ORGANOALUMINUM CHEMISTRY

II. THE OXIDATION OF SOME UNSATURATED ALUMINUM COMPOUNDS WITH COBALT CHLORIDE

MARTIN I. PRINCE AND KARL WEISS*
William H. Nichols Chemical Laboratory and Department of Chemical Engineering, New York University, New York (U.S.A.)

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In the previous paper[1], the reaction of a variety of aluminum alkyls with transition metal halides was described. Evidence was presented that radicals are produced in these reactions and that the gaseous hydrocarbons result, at least in part, from radical interactions with aluminum-bound alkyl groups. With the three unsaturated aluminum compounds examined [1-butynyldiethylaluminum (I), 1-butenyldiethylaluminum (II), and (4-methyl-1-pentenyl)diisobutylaluminum (III)], the gaseous hydrocarbons were derived primarily from the alkyl groups. In diethyl ether, the cobalt chloride oxidation of aluminum compounds bearing only simple alkyl groups produced no new liquid products[1]. However, gas chromatographic examination of the liquid phase from the oxidation of compounds (I), (II), and (III) under similar conditions showed new components. These reactions have been repeated on larger scales, and this paper describes the products.

$(C_2H_5)_2AlC{\equiv}CC_2H_5$ (I) $(C_2H_5)_2AlCH{=}CHC_2H_5$ (II) $(iso\text{-}C_4H_9)_2AlCH{=}CHCH_2CH(CH_3)_2$ (III)

RESULTS

The aluminum compounds were prepared as described by Wilke and Müller[2], and the oxidations were carried out as described in the first paper[1]. After cessation of gas evolution the unreacted aluminum alkyl was destroyed with water, and the liquid products were isolated by distillation of the organic phase.

With 1-butynyldiethylaluminum, the butynyl groups were completely converted into other products by the cobalt chloride. The gas produced during the reaction contained no 1-butyne, and hydrolysis furnished gas containing 99 % ethane. Distillation afforded benzene as the sole volatile product, which was identified by its infrared spectrum and analysis, and by gas chromatography. No pure components could be isolated from the non-volatile residue, which amounted to about one half of the organic product.

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* To whom enquiries should be addressed: Department of Chemistry, Northeastern University, Boston 15, Massachusetts.

The oxidation of 1-butenyldiethylaluminum produced gaseous hydrocarbons, about one quarter of which were derived from the butenyl groups. The complete reaction of these groups was indicated by the hydrolysis, which gave essentially pure ethane. The liquid products were a *ca.* 20:1 mixture of *trans*-4-octene and *trans*-3-octene (27 % yield), and an unidentified higher boiling fraction consisting of several components. For comparison, the oxidation of 1-butenylmagnesium bromide with excess cobalt chloride in tetrahydrofuran was examined. This reaction produced a large amount of non-volatile, polymeric material, two unidentified higher boiling fractions containing several compounds, and *trans*-4-octene in 4 % yield.

The oxidation of (4-methyl-1-pentenyl)diisobutylaluminum was more complex than those of compounds (I) and (II). The reaction and subsequent hydrolysis gave only C_4 hydrocarbons. Three pure compounds, whose detailed structures remain to be elucidated, were isolated by several distillations. On the basis of boiling points, analyses, molecular weights, and hydrogenation data they are tentatively identified as follows: (A) and (B), isomeric $C_{20}H_{38}$ hydrocarbons, and (C) a $C_{28}H_{54}$ hydrocarbon. While carbon and hydrogen analyses are not particularly sensitive criteria for the molecular formulas of hydrocarbons, and the molecular weights as determined by "Osmometer" were lower than the calculated values, the hydrogenation results are inconsistent with alternative formulations based on the available hydrocarbon fragments. The infrared spectra of compounds (A) and (C) are almost identical, and show strong *trans* $-CH{=}CH-$ bands at 10.36 μ and 10.35 μ respectively. In compound (B), this band is replaced by two others at 10.12 μ (strong) and 10.60 μ (medium) respectively which may be ascribed to the presence of the conjugated *trans* diene structure[*]. Compounds (A) and (B) have identical carbon skeletons, since hydrogenation produced the same alkane from each.

DISCUSSION

The oxidative cleavage of the unsaturated alkyls is seen to follow a more complex pattern than that of the saturated compounds. In each case the unsaturated group reacted preferentially and completely, yielding sizable quantities of polymeric materials as well as the products described. The seemingly divergent results may, however, be satisfactorily rationalized in terms of the initial formation of radicals[1], which react further with aluminum-bound alkyl or alkenyl groups, or with solvent.

The production of benzene from compound (I) proceeds via 1-butyne (equation 1, al = 1/3 Al). The fact that this hydrocarbon was completely absent in the gas

$$\text{alC}{\equiv}\text{CC}_2\text{H}_5 \xrightarrow{\text{CoCl}_2} \text{alCl} + \text{C}_2\text{H}_5\text{C}{\equiv}\text{C}^{\bullet} \longrightarrow \text{C}_2\text{H}_5\text{C}{\equiv}\text{CH} \tag{1}$$

evolved during the reaction, suggested that it was consumed in a subsequent step. To test this idea, 1-butyne was passed into a refluxing solution of triethylaluminum containing suspended cobalt chloride. Benzene was produced and, although there was no change in the appearance of the metal halide, the solution became brown

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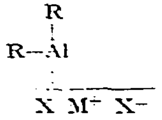
[*] Conjugation is reported to shift the *trans*-ethylenic absorption to higher frequencies[3], and this assignment correlates well with the bands at 10.10–10.15 μ and 10.43–10.68 μ observed with a number of *cis–trans* and *trans–trans* conjugated dienes[4].

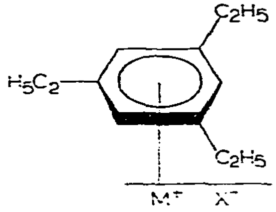
and subsequent hydrolysis showed that 59 % of the aluminum-bound ethyl groups had been consumed during the reaction. Since aluminum alkyls do not react with acetylenic hydrogen[2], the alkyne as such must be involved in benzene formation.

The cyclization of substituted alkynes can be achieved by a variety of catalysts. Without exception the products are benzene derivatives, although the present work suggests that benzene might be an unsuspected and hitherto undetected side product in these reactions. Ziegler-type catalytic systems based on aluminum alkyl–titanium halide combinations produce polymers[5] or substituted benzenes[6], depending on the conditions. The reaction of alkynes with metal carbonyls furnishes acetylenic complexes and benzene derivatives[7]. The cyclizations described by Zeiss and coworkers, which are brought about by transition metal aryls and alkyls[8] appear to be particularly pertinent to the aluminum alkyl–cobalt chloride system. Bisarenemetal π-complexes as well as aromatic hydrocarbons are the products, and organocobalt compounds are unique in that they are capable of acting in a catalytic manner[8e]. With the possible exception of the cobalt compounds, the π-complexes as such appear not to be intermediates in the formation of the cyclic trimers[8b]. The formation of a bridged bisbenzenechromium complex from the reaction of chromic chloride with triethylaluminum and stilbene has also recently been reported[9].

The oxidation of aluminum alkyls has been proposed[1] to involve intermediates such as (IV). It is suggested that the univalent cobalt ion in this intermediate coordinates with 1-butyne molecules to furnish a π-arenecobalt(I) surface complex of type (V). Analogously to the system described by Tsutsui and Zeiss[8e], intermediate



(IV)



(V)

(V) may catalytically trimerize more butyne or furnish bisarenecobalt(I) in solution. Diversion of intermediate (IV) to intermediate (V) would explain the complete suppression of the formation of black metallic cobalt which occurs in the oxidation of triethylaluminum by cobalt chloride in the absence of alkyne[1]. According to this reaction sequence, the benzene arises from triethylbenzenes by dealkylation. Such reactions are brought about by Friedel-Crafts catalysts[10] and, under relatively mild conditions, are reported to be equilibrium processes[11]. The absence of ethylbenzene, diethylbenzenes, and higher alkylated benzenes in the oxidation of compound (I) clearly precludes an equilibrium in this system. Evidently the conditions are sufficiently drastic that the alkylaluminum halides, which are the most probable disproportionation agents, ultimately convert all alkylbenzenes into intractable polymers*.

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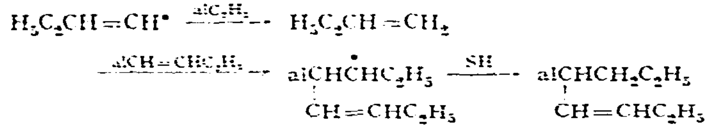
* Temperature and contact time appear to be important variables in dealkylation. Thus in the presence of hydrogen fluoride–boron trifluoride catalyst *tert*-butylbenzene disproportionates smoothly in 10 min at 0°, while in the same time at 45° mainly benzene and much higher boiling material is produced[11b]. Even benzene is largely converted to tar when in contact with hydrogen bromide–aluminum bromide catalyst at 25° for 8 days[11c].

Dimerization or addition to 1-butyne represent alternative modes of reaction for butynyl radicals generated according to equation 1. The oxidative coupling of alkynes to diynes by cupric salts has been formulated to proceed in this manner[12]. If such processes occur in the oxidative degradation of compound (I), the coupled products must be converted into high molecular weight material.

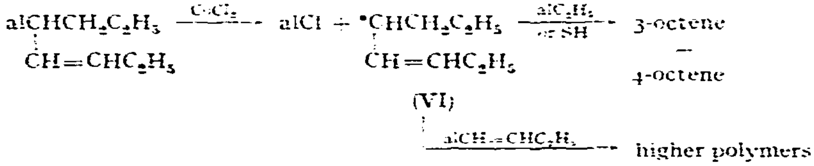
A reasonable explanation can now be offered for the trimerization of alkynes by aluminum alkyl–titanium tetrachloride systems. Chemisorption of alkyne on the catalyst has been suggested as the first step[6c]. A logical extension of this idea leads to an π-arenetitanium surface complex, and relates the Zeiss and Ziegler catalyst systems*. Maximum yields of trimers are obtained when the aluminum to titanium ratio in the catalyst is about 3 (ref. 6d), which corresponds to an average valence state of 2 for the titanium[13]. It can be reasoned, therefore, that the cyclization proceeds via an arenetitanium complex which incorporates divalent titanium**.

Several possibilities may be considered for the formation of octenes in the oxidation of compound (II). Thermal reaction between two molecules of this aluminum compound followed by oxidative scission of aluminum–carbon bonds may be ruled out since branched C_8 hydrocarbons would result***. Similarly, a growth reaction which terminates at the dimer stage and involves the AlCH=CHR group and 1-butene (from hydrogen abstraction by butenyl radicals) would be expected to give a branched alkene since such additions normally follow Markownikov's rule[19]. A sequence which accounts for the results, and which would take place on the surface of the cobalt chloride as proposed earlier[1], is shown in equations (2), (3), and (4) (SH is solvent). This mechanism implies that the surface is sufficiently populated with aluminum

$$\text{alCH}{=}\text{CHC}_2\text{H}_5 \xrightarrow{\text{CoCl}_2} \text{alCl} + \text{H}_5\text{C}_2\text{CH}{=}\text{CH}^{\bullet} \qquad (2)$$



$$\text{H}_5\text{C}_2\text{CH}{=}\text{CH}^{\bullet} \xrightarrow{\text{alC}_2\text{H}_5} \text{H}_5\text{C}_2\text{CH}{=}\text{CH}_2 \xrightarrow{\text{alCH}=\text{CHC}_2\text{H}_5} \underset{\text{CH}=\text{CHC}_2\text{H}_5}{\text{alCH}\dot{\text{C}}\text{HC}_2\text{H}_5} \xrightarrow{\text{SH}} \underset{\text{CH}=\text{CHC}_2\text{H}_5}{\text{alCHCH}_2\text{C}_2\text{H}_5} \qquad (3)$$



$$\underset{\text{CH}=\text{CHC}_2\text{H}_5}{\text{alCHCH}_2\text{C}_2\text{H}_5} \xrightarrow{\text{CoCl}_2} \text{alCl} + \underset{\substack{\text{CH}=\text{CHC}_2\text{H}_5\\ \text{(VI)}}}{{}^{\bullet}\text{CHCH}_2\text{C}_2\text{H}_5} \xrightarrow[\text{or SH}]{\text{alC}_2\text{H}_5} \text{3-octene} + \text{4-octene} \qquad (4)$$

$$\text{(VI)} \xrightarrow{\text{alCH}=\text{CHC}_2\text{H}_5} \text{higher polymers}$$

alkenyl molecules to allow reactions to occur between radicals from one molecule and alkenyl groups not attached to the same aluminum atom. The formation of radicals

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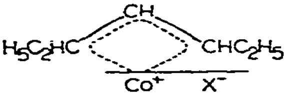
* Franzus *et al.*[6a] have already commented on the possibility of a relationship between the actions of these catalysts.

** A π-complexed compound of titanium(II), biscyclopentadienyltitanium dicarbonyl, has been prepared by Murray[14]. Further, the appearance of hydrogen among the gases obtained by hydrolysis of triethylaluminum–titanium tetrachloride catalyst is possibly due to divalent titanium[15]. The presence of this oxidation state was also inferred by Simon *et al.*[16]. See, however, ref. 17.

*** Thus heating compound(II) at 80°–150° with subsequent hydrolysis yields, amongst other products, 3-methyl-4-heptene or 2-ethyl-1-hexene; *cf.* refs. 2 and 18.

such as (VI) may be enhanced by association with cobalt as shown in (VII). A butadienylcobalt carbonyl compound of similar structure has been reported[20]. The relative



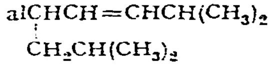
(VII)

inertness of the solvent (ether), and the excess of ethylene over ethane in the gas evolved during the oxidation strongly support the contention that AlC_2H_5 groups serve as hydrogen donors.

The dimerization of alkenyl radicals is not extensive in the gas phase[21], but may participate in the reaction of germanium tetrachloride with vinylmagnesium bromide[22]. In any case, the 3,5-octadiene which would result if this reaction occurs in the oxidation of compound (II) is not a likely precursor of the octenes.

The oxidation of 1-butenylmagnesium bromide evidently follows a similar course*. The lower yield of octene may be ascribed to the absence of metal-bound alkyl groups, which forces hydrogen abstraction to occur primarily from the solvent.

A more complicated reaction path emerges from the results of the oxidation of compound (III). No 2,9-dimethyldecenes, corresponding to the octenes from compound (II), were identified, although small amounts of these compounds may have been present in early distillation fractions. In the absence of further structural data, the formation of C_{20} and C_{28} hydrocarbons can only be rationalized in terms of the available building blocks. It is immediately apparent that additional isobutyl groups are incorporated in these products. The addition of an isobutyl radical to the alkenyl group (*cf.* equation 3) followed by loss of hydrogen would give structure (VIII). The $C_{20}H_{38}$ compounds can arise from oxidative scission of (VIII) and dimerization



$$\begin{array}{l} \text{alCHCH}{=}\text{CHCH(CH}_3)_2 \\ \;\;\;\text{CH}_2\text{CH(CH}_3)_2 \end{array}$$

(VIII)

of the resulting radicals. The addition of another isobutyl radical to (VIII) with subsequent loss of hydrogen, oxidation, and dimerization would furnish a $C_{28}H_{54}$ compound.

EXPERIMENTAL

General

All reactions were carried out with the rigorous exclusion of air[1]. The boiling points are uncorrected. The carbon and hydrogen analyses and molecular weight determina-

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* Fo-Sun Van *et al.*[23] and Kropachev *et al.*[23] have investigated the reactions of ethylmagnesium bromide and ethyllithium with titanium and cobalt halides. Based on the absence of drastic changes in the yield and composition of the gases evolved in the presence of styrene, α-methylstyrene, and 1-heptene, these authors concluded that radicals do not participate. If, however, as is proposed here and elsewhere[1,24] radical interactions occur primarily on the salt surface with metal-bound alkyl groups, the gas should be relatively independent of small changes in solvent composition.

tions were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y. The aluminum analyses, quantitative hydrolyses, and gas chromatographic analyses were carried out as described previously[1]. Infrared spectra were measured with a Baird Model 4-55 spectrometer. Active aluminum compounds were examined as liquid smears between sodium chloride plates; lateral seepage led to the formation of oxidation products at the edge of the film, which acted as an effective seal against further oxidation.

Oxidations with cobalt chloride

(*a*) *1-Butenylmagnesium bromide*. The Grignard reagent was prepared according to the general method of Normant[25]. 1-Bromo-1-butene (redistilled material from Columbia Organic Chemicals Co., Columbia, S.C.) (135 g, 1.00 mole) in 250 ml of tetrahydrofuran (purified as described by Fieser[26]) was added dropwise to a suspension of freshly crushed magnesium turnings (24.3 g, 1.00 mole) in 250 ml of tetrahydrofuran. The reaction was initiated by a few drops of separately prepared ethylmagnesium bromide solution. Refluxing for an additional hour after addition left only a few pieces of unreacted metal.

The filtered Grignard solution was added slowly to cobalt chloride (130 g, 1.00 mole) in 300 ml of refluxing tetrahydrofuran. An exothermic reaction ensued with immediate darkening of the solid, but no gas evolution was observed. Heating was continued for 14 h, after which the cooled mixture was filtered and the solid was extracted with ether. Distillation of the solvent from the combined liquids followed by total distillation of all volatile material from the semi-solid residue under high vacuum at 120° gave a pale yellow liquid. Three fractions were obtained by redistillation: (*1*) 2.77 g, b.p. 123° (760 mm), (*2*) 3.08 g, b.p. 60° (7 mm), and (*3*) 1.26 g, b.p. 78° (1 mm). Fraction (*1*) had an infrared spectrum identical with that of authentic *trans*-4-octene (obtained from the Phillips Petroleum Co., Bartlesville, Okla.). This identity was confirmed by gas chromatography using a "Ucon" 525 column. A 91.8 mg sample of fraction 1 in 5 ml of ethyl acetate with 40.4 mg of 5 % Palladium-on-charcoal absorbed 17.5 ml (S.T.P.) of hydrogen, and produced *n*-octane. (Found: C, 86.1; H, 14.0; H_2 abs., 0.95 moles/mole. C_8H_{16} calcd.: C, 85.6; H, 14.4 %; H_2 abs., 1.0 moles/mole.)

Gas chromatography of fractions (*2*) and (*3*) showed several components in each. The hydrogenation results (147 ml/g and 167 ml/g at S.T.P. respectively) are indicative of mixtures of compounds with different molecular weights.

(*b*) *1-Butynyldiethylaluminum*. The aluminum compound was prepared from redistilled diethylaluminum chloride (54.98 g, 0.456 mole) and 1-butynylsodium (36.7 g, 0.482 mole) in 300 ml of hexane[2]. Filtration of the sodium chloride and distillation of the red-colored liquid afforded 21.7 g of 1-butynyldiethylaluminum, b.p. 76° (0.07 mm), λ_{max}^{neat} 4.62, 4.72 μ (C≡C). (Found: Al, 19.6. $C_8H_{15}Al$ calcd.: Al, 19.6 %.)

A solution of the aluminum alkyl (17.94 g, 0.130 mole) in 35 ml of anhydrous ether* was slowly added to a suspension of anhydrous cobaltous chloride* (25.97 g, 0.200 mole) in 165 ml of refluxing ether. The solid became black immediately, and altogether 0.0223 mole of gas (60 % ethylene, 38.5 % ethane, 0.5 % C_4) was evolved overnight. Hydrolysis with 60 ml of water furnished gas containing at least 99 %

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* The purification of solvents and reagents is described in ref. 1.

ethane. Distillation of the dried organic layer gave 3.5 g of dark, solid residue and 3.3 g (0.042 mole) of benzene which, after redistillation had b.p. 78.5–80° (760 mm) and n_D^{20} 1.5047 [reported[27] b.p. 80.099° (760 mm), n_D^{20} 1.50112]. The infrared spectrum and the retention time on a diisooctyl isosebacate column were identical with those of an authentic sample. The usual purification techniques failed to produce identifiable material from the solid.

The formation of benzene from 1-butyne was demonstrated as follows. A suspension of cobalt chloride (1.3 g, 10 mmoles) in 10 ml of ether was refluxed while a stream of 1-butyne was passed in. Triethylaluminum (0.76 g, 6.7 mmoles) in 10 ml of ether was added slowly, and the gas stream was continued for several hours. The solution became progressively darker, but no change occurred in the appearance of the solid. Hydrolysis furnished 8 mmoles of gas, and gas chromatographic examination of the organic liquid showed the presence of a sizable quantity of benzene.

(*c*) *1-Butenyldiethylaluminum*. The reaction of triethylaluminum and acetylene furnished 1-butenyldiethylaluminum[2]. The pale yellow, viscous product, λ_{max}^{neat} 6.43 μ (C=C), was decanted from a small quantity of dark solid prior to use. [Found: Al, 20.0; gas, 3.1 moles/mole (C_2:C_4, 2.3:1). $C_8H_{17}Al$ calcd.: Al, 19.3%; gas, 3.0 moles/mole (C_2:C_4, 2:1).]

Cobalt chloride (25.97 g, 0.200 mole) in 165 ml of ether was refluxed, and a solution of 1-butenyldiethylaluminum (18.62 g, 0.130 mole) in 35 ml of ether was added gradually. Gas evolution was slow, and ceased after 18 h at reflux temperature. During this time the solid became dark and 0.074 mole of gas (60% ethylene, 13.5% ethane, 0.8% *n*-butane, 19% 1-butene, and 5.5% 2-butene) was produced. The mixture was hydrolyzed with 50 ml of water; the gas evolved contained only ethane and a trace of 1-butene. Distillation of the dried organic layer afforded three fractions, (*1*) 0.51 g, b.p. 127° (760 mm), (*2*) 1.50 g, b.p. 127–133° (760 mm), (*3*) 0.73 g, b.p. 60° (7 mm), and a non-volatile residue of 0.54 g. Gas chromatographic analysis of fractions (*1*) and (*2*) showed two components in each. By comparison with authentic specimens (obtained from the Phillips Petroleum Co., Bartlesville, Okla.), they were identified as *trans*-4-octene and *trans*-3-octene in the approximate ratio of 20:1.

d) *(4-Methyl-1-pentenyl)diisobutylaluminum*. Triisobutylaluminum was treated with acetylene to yield the unsaturated aluminum compound[2] as a pale orange-colored solid, λ_{max}^{neat} 6.45 μ (C=C), which was used without further purification. (Found: Al, 11.6. $C_{14}H_{29}Al$ calcd.: Al, 12.05%.)

(4-Methyl-1-pentenyl)diisobutylaluminum (67.74 g, 0.305 mole) in 100 ml of ether was slowly added to a refluxing suspension of cobalt chloride (61.49 g, 0.473 mole). Overnight 0.0365 mole of gas, consisting of isobutane and isobutene, was evolved. Hydrolysis with 50 ml of water produced only isobutane. The organic layer from this run and from three other runs, corresponding to a total of 1.00 mole of aluminum compound, were combined, washed, dried, and distilled. After removal of the ether (containing only traces of other compounds), the volatile components of the residue were totally distilled and collected at −78°. At 1–2 mm pressure and pot temperature from 45–200°, 41.3 g of pale-yellow liquid was collected, and a dark residue of 13.1 g remained. Fractional distillation afforded four fractions, (*1*) 2.83 g, b.p. 52–63° (4 mm), (*2*) 10.72 g, b.p. 52–56° (1 mm), (*3*) 8.54 g, b.p. 100–110° (0.5 mm), (*4*) 1.63 g, b.p. 109–130° (0.1 mm), and another non-volatile residue of 15.5 g. Gas chromatography ("Ucon" 525 column) showed many components in fractions (*1*) and

(*4*), but only three in fractions (*2*) and (*3*). The latter fractions were combined and redistilled at low pressure to prevent further decomposition (Nester and Faust Spinning Band Column, 45 cm × 0.6 cm, packed with stainless steel gauze). Six fractions were collected (b.p., pressure in mm): (*1*) 28°, 0.1; (*2*) 29.5°, 0.1; (*3*) 29.75°, 0.1; (*4*) 34°, 0.1; (*5*) 54°, 0.08; (*6*) 56°, 0.08. Of these fractions, (*2*), (*3*) and (*6*) contained only one component each, (A), (B), and (C) respectively, identical with the three components of fractions (*2*) and (*3*) of the first distillation. Intermediate cuts consisted of varying amounts of these materials. All three compounds gave positive unsaturation tests. Infrared spectra: (A), $\lambda_{\max}^{\text{neat}}$ 7.25, 7.36, 8.56, 10.36 μ; (B), $\lambda_{\max}^{\text{neat}}$ 7.25, 7.36, 8.58, 10.12, 10.60 μ; (C) $\lambda_{\max}^{\text{neat}}$ 7.25, 7.36, 8.53, 10.35 μ.

ANALYSES OF (A), (B), AND (C)

Compound		*Found (calculated)*			
		C	*H*	*Mol.wt.*	*H_2 abs. moles/mole*
(A)	$C_{20}H_{38}$	86.1 (86.3)	13.8 (13.7)	213[a] (278) 295[b]	1.9 (2.0)
(B)	$C_{20}H_{38}$	86.3 (86.3)	13.5 (13.7)	246[a] (278) 257[a] 250[b]	2.2 (2.0)
(C)	$C_{28}H_{54}$	86.3 (86.2)	13.6 (13.8)	330[a] (390) 335[a] 384[b]	2.0 (2.0)

[a] Determined by "Osmometer". [b] Based on hydrogenation data.

Catalytic hydrogenation in 5 ml of ethyl acetate at room temperature and atmospheric pressure gave these results (mg, sample, mg 5 % Palladium-on-charcoal, ml hydrogen at S.T.P.): (A), 177.0, 48.0, 26.7; (B), 113.3, 38.1, 20.3; (C), 192.1, 37.1, 21.8. The hydrogenation products from fractions (*2*) and (*3*) were found to be identical by gas chromatography.

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SUMMARY

1-Butynyldiethylaluminum (I), 1-butenyldiethylaluminum (II), and (4-methyl-1-pentenyl)diisobutylaluminum (III) react with cobalt chloride in ether to furnish a complex array of products including much polymeric material. Benzene, which was isolated from the oxidation of compound (I), was shown to arise from initially formed 1-butyne by trimerization and subsequent dealkylation. A π-arenecobalt(I) surface complex is postulated to account for the cyclization. The oxidation of compound (II) yields *trans*-3-octene and *trans*-4-octene, while compound (III) gives rise to two $C_{20}H_{38}$ hydrocarbons which differ only in the position of the double bonds, and a $C_{28}H_{54}$ hydrocarbon. These results are shown to be consistent with the previously proposed mechanism for the oxidation of aluminum alkyls by metal halides[1].

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