15 hr followed by the addition of 23 ml of water gave 10.8 g of material, bp 38–55°. Distillation through a 5-in. Vigreux column yielded 9.6 g (47%) of 3-methyl-1,2-butadiene: bp 39.5–41.0°; nmr, τ 5.55 (septet, 2, $J = 2.9$ Hz, $C{=}C{=}CH_2$) and 8.37 (t, 6, $J = 2.9$ Hz, CH_3). Glpc analysis indicated that this material was homogeneous. The absence of 3-methyl-1-butyne, 3-methyl-1-butene, and 3-methyl-2-butene was shown by glpc retention time comparison.

3-Methyl-1,2-butadiene-1-d_1.—Treatment of 2.05 g of **1a** with 0.42 g of lithium aluminum deuteride gave 0.75 g (55%) of 3-methyl-1,2-butadiene-1-d_1 of 96% purity by glpc analysis: bp 35–55°; nmr, τ 5.58 (m, 1.00 ± 0.1 H, $C{=}C{=}CH$) and 8.37 (d, 6, $J = 3.1$ Hz, CH_3).[15] Mass spectral analysis indicated 5% d_0, 94% d_1, 1% d_2.

One-Step Preparation of 3-Methyl-1,2-butadiene.—2-Methyl-3-butyn-2-ol (84 g) was added dropwise to a vigorously stirred slurry of 111 g of calcium chloride, 420 ml of concentrated hydrochloric acid, and 1.0 g of hydroquinone. After stirring for 45 min, the top layer was separated and dried over sodium carbonate. After filtration, 54 g of the crude filtrate (90 g total) was treated for 15 hr with 5.7 g of lithium aluminum hydride in 150 ml of diethyl carbitol. After addition of 25 ml of water, material of boiling point range 40–55° was collected. Distillation gave 12.0 g (29%) of 3-methyl-1,2-butadiene which was homogeneous by glpc.

3-Methyl-1-butyne.—Treatment of 14.7 g of **2b** with 1.9 g of lithium aluminum hydride in 60 ml of diethyl carbitol for 15 hr followed by the addition of 8 ml of water gave 4.9 g (72%) of material, bp 30–35°, which was identified as 3-methyl-1-butyne (90%) [ir, 3.05 ($C{\equiv}CH$), 4.72 ($C{\equiv}C$), 7.28 and 7.38 μ (CH_3); nmr, τ 7.55 (septet of doublets, 1, $C{\equiv}CCH$), 8.13 (d, 1, $J = 2$ Hz, $C{\equiv}CH$), and 8.86 (d, 3, $J = 6.5$ Hz, CH_3)] and 3-methyl-1-butene (10%).

3-Methyl-1-butyne-3-d_1.—Treatment of 4.3 g of 1-bromo-3-methyl-1,2-butadiene (**2b**) with 0.57 g of lithium aluminum deuteride gave 1.35 g (65%) of material, bp 25–35°, 90% of which was 3-methyl-1-butyne-3-d_1: nmr, τ 8.16 (s, 1, $C{\equiv}CH$) and 8.85 (t, 6, $J = 1$ Hz, CH_3). No signal was observed for the methine proton.

1,2-Hexadiene.—Treatment of 5.8 g of **3b** with 0.95 g of lithium aluminum hydride in 20 ml of diethyl carbitol for 12 hr followed by the addition of 4 ml of water gave 3.3 g of material of boiling range 66–90°. Distillation through a 5-in. Vigreux column yielded 2.9 g (72%) of product which consisted of 1,2-hexadiene (93%): ir, 5.13 ($C{=}C{=}C$), 7.28 (CH_3), 11.5, and 11.9 μ; nmr, at τ 5.04 (quartet, 1, $J = 6.5$ Hz, $C{=}C{=}CH$), 5.4 (m, 2, $C{=}C{=}CH_2$), 8.1 and 8.6 (m, 4), and 9.05 (t, 3, $J = 7$ Hz, CH_3); and an unknown terminal olefin (7%) with infrared absorption at 6.1, 10.1, and 11.0 μ, which was not 1-hexene.

Reduction of 1-Hexyn-3-yl Mesylate.—A slurry of 11 g of lithium aluminum hydride in 300 ml of diethyl carbitol was maintained below 0° in an ice–methanol bath during the dropwise addition of 53 g of crude **3c**. The mixture was then stirred for 5 hr. After recooling to 0°, 46 ml of water was added dropwise. When reaction ceased, volatile material was distilled from the reaction mixture to give 19.8 g (80%) of crude product, bp range 60–90°, which was identified as 89% 1,2-hexadiene and 11% 1-hexyne.

Lithium aluminum hydride reduction of 1-hexyn-3-yl mesylate which had been purified by distillation gave a identical result.

Registry No.—Lithium aluminum hydride, 1302-30-3; **3b**, 761-79-5; **3c**, 17159-63-6; 3-methyl-1,2-butadiene, 598-25-4; 3-methyl-1,2-butadiene-1-d_1, 17159-64-7; 3-methyl-1-butyne, 598-23-2; 3-methyl-1-butyne-3-d_1, 17159-65-8; 1,2-hexadiene, 592-44-9.

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The Aluminum Alcoholate of a Hemiacetal. An Intermediate in the Tishchenko Reaction

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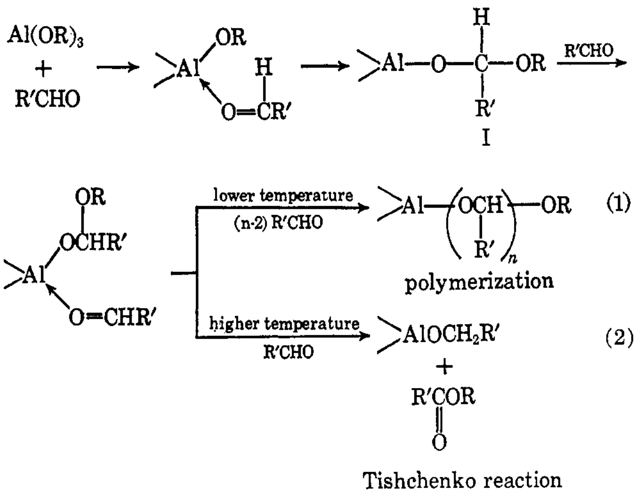
Previously,[1-4] the aluminum alcoholate of a hemiacetal (I) has been formulated as the key intermediate in the polymerization of aldehyde by aluminum alcoholate and in the Tishchenko reaction (eq 1 and 2).



However, other possible mechanisms of the Tishchenko reaction which do not involve the intermediate I have also been presented.[5,6]

In the present study, the aluminum alcoholate of a hemiacetal corresponding to I was isolated in a specified combination of reaction components, *i.e.*, aluminum *t*-butoxide and trichloroacetaldehyde (chloral), and the reactivity of I was examined to obtain support for the scheme shown in eq 1 and 2.

When the reaction was carried out at 30° in *n*-heptane, the aluminum alcoholate of a semiacetal (II) ($R = t\text{-Bu}$, $R' = Cl_3C$ in I) separated as a white crystalline solid from the yellow reaction mixture after 10 days. The amount of II increased progressively up to 30 days (yield 67%). The reaction temperature is quite important for the isolation of II. In the reaction at 0°, only the polymerization of chloral took place to produce an insoluble polymer of chloral. At 60°, only the Tishchenko ester, 2,2,2-trichloroethyl trichloroacetate, was isolated.

The success in isolation of II is also ascribed to the choice of the reaction components. The trichloromethyl group of hemiacetal alcoholate II suppressed the hydride transfer from II to chloral (eq 2) by its

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

[2] J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 94–103.

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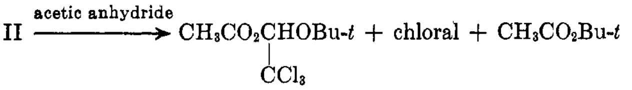
[5] I. Lin and A. R. Day, *J. Amer. Chem. Soc.*, **74**, 5133 (1952).

[6] O. Neunhoffer and E. Ruske, *Chem. Ber.*, **93**, 623 (1961).

electron-withdrawing effect at 30°. The Meerwein–Ponndorf–Verley reduction is another possible reaction of aluminum alcoholate with a carbonyl compound. The possibility of this reaction, however, was eliminated because of the absence of a hydrogen atom on the α-carbon atom in the *t*-butoxy group.

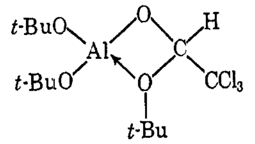
The structure of II was confirmed by elemental analysis and by the products of acid hydrolysis and of acetylation with acetic anhydride, as well as by the nmr spectrum of its benzene solution. Acid hydrolysis of II with acetic acid produced 3 mol of *t*-butyl alcohol per gram atom of aluminum. Treatment of II with acetic anhydride gave the hemiacetal acetate (III) and chloral in addition to *t*-butyl acetate. The combined amount of III and chloral was 0.97 mol/g-atom of aluminum (calcd, 1.00).



$$\mathrm{II} \xrightarrow{\text{acetic anhydride}} \underset{\displaystyle \mathrm{CCl_3}}{\mathrm{CH_3CO_2\underset{|}{C}HOBu\text{-}}t} + \text{chloral} + \mathrm{CH_3CO_2Bu\text{-}}t$$

III

The nmr spectrum of a benzene solution of II showed four signals, *i.e.*, δ 1.36 (s, 9 H), 1.39 (s, 9 H), 1.55 (s, 9 H), and 4.55 (s, 1 H). The three singlets at lower fields were assigned to the three kinds of protons of the *t*-butyl group. The last singlet was ascribed to the hydrogen of the hemiacetal group. Cryoscopic molecular weight of II in benzene was 394 ± 20 (calcd for the monomer, 394). A monomeric structure may reasonably be assumed to be as follows:



IV

Nonequivalence of two *t*-butoxyl groups may be due to the difference in their spatial relations to the trichloromethyl group. The monomeric structure of II in benzene was not stable. After 10 days at room temperature, the nmr spectrum changed to a more complex one. The four sharp singlets broadened and some new signals appeared in the vicinities of the original four singlets. However, the area ratio of the peaks at lower fields to the groups of peaks at higher fields was still 1:27. This finding is interpreted as indicating the retention of the hemiacetal structure.

The reactivity of the hydrogen of compound II with carbonyl compounds was then examined. Among the ketones employed in the present study, only trifluoroacetone was reduced by II to 1,1,1-trifluoropropanol-2. The decreased activity of the hemiacetal hydrogen of II is due to the electron-withdrawing effect of the trichloromethyl group. In addition, II itself induced the polymerization of chloral at 0°.

In conclusion, the scheme of the aldehyde polymerization and the Tishchenko reaction has been supported by the findings of the present study.

Experimental Section

Reaction of Chloral with Aluminum *t*-Butoxide.—A mixture of 0.0132 mol of chloral and 0.0130 mol of aluminum *t*-butoxide in 20 ml of *n*-heptane was kept at 30°. A white crystalline material (II) began to separate from the yellowish reaction system after 10 days. The amount of II increased progressively up to 30 days. Product II was isolated by filtration, washed several times with *n*-heptane, and finally dried *in vacuo* at room temperature. The yield of II was 66.5% (calcd as the 1:1 adduct.).

Anal. Calcd for $C_{14}H_{28}AlCl_3O_4$: Al, 6.85. Found: Al, 6.81. In the glpc analysis of the filtrate, none of the Tishchenko products were detected. Unreacted chloral was 10.4%.

Attempts at further purification of II were futile. Compound II decomposed without melting and subliming *in vacuo*. It was only slightly soluble in benzene and in methylene dichloride. Recrystallization from these solvents was unsuccessful because of the decomposition of II.

The total *t*-butoxyl groups of II was determined by the glpc analysis of *t*-butyl alcohol produced by treatment with an excess acetic acid at room temperature. The ratio of *t*-BuOH/Al was 3.00 (calcd for II, 3.00).

At 60°, a mixture of 0.1 mol of chloral and 0.01 mol of aluminum *t*-butoxide in 20 ml of benzene was kept for 1 day. The reaction mixture was thereafter treated with 1 *N* HCl, and was extracted with ether. The ether extract was analyzed by glpc. The Tishchenko reaction products, trichloroethyl trichloroacetate (5.3%), *t*-butyl trichloroacetate (0.1%), and trichloroethanol (6.8%), were obtained.

Reaction of II with Acetic Anhydride.—A solution of II in toluene was treated with an excess acetic anhydride at 100°. Product III and chloral as well as *t*-butyl acetate were produced. The structure of III was established by elemental analysis and ir and nmr spectra: nmr, δ 6.14 (s, 1 H), 2.06 (s, 3 H) and 1.30 (s, 9 H).

Anal. Calcd for $C_8H_{13}Cl_3O_3$: C, 36.46; H, 4.97; Cl, 40.36. Found: C, 36.71; H, 5.18; Cl, 40.46.

The amounts of III and chloral (mole ratios to aluminum) were 0.695 and 0.274, respectively. The combined amount of the two products was 0.97 (calcd, 1.00).

Reaction of II with 1,1,1-Trifluoroacetone.—A mixture of 0.001 mol of II and 0.01 mol of 1,1,1-trifluoroacetone was heated at 60° for 45 hr. Then the reaction system was treated with an excess acetic acid. 1,1,1-Trifluoroisopropyl alcohol (5.7% based upon the initial aluminum compound) was found by glpc analysis. In the reactions with other ketones such as acetone and benzophenone of less reactivities, however, no corresponding alcohols were detected.

Registry No.—II, 17192-31-3; III, 17203-07-5.

Chemotaxonomy of the Rutaceae. III.[1] Isolation of Halfordinol Derivatives from *Aeglopsis Chevalieri* Swing.

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The isolation of isopimpinellin from the seeds of one of the hard shell citrus, *Aeglopsis chevalieri* Swing. (Rutaceae),[4] was described in a previous communication from this laboratory.[5] This paper describes the isolation, from the whole fruit of this plant, of several coumarins of a type widespread in the Rutaceae as well as a new alkaloid which is shown to be O-isopentenylhalfordinol (**3**).

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[2] Department of Chemistry, San Francisco State College, San Francisco, Calif.

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