tions from 50% ethanol gave 2.27 g. (45%) of acid melting 145–149°. This product was identical with that obtained in the hydrogenation in alkaline solution.

The last three fractions from the fractional acidification were combined to give 0.86 g. (16.8%) of crude 1,2,3,4-tetrahydro-1-naphthoic acid, m.p. 68–75°.

(*c*) *With Platinum in Acetic Acid.*—A suspension of 25 g. (0.145 mole) of 1-naphthoic acid and 1.0 g. of platinum oxide in 200 ml. of acetic acid was hydrogenated at room temperature and a pressure of three atmospheres. During the hydrogenation, some solid precipitated. The reaction mixture was warmed and filtered and upon cooling, 9.2 g. (34.8%) of 5,6,7,8-tetrahydro-1-naphthoic acid, m.p. 146–150°, precipitated. Concentration of the filtrate to 100 ml. yielded an additional 7.3 g. (27.7%) of material melting 146–150°. After removal of all of the acetic acid and fractional crystallization from 50% ethanol, 2.3 g. (9.5%) of the 1,2,3,4-tetrahydro isomer, m.p. 65–75°, was obtained.

Berkeley 4, California Received October 16, 1950

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

Ketene Acetals. XXIII. Dealcoholation of Orthoesters with Aluminum *t*-Butoxide

By S. M. McElvain and William R. Davie

Aluminum *t*-butoxide is shown to be an efficient reagent for the dealcoholation of orthoesters to the corresponding ketene acetals. It is particularly valuable for the dealcoholation of the low-boiling orthoesters, *e.g.*, methyl orthoisobutyrate, which distil unchanged from aluminum methoxide and ethoxide. The superiority of aluminum *t*-butoxide over its lower homologs in this reaction is attributed to a greater coördinative capacity resulting from a simpler molecular structure. The properties of two new ketene acetals, dimethylketene diethylacetal and ethoxyketene diethylacetal, are reported.

In paper XXI of this series the facile and practically quantitative dealcoholation of methyl orthophenylacetate to the corresponding ketene acetal with the aprotic acid, aluminum methoxide, was reported.[1] The higher boiling point and the greater reactivity of the α-hydrogen of this orthoester made it possible to effect this dealcoholation by heating the reactants together at 210°. However, the lower boiling and less reactive aliphatic orthoesters, methyl orthopropionate and methyl orthoisobutyrate, simply distilled unchanged from the alkoxide under such conditions. Only partial dealcoholations (8–16%) of these aliphatic orthoesters were effected by passing their vapors through a column of aluminum methoxide heated to 240–290°.

In extending the study of these dealcoholations to the homologous aluminum alkoxides, it has been found that aluminum *t*-butoxide is a particularly effective agent for the dealcoholation of orthoesters to the corresponding ketene acetals. The temperatures of dealcoholation and the yields of the ketene acetals from some representative orthoesters are listed in Table I. In general these dealcoholations occur at much lower temperatures than those previously observed[1] with aluminum methoxide and for this reason each of them may be carried out by heating a mixture of the orthoester and the aluminum *t*-butoxide.

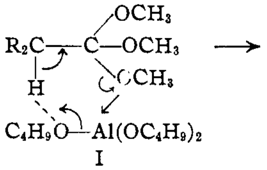
Table I

Dealcoholations of Orthoesters with Aluminum *t*-Butoxide

Orthoester	Mole ratio alkoxide: ester	Reaction temp., °C.	Yield of *t*-C_4H_9-OH, %	Yield of ketene acetal, %
$C_6H_5CH_2C(OCH_3)_3$	1:3	165–180	77	85[a]
$C_6H_5CH_2C(OC_2H_5)_3$	1:3	160–180	82	85[a]
$CH_3C(OC_2H_5)_3$	1:1	180–185	70	65
$CH_3CH_2C(OC_2H_5)_3$	1:1	180–185	86	83
$(CH_3)_2CHC(OCH_3)_3$	1:1	185–190	63	54
$(CH_3)_2CHC(OC_2H_5)_3$	1:1	185–190	82	62
$C_2H_5OCH_2C(OC_2H_5)_3$	1:1	175–180[b]	80	61

[a] This product was contaminated with some of the alkoxide that sublimed during the distillation of the ketene acetal. [b] This dealcoholation was carried out under diminished pressure (see experimental).

A noteworthy feature of these dealcoholations is that pure *t*-butyl alcohol distils from the reaction of methyl and ethyl orthoesters with aluminum *t*-butoxide. This fact supports the earlier suggestion[1] that the alkoxide functions by coördination with the orthoester followed by the concerted elimination of the reaction products from the complex (I):



I

$$C_4H_9OH + \underset{\text{II}}{R_2C{=}C(OCH_3)_2} + \underset{\text{III}}{CH_3O{-}Al(OC_4H_9)_2}$$

With the more reactive methyl orthophenylacetate all of the *t*-butyl groups of aluminum *t*-butoxide may be eliminated as *t*-butyl alcohol, *i.e.*, one mole of the alkoxide converts three moles of the orthoester to the ketene acetal. With the lower-boiling aliphatic orthoesters, it was found necessary to use a molecular equivalent of the alkoxide to prevent distillation of the orthoester and to obtain maximum yields of the ketene acetals.

When either aluminum ethoxide or isopropoxide was used for the dealcoholation of methyl orthophenylacetate, a mixture of methyl and ethyl (or isopropyl) alcohols and non-homogeneous ketene acetals were obtained. These products are doubtless the result of the addition of the more reactive ethyl (or isopropyl) alcohol to the initially formed ketene acetal followed by dealcoholation of the resulting mixed orthoester. While aluminum ethoxide dealcoholates ethyl orthophenylacetate successfully, it is as ineffective with the lower-boiling aliphatic orthoesters, such as ethyl orthoacetate and ethyl orthopropionate, as the methoxide is with the corresponding methyl orthoesters.

It is apparent from Table I that a wide variety of orthoesters may be dealcoholated to the corresponding ketene acetals in good yields with alu-

---

[1] S. M. McElvain and J. T. Venerable, This Journal, **72**, 1661 (1950).

minum *t*-butoxide. This reaction is especially valuable for the dealcoholation of the lower boiling orthoesters and makes available for further study the dialkylated compounds, dimethylketene dimethyl and diethylacetals. In the preparation of the higher boiling ketene acetals, such as the phenylketene acetals, the volatility of the aluminum *t*-butoxide (and the ethoxide) causes some contamination of the acetal. In such cases it is preferable to use the non-volatile aluminum methoxide with a methyl orthoester to obtain a ketene dimethylacetal.

Ethoxyketene diethylacetal, $C_2H_5OCH{=}C(OC_2H_5)_2$, which results from the dealcoholation of ethyl orthoethoxyacetate, has been reported by Scheibler and Marhenkel[2] to have been prepared by the action of sodium ethoxide on ethyl ethoxyacetate. However, the properties of the compound obtained by these German workers do not correspond to those of the ketene acetal obtained by the dealcoholation of ethyl orthoethoxyacetate (see footnote (*f*) Table II). This ketene acetal was characterized by analyses, and by its facile addition of both alcohol and water to form ethyl orthoethoxyacetate and ethyl ethoxyacetate, respectively.

It is tempting to speculate on the cause of the greater effectiveness of aluminum *t*-butoxide, in comparison with the lower alkoxides, for the dealcoholation of orthoesters. It seems certain that the butoxide has a greater ability to coördinate with the orthoesters, in spite of its larger alkyl groups, than the lower alkoxides have. Because of this coördinative capacity, the lower-boiling orthoesters are prevented from distilling away from the *t*-butoxide before they are dealcoholated to the corresponding ketene acetals. This conclusion would suggest that the structures of the lower aluminum alkoxides are more polymeric due to intermolecular coördination between oxygen and aluminum than is that of aluminum *t*-butoxide.

The physical properties of these substances support this conclusion (see Table III). Aluminum methoxide is a fine, infusible powder, which is quite insoluble in organic solvents. In contrast, aluminum *t*-butoxide sublimes at 180°, may be recrystallized from benzene, and is very soluble in orthoesters. Both aluminum ethoxide and isopropoxide melt at about 130° and may be distilled. While the ethoxide is quite soluble in ethyl orthoesters at or above 130°, its coördination complex with such an orthoester as ethyl orthopropionate is not sufficiently stable to prevent distillation of the orthoester before the temperature of dealcoholation is reached. The aluminum isopropoxide has a solubility in orthoesters approaching that of the *t*-butoxide and appears to form a sufficiently stable coördination complex to permit dealcoholation, but the interaction of the products (isopropyl alcohol and the ketene acetal) causes a mixture of alcohols and ketene acetals to be produced. It seems likely that aluminum isopropoxide would be effective for the dealcoholation of isopropyl orthoesters, if such compounds were available.

Aluminum methoxide is too insoluble for molecular weight determination. Cryoscopically in camphor (*ca.* 165°) aluminum *t*-butoxide has the molecular weight of the monomer and aluminum ethoxide has that of a dimer. Ebullioscopically in benzene the aluminum *t*-butoxide gives a value of about 1.9 times the monomer while the isopropoxide appears to be a pentamer; the ethoxide is too insoluble in this solvent to permit determination of its molecular weight.

Experimental

Dealcoholations with Aluminum *t*-Butoxide.—The general procedure consisted of heating in an oil-bath a mixture of aluminum *t*-butoxide[3] and orthoester, in the molecular ratio and at the bath temperature shown in Table I, in a flask connected through a Vigreux column to a condenser. When the *t*-butyl alcohol stopped distilling—in certain cases it was necessary to apply a vacuum of approximately 120 mm. to the system to remove the last portion of the alcohol—the pressure in the system was lowered until the remaining ketene acetal distilled without raising the bath temperature above 190°, at which temperature the alkoxide begins to dehydrate *t*-butyl alcohol to isobutylene.[4] The lower boiling ketene acetals generally distilled with the *t*-butyl alcohol from the reaction flask at atmospheric pressure. The ketene acetal then was fractionated to remove small amounts of the alkoxide that sublimed and other contaminants, *e.g.*, normal ester and unchanged orthoester.

The following ketene acetal preparations, which represent the greatest deviations from the above general procedure, are given in detail to illustrate certain necessary variations.

Dimethylketene Dimethylacetal.—In a 100-ml. round-bottom flask equipped with a 25-cm. Vigreux column was placed 32.2 g. (0.22 mole) of methyl orthoisobutyrate and 54.5 g. (0.22 mole) of aluminum *t*-butoxide. The flask was immersed in an electrically heated oil-bath, which was kept at 185–190°. The *t*-butyl alcohol distilled out with the dimethylketene dimethylacetal over a period of about 2 hours at a temperature of 83–105° at the top of the column. If the temperature of distillation was allowed to exceed 105°, the distillate contained a considerable amount of unchanged orthoester. When distillation stopped, the receiver was removed and the last portion of the product was removed and condensed in a cold trap with the system under the vacuum of a water-pump.

The distillates were combined and fractionated through a 25-cm. Fenske column. The ketene acetal, collected at 104–110°, amounted to 13.4 g. (54%); most of this product boiled 107–109°; 6.5 g. (20%) of methyl orthoisobutyrate was recovered.

Ethoxyketene Diethylacetal.—In a 100-ml. round-bottom flask equipped with a 30-cm. Vigreux column was placed 30 g. (0.145 mole) of ethyl orthoethoxyacetate[5] and 36 g. (0.145 mole) of aluminum *t*-butoxide. The flask was immersed in an oil-bath at 175–180°. The system was kept under 120 mm. pressure by means of a pressure regulator connected to a water-pump. *t*-Butyl alcohol distilled out at 48°. After approximately 55% of the theoretical amount of the alcohol had been collected, the distillation practically stopped. The pressure then was reduced to 30 mm. and all material that would distil was collected; finally, the pressure was reduced to 10 mm. to remove the remainder of the volatile material. During this time sufficient *t*-butyl alcohol collected in the cold trap to bring the total yield to 80%. The product then was distilled rapidly through a 12-inch Vigreux column under 8 mm. pressure (b.p. 54–68°)

---

[2] H. Scheibler and E. Marhenkel, *Ann.*, **458**, 36 (1927).

[3] This compound was prepared by the procedure of Fieser "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., p. 445, except that the benzene solution of the alkoxide was filtered rather than treated with moist ether to obtain a clear solution.

[4] This isobutylene is derived from *t*-butyl alcohol rather than from the pyrolysis of the aluminum *t*-butoxide, because the latter compound when pure neither decomposes nor melts when heated in a sealed melting point tube as high as 300°. However, traces of moisture or *t*-butyl alcohol cause this alkoxide to melt in the range of 160–200° and to evolve isobutylene at the higher temperature.

[5] S. M. McElvain and P. M. Walters, THIS JOURNAL, **64**, 1965 (1942).

Table II

Ketene Acetals, $R_1R_2C{=}C(OR)_2$, from Dealcoholation of Orthoesters, $R_1R_2CHC(OR)_3$

R_1	R_2	R	Formula	B. p., °C.	Mm.	$n^{25}D$	d^{25}_4	Analyses, % Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
C_6H_5	H	CH_3	.....[a]	123–126	13	1.5631	...	...	...	...	...
C_6H_5	H	C_2H_5	$C_{12}H_{16}O_2$[b]	80–81	0.15	1.5395	0.998	74.96	75.09	8.39	8.34
H	H	C_2H_5	.....[c]	123–126	740	1.4095	...	...	...	...	...
CH_3	H	C_2H_5	.....[d]	132–137	740	1.4100	...	...	...	...	...
CH_3	CH_3	CH_3	$C_6H_{12}O_2$[e]	107–109	740	1.4081	0.871	62.0	62.2	10.3	10.4
CH_3	CH_3	C_2H_5	$C_8H_{16}O_2$	139–140	740	1.4115	.870	66.6	66.7	11.1	11.3
C_2H_5O	H	C_2H_5	$C_8H_{16}O_3$[f]	57–58	7	1.4188	.919	60.0	59.6	10.1	10.1
				174–176	740						

[a] See ref. 1, pp. 1667 and 1668. [b] This compound was prepared with catalytic amounts of aluminum ethoxide; it contained 46.5% ethoxyl (calcd. 46.8%); the product from the pyrolysis of ethyl orthophenylacetate had $n^{25}D$ 1.5385 (McElvain and Stevens, This Journal, **68**, 1920 (1946)). [c] Beyerstedt and McElvain, *ibid.*, **58**, 529 (1936). [d] Walters and McElvain, *ibid.*, **62**, 1482 (1940). [e] McElvain and Venerable (ref. 1) report for this compound: b.p. 103–105°, $n^{25}D$ 1.4046. [f] Ethoxyl content 80.5% (calcd. 84.3%); Scheibler and Marhenkel (ref. 2) report the following properties for this compound: b.p. 163–165°, $n^{22}D$ 1.4038, d^{22}_4 0.9047.

to remove traces of the alkoxide that it contained and then this distillate was fractionated carefully through a 40 cm. Podbielniak column. The ethoxyketene diethylacetal, boiling at 55–59° (7 mm.), amounted to 14 g. (61%); most of this material boiled at 57–58° (7 mm.).

Ethoxyketene diethylacetal (5 g.) reacted vigorously with water (3 ml.) containing one drop of 5% hydrochloric acid to yield 5 g. of ethyl ethoxyacetate, b.p. 155–158°, $n^{25}D$ 1.4009. Treatment of this ester with concentrated ammonia water converted it to ethoxyacetamide,[6] m.p. 81–82°.

When ethoxyketene diethylacetal (2 g.) was treated with ethyl alcohol (0.5 g.) containing a trace of hydrogen chloride, considerable heat was evolved. Distillation of the resulting product yielded ethyl orthoethoxyacetate, b.p. 180–185°, $n^{25}D$ 1.4025.

The properties and analyses of the ketene acetals prepared from the corresponding orthoesters with aluminum *t*-butoxide are listed in Table II.

Dealcoholations with Other Aluminum Alkoxides.—A mixture of 30 g. (0.126 mole) of ethyl orthophenylacetate and 2 g. of aluminum ethoxide was heated in the apparatus described above for the preparation of dimethylketene dimethylacetal at a bath temperature of 160°. After the ethyl alcohol (*ca.* 5 g.) had distilled out, the crude ketene acetal was distilled from the reaction flask under 0.1 mm. pressure. Redistillation of this product gave 15.6 g. (65%) of phenylketene diethylacetal, the properties of which are listed in Table II. If larger amounts of aluminum ethoxide were used, it was difficult to obtain a ketene acetal free of the alkoxide.

When a mixture of 36 g. (0.184 mole) of methyl orthophenylacetate and 18.7 g. (0.092 mole) of supercooled liquid aluminum isopropoxide was heated in an oil-bath at 140°, the liquid foamed and turned solid. When the bath temperature was increased to 210–240°, a mixture of methyl and isopropyl alcohols (refractive index and boiling point) distilled out. Bath temperatures of 260–270° at 10 mm. were required to distil any further material from the alkoxide. These temperatures caused considerable decomposition and gave a mixture of normal esters and ketene acetals which boiled 93–110° (10 mm.).

In an attempt to determine the nature of the intermediate products in the reaction between methyl orthophenylacetate and aluminum isopropoxide, 10.8 g. (0.055 mole) of methyl orthophenylacetate was heated with 11.1 g. (0.055 mole) of liquid aluminum isopropoxide. After a few minutes at 140°, the mixture became solid. The heating was discontinued and, after the reaction mixture had cooled, it was extracted with ether. The solid was filtered off, washed well with ether and dried. The weight of solid material obtained was 8.2 g., which was the weight of alkoxide expected if two isopropoxyl of the aluminum isopropoxide had been replaced by methoxyl groups. This solid was very similar to aluminum methoxide, *i.e.*, it was infusible and insoluble in organic solvents (see Table III).

Distillation of the ether solution yielded a mixture of orthoesters boiling at 109–128° (10 mm.); $n^{25}D$ ranged from 1.4996–1.5187. Methyl orthophenylacetate boils at 116–117° (13 mm.); $n^{25}D$ 1.4950.

A mixture of aluminum ethoxide and methyl orthophenylacetate behaved similarly when heated. The aluminum ethoxide was solid at the beginning of the reaction but instead of dissolving as the temperature increased as it does in ethyl orthoesters it remained as a solid gel-like mass in the reaction mixture. At temperatures above 200° a mixture of alcohols distilled at atmospheric pressure and after this a mixture of normal esters and mixed ketene acetals (bromine absorption) distilled at 95–118° (10 mm.). A small amount of acetaldehyde was collected in a cold trap attached to the system.

The non-volatile aluminum methoxide is the most satisfactory dealcoholating agent for the higher boiling methyl orthoesters such as methyl orthophenylacetate. It may be used in the ratio of 2 g. of the alkoxide to 50 g. of the orthoester. Even when one mole of aluminum *t*-butoxide is used with three moles of this orthoester, there is some contamination of the ketene acetal with the alkoxide (see footnote (*a*), Table I).

Aluminum Alkoxides.—Some properties of these compounds, prepared by previously described procedures,[1,3] are listed in Table III.

Table III

Properties of Aluminum Alkoxides, $Al(OR)_3$

R	M.p., °C.	B. p., °C.	Mm.	Mol. wt. (monomer)n n in camphor (m.p.)	in benzene (b.p.)	Solubilities in organic solvents
CH_3	None	None		Too insoluble to determine		None
C_2H_5	130	200–205	14	2	Insoluble	Insoluble below m.p.[b]
$(CH_3)_2CH$	130[a]	145–150	5	..[c]	5–6	Very soluble
$(CH_3)_3C$	Sublimes at 180			1	1.9	Very soluble[d]

[a] Usually distils as a supercooled liquid. [b] Quite soluble in ethyl orthoesters above 130°. [c] M.p. in camphor not constant indicating reaction of alkoxide with solvent. [d] May be recrystallized from benzene; 5 g. of ethyl orthopropionate dissolves approximately 9 g. of this alkoxide at 120°.

Madison, Wisconsin Received September 18, 1950