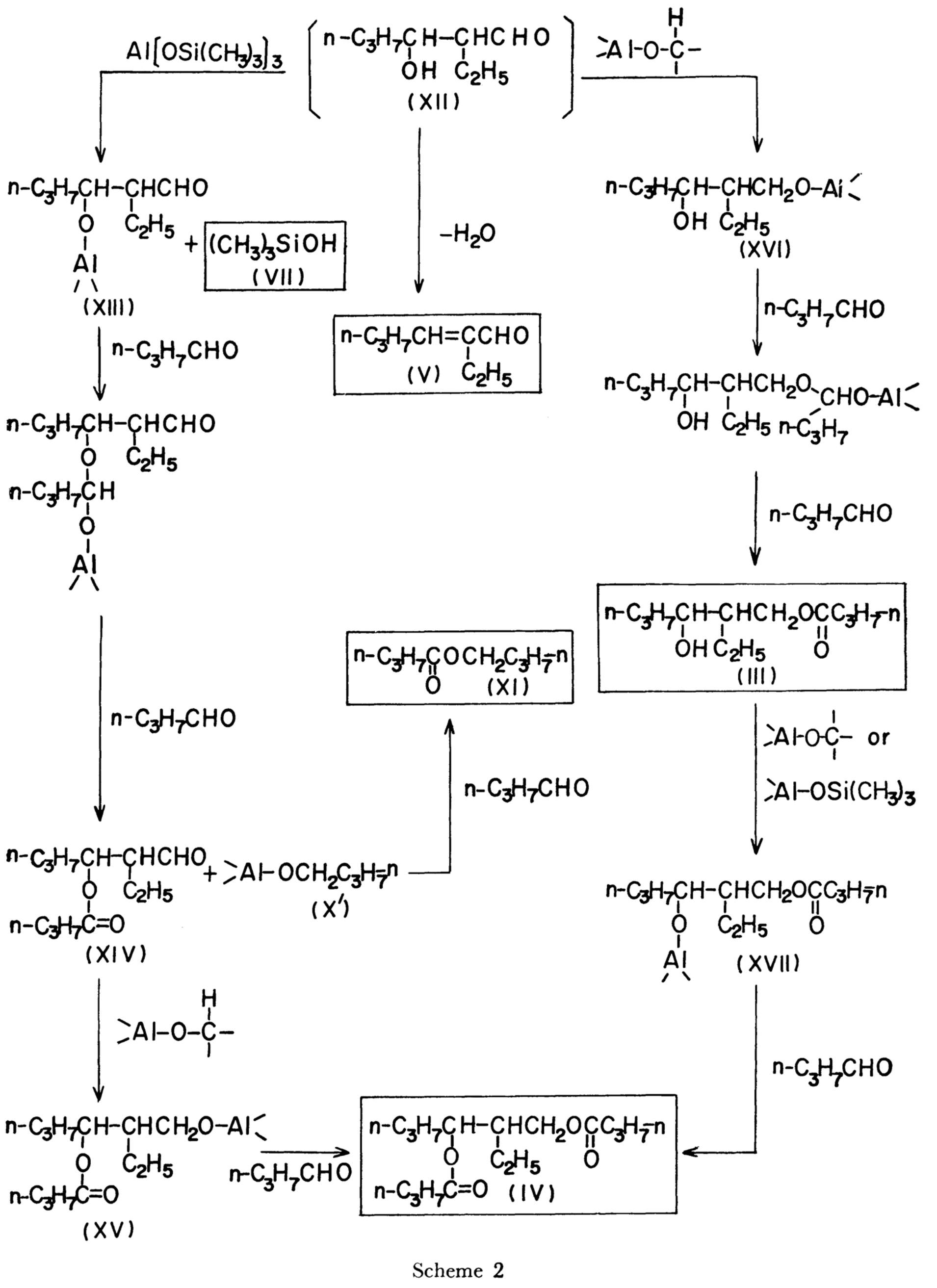
TABLE 2. REACTION OF *n*-BUTYRALDEHYDE WITH Al[OSi(CH$_3$)$_3$]$_3$ CATALYST[a)]

| Reaction time hr | Conversion % | Product, mmol | | | |
|---|---|---|---|---|---|
| | | (CH$_3$)$_3$SiOH | *n*-Butyl *n*-butyrate | III[b)] | IV[c)] |
| 1/6 | 4.9 | 1.36 | 0.66 | | |
| 1/2 | 8.1 | 2.46 | 1.87 | 0.0432 | 0.0560 |
| 1 | 12.5 | 2.95 | 5.75 | 0.0405 | 0.129 |
| 3 | 45.1 | 3.38 | 30.1 | 0.131 | 0.445 |
| 6 | 73.2 | 4.58 | 50.0 | 0.228 | 0.875 |
| 11 | 83.1 | 5.96 | 58.1 | 0.259 | 1.16 |
| 24 | 91.8 | 7.92 | 62.7 | 0.765 | 2.11 |

a) A mixture of 169 mmol of *n*-butyraldehyde, 17.8 mmol of Al[OSi(CH$_3$)$_3$]$_3$ and 70 m*l* of *n*-heptane were maintained at 20±1°C. Several portions were drawn for analysis at appropriate intervals.

b) III:

$n\text{-}C_3H_7\underset{OH}{C}H\text{-}\underset{C_2H_5}{C}HCH_2O\underset{O}{C}C_3H_7\text{-}n$

c) IV:

$\begin{matrix}n\text{-}C_3H_7\\ n\text{-}C_3H_7\underset{O}{C}O\end{matrix}\Big\rangle CH\underset{C_2H_5}{C}HCH_2O\underset{O}{C}C_3H_7\text{-}n$



Scheme 2

the hydride transfer from IX to the second *n*-butyraldehyde produces VI and the aluminum *n*-butoxide species (X). A similar process starting from X affords *n*-butyl *n*-butyrate (XI), the principal product of the Tishchenko reaction.

In the reaction caused by I as the catalyst, VII was found in the vacuum distillate prior to hydrolysis, but trimethylsilyl *n*-butyrate was not. This finding, as well as the difference in product composition between the reactions caused by I and II at 80°C, suggests a difference in catalytic mechanism between I and II.

Table 2 illustrates the change in product composition in the progress of the reaction caused by I. It may be seen that the formation of VII prevails over that of XI in the initial stage of reaction (up to a half hour), and that mono-ester (III) and di-ester (IV), which are derived from the aldol condensation products, are produced in considerable amounts even at the beginning of the reaction.

The foregoing observation on the reaction caused by I can be explained by Scheme 2. Aldol (XII) is first formed, probably by the catalysis with I; this then reacts with I to produce the aluminum alkoxide species (XIII) and VII. Starting from XIII, the Tishchenko reaction between aldehydes (*n*-butyraldehyde, XII, and XIV) and aluminum alkoxide species (XIII, X′, XV, XVI and XVII) produces various ester products. The compounds enclosed by squares in Scheme 2 were found in the reaction system.

The assumption that the initiation of the Tishchenko reaction in the system with I is to be ascribed to the aluminum alkoxide species of aldol, but not to I itself, has been supported by the results of the reaction of benzaldehyde. A mixture of 27.8 mmol of benzaldehyde and 2.68 mmol of II in 3.0 m*l* of *n*-heptane maintained at 20°C gave benzyl benzoate in a yield of 98%. However, a similar reaction with I did not afford any benzyl benzoate. In principle, the aldol condensation of benzaldehyde is not considered; hence, the aluminum alkoxide species responsible for the Tishchenko reaction is not formed. The addition of an equimolar amount of butyraldol to I in the benzaldehyde system caused the Tishchenko reaction to afford benzyl benzoate in a yield of 3.3%.