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FACTORS INFLUENCING THE COURSE AND MECHANISM OF GRIGNARD REACTIONS. XXI. THE REACTION OF HALOALKYL PHENYL ETHERS WITH GRIGNARD REAGENTS IN THE PRESENCE OF COBALTOUS HALIDES

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It has been shown (1) that the cleavage of ethers by Grignard reagents and cobaltous halides is in many respects similar to the hydrogenolysis of ethers in the presence of Raney nickel (2). Furthermore,¹ Grignard reagents react with cobaltous halides to give unstable intermediates (sub-cobaltous halides) which abstract a halogen atom from an alkyl or aryl halide. It, therefore, seemed of interest to investigate the reaction of haloalkyl phenyl ethers with Grignard reagents in the presence of cobaltous halides.

 $\mathrm{RMgX} \ + \ \mathrm{C}_{6}\mathrm{H}_{5}\,\mathrm{O}(\mathrm{CH}_{2})_{\mathrm{n}}\mathrm{Br} \xrightarrow{\mathrm{CoBr}_{2}} \ \mathrm{R}_{-\mathrm{H}} \ + \ \mathrm{R}_{+\mathrm{H}} \ + \ \mathrm{C}_{6}\mathrm{H}_{5}\,\mathrm{O}(\mathrm{CH}_{2})_{\mathrm{n}} \cdot$

In this way a new class of free radicals might well be generated.

GENERAL PROCEDURE

RESULTS

Table I shows that as the length of the haloalkyl chain is increased there is an abrupt change in the character of the reaction of the haloalkyl phenyl ethers $[C_6H_5O(CH_2)_nBr]$ with the Grignard reagents modified by the addition of cobaltous halide. Thus, where n = 2, the over-all reaction may be represented by the following scheme:

$$\begin{array}{rcl} \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{MgX} & + & \mathrm{C}_{6}\mathrm{H}_{5}\,\mathrm{OCH}_{2}\,\mathrm{CH}_{2}\mathrm{Br} & \xrightarrow{\mathrm{C}_{0}\mathrm{Br}_{2}} & \mathrm{C}_{6}\mathrm{H}_{5}\,\mathrm{C}_{6}\mathrm{H}_{5} \\ & & + & \mathrm{C}_{6}\mathrm{H}_{5}\,\mathrm{OMgX} & (50\text{--}90\%) & + & \mathrm{CH}_{2}\text{---}\mathrm{CH}_{2}(65\text{---}81\%) & + & \mathrm{C}_{6}\mathrm{H}_{5}\,\mathrm{OC}_{2}\mathrm{H}_{5}(3\text{--}4\%). \end{array}$$

Phenol (60–70%) and phenoxypropane (17–27%) are also formed from γ -bromopropoxybenzene (n = 3), but the gas (65–71%) consists mainly of cyclopropane; there is also some propylene (maximum 10% by infrared analyses). The yields

¹ See earlier papers in this series.

of phenol and/or ethylene and cyclopropane from the haloalkyl phenyl ethers (n = 2 or 3) depend upon the particular Grignard reagent and the experimental conditions used, but under all conditions two moles of the Grignard reagent per mole of the haloalkyl phenyl ether are required.

When n > 3 the reaction of haloalkyl phenyl ethers $[C_6H_5O(CH_2)_nBr]$ with Grignard reagents, in the presence of cobaltous halides, is altered in three significant aspects: (a) First, the ether cleavage reaction is largely suppressed. When n = 4, 5, and 6, only 7-8% of phenol is formed. Note that cleavage occurs with the haloalkyl phenyl ethers $[C_6H_5O(CH_2)_nBr]$, but not with the alkyl phenyl ethers $[C_6H_5O(CH_2)_nH]$. (b) Second, when n = 4, 5, and 6, the alkyl

RMGX (consumed)		d)	C ₆ H ₅ O(CH ₂) _{II}		REACTION PRODUCTS, %				
	R	Mole	-(CH ₂) _n Br	Mole	C ₆ H ₆ OH	(CH2)n	$\begin{array}{c} \operatorname{RO}(\operatorname{CH}_2)_n \\ + \mathrm{H}, \\ \operatorname{RO}(\operatorname{CH}_2)_n \\ - \mathrm{H} \end{array}$	C ₆ H ₈ O(CH ₂) _n (CH ₂) _n OC ₆ H ₈	
1	C ₆ H ₅	0.32	—C₂H₄Br	0.2	70	C_2H_4 (65%)	4	None	
2	C ₆ H ₅	.32	C₂H₄Br	.18	58	C_2H_4 (81%)	3	None	
3	$(CH_3)_2CH$.13	$-C_2H_4Br$.08	90	$C_{2}H_{4}$ (81%)			
4	C_6H_5	.09	C ₃ H ₆ Br	.05	59	Cyclopropane (71%)	27	Trace	
5	$(CH_3)_2CH^a$.22-	C ₃ H ₆ Br	.10	70	Cyclopropane (70%)	18	Trace	
6	(CH ₃) ₂ CH	.04	C₄H ₈ Br	.02			85	Trace	
7	(CH ₃) ₂ CH	.15	—C₄H₅Cl	.09	8		74	Trace	
8	(CH ₃) ₂ CH	.17	C ₅ H ₁₀ Cl	.09			87	Trace	
9	C_2H_5	.15	$-C_{6}H_{12}Br$.08	—	_	70	25	
10	(CH ₃) ₂ CH	.09	$-C_6H_{12}Br$.076	7	_	44	18	

TABLE I REACTION OF HALOALKYL PHENYL ETHERS WITH GRIGNARD REAGENTS IN THE PRESENCE

OF COBALTOUS SALTS (1-5 Mole-%)

^a The amount of gas to be attributed to the cleavage of the ether was calculated on the basis of phenol isolated from the reaction mixture. This value, when subtracted from the total gas formed in the reaction, gave the value of the gas formed from the Grignard reagent. The composition of the gas was 46% propane and 54% propylene.

phenyl ethers $[C_{\theta}H_{\delta}O(CH_2)_{n}H]$ become the predominant products. (c) Third, although traces of the "dimer" are formed when n = 3, 4, and 5, the yield of

$$\mathrm{RMgX} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{O}(\mathrm{CH}_{2})_{n}\mathrm{Br} \xrightarrow{\mathrm{CoBr}_{2}} \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{O}(\mathrm{CH}_{2})_{n}\mathrm{OC}_{6}\mathrm{H}_{2}$$

the "dimer" becomes appreciable (25%) when n = 6. It is highly significant that no dodecane is formed when isopropylmagnesium bromide is treated with n-hexyl bromide in the presence of cobaltous bromide. Here hexane and hexene are formed together with a small amount of 2-methyloctane. The formation of the "dimer" $[C_6H_5O(CH_2)_6]_2$ may, therefore, be due to the stabilization of the free radical $[C_6H_5O(CH_2)_5CH_2]$.

When n = 2 or 3, the ethers [C₆H₅O(CH₂)_nH] produced by the reaction are saturated. They do not react with ozone or with hydrogen in the presence of Adams' catalyst. When n = 4, 5, and 6, a mixture of saturated and unsaturated

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ethers is formed. When the halogen in the starting material $[C_6H_5O(CH_2)_nX]$ is bromine about 12% of unsaturated ether is formed; when the halogen is chlorine about 30% of the ether product is unsaturated. When n = 4 or 5 ozonolysis indicates terminal double bonds (exclusive formation of formaldehyde). When n = 6, along with much formaldehyde a small amount of acetaldehyde is formed by ozonolysis of the mixture of saturated and unsaturated ether. This fact suggests that the bromide used may have contained as an impurity a small amount of $[C_6H_5O(CH_2)_4CHBrCH_3]$. Halides of this type (2-bromoöctane) readily dimerize (unpublished work). But the "dimer" found in the reaction, here carried out, contains no bands in the infrared other than those found in the infrared spectrum of an authentic sample of $[C_6H_5O(CH_2)_4OC_6H_5]$. The "dimer", therefore, did not arise from $[C_6H_5O(CH_2)_4CHBrCH_3]$.

The possibility was considered that some of the saturated and unsaturated ether (n = 4, 5, and 6) contain the saturated cyclic ethers. To exclude this possibility the entire fractions of the respective ethers were hydrogenated. The indices of refraction of the products thus formed were compared with the figures given in the literature for the pure saturated ethers (Table II). Since the cyclic

INDICES OF REFRACTION $(n_{\rm D})$ OF LTHERS $\rm KO(On_2)_{\rm B} \Pi$					
FROM REACTION \rightarrow	4	5	6		
Saturated and unsaturated	1.5025	1.5001	1.4951		
After hydrogenation	1.4979	1.4949	1.4929		
Literature value ^a	1.4971	1.4947	1.4920		

TABLE II

Indices of Refraction (n_p^{20}) of Ethers $\mathrm{RO}(\mathrm{CH}_2)_{n}\mathrm{H}$

^a A. I. Vogel, J. Chem. Soc., 622 (1948).

ethers have very high refractive indices, there can not have been more than traces of these (if any) in any of the products obtained.

A detailed discussion of the mechanism of these reactions will be given in a subsequent paper.

EXPERIMENTAL

Reagents. The haloalkyl phenyl ethers used in this study were prepared from sodium phenoxide and a five-fold excess of the corresponding dihalides. (a) $C_6H_5OC_2H_4Br$ (b.p. 114-115°/10 mm.; m.p. 32°); (b) $C_6H_5OC_2H_6Br$ (b.p. 132-133°/13 mm.); (c) $C_6H_5O(CH_2)_4Br$ (b.p. 153-156°/18 mm.; m.p. 39-40°).

Anal. Calc'd for C10H13BrO: Br, 34.9. Found: Br, 34.6.

(d) $C_6H_5O(CH_2)_4Cl$ (b.p. 133-134°/9 mm.).

Anal. Calc'd for C10H13ClO: Cl, 19.2; Found: Cl, 19.1.

(e) $C_{6}H_{5}O(CH_{2})_{5}Cl$ (b.p. 139-141°/9 mm.).

Anal. Calc'd for C₁₁H₁₅ClO: Cl, 17.9; Found: Cl, 17.3.

(f) $C_6H_5O(CH_2)_6Br$ (b.p. 132-133°/1 mm.; n_D^{20} 1.530).

Anal. Calc'd for C12H17BrO: Mol. wt., 257. Found: Mol. wt., 257.

The Grignard reagents were prepared in the usual way in ethyl ether, filtered under nitrogen pressure, and the concentration of the reagents determined by titration of aliquot portions for halide ions. An excess of magnesium (50%) was used in the preparation of the Grignard reagents.

Apparatus. The apparatus consisted of a three-necked flask fitted, through ground-glass joints, with a mercury-sealed stirrer, a graduated dropping-funnel, and an adapter connected to a reflux condenser and a tube containing the cobaltous bromide. The gases evolved in the reactions were collected and analyzed by the method described by Kharasch, Lewis, and Reynolds (3).

Procedure. The Grignard reagent (3-4 moles) was introduced into the three-necked flask, cooled to 0°, and the cobaltous bromide added in small portions (3-5 mole-%). The mixture was then allowed to come to room temperature, and the air in the apparatus was displaced by nitrogen gas. The solution of the haloalkyl phenyl ether (1 mole), dissolved in anhydrous ethyl ether, was then added. The rate of addition of the Grignard reagent was adjusted to maintain the reaction mixture at the boiling point of the ethyl ether. The evolved gases were collected either over water or water saturated with sodium chloride, or condensed in a cold trap.

The reaction mixture was finally refluxed gently until evolution of gas had ceased. In some cases additional cobaltous bromide (2-3 mole-%) was added before heating the mixture to insure complete reaction of the haloalkyl phenyl ether. The gas in the apparatus was then displaced by nitrogen. The mixture was then decomposed with ice and dilute sulfuric acid, the layers separated, and the water solution extracted twice with ether, and all the ether portions combined.

The phenol formed in the reactions was obtained by extraction of the ether solution with dilute (5%) aqueous sodium hydroxide. The alkaline extract was washed twice with ether, and all the ether portions were combined. After acidification the liberated phenol was extracted with ether, the solution dried, and the solvent removed. The phenol was distilled at reduced pressure. It was further identified (in the usual way) by the preparation of 2,4,6-tribromophenol.

The combined ethereal extracts were dried with sodium sulfate, the ether removed and the residue subjected to distillation. The types and amounts of the non-phenolic products isolated are recorded in Table I. Additional data for the compounds isolated are indicated below.

1. The ether $C_6H_5OC_2H_5$ (4%) (b.p. 67-70°/18 mm.) was obtained when $C_6H_5O(CH_2)_2Br$ was treated with C_6H_5MgBr and cobaltous bromide. The nitrated material melted at 58°. The material did not depress the melting point of an authentic sample of p-NO₂C₆H₄OC₂H₅.

2. The ether $C_6H_5OCH_2CH_2CH_3$ (27%) (b.p. 64-66°/7 mm.) was obtained when $C_6H_5O-(CH_2)_3Br$ was treated with C_6H_5MgBr in the presence of cobaltous bromide.

Anal. Calc'd for C₉H₁₂O: C, 79.4; H, 8.9; Mol. wt., 136.

Found: C, 79.4; H, 8.9; Mol. wt., 136.

The compound contains no unsaturation as indicated by hydrogenation and ozonolysis. After removal of the $C_6H_6OC_3H_7$ material a small amount of a brown oil was obtained. From this oil a small amount of the compound $C_6H_6O(CH_2)_6OC_6H_5$ (m.p. 80°) was isolated. The material here obtained did not depress the melting point of an authentic sample.

The gas formed in this reaction (71%) had a molecular weight of 42. Infrared measurements indicated that the gas was mainly cyclopropane (not more than 10% propylene).

3. (a) The mixture of the two ethers $C_6H_6OC_4H_9$ and $C_6H_6OC_4H_7$, obtained from interaction of $C_6H_6O(CH_2)_4Cl$ with isopropylmagnesium bromide and cobaltous bromide, boiled at 81-83°/8 mm., and had the refractive index n_b^{20} 1.5025. Hydrogenation and ozonolysis of this material indicated that it contained 26% of the olefin $C_6H_6O(CH_2)_2CH=CH_2$. The analyses of this material gave C, 80.4; H, 9.22. The calculated values for carbon and hydrogen of a mixture of $C_6H_6OC_4H_3$ (74%) and $C_6H_4OC_4H_7$ (26%) are C, 80.2; H, 9.12.

(b) The mixture of the two ethers $C_6H_5OC_4H_9$ and $C_6H_5OC_4H_7$, obtained from interaction of $C_6H_5O(CH_2)_4Br$ and isopropylmagnesium bromide, boiled at 81-83°/8 mm. $(n_p^{20}$ 1.5022). Hydrogenation and ozonolysis indicated that the material contained 11% of the ether $C_6H_5O(CH_2)_2CH=CH_2$.

When the mixture of the ethers $C_6H_5OC_4H_9$ and $C_6H_5OC_4H_7$ [from either (a) or (b)] was hydrogenated and distilled, the index of refraction was n_2^{20} 1.4979. The index of refraction for $C_6H_5OC_4H_9$ recorded in the literature is n_2^{20} 1.4971.

After removal of these ethers the small amount of residue was crystallized from methanol. A very small amount of a material was obtained which melted at 80-81°. This compound is presumably $C_6H_5O(CH_2)_8OC_6H_5$.

4. The mixture of the two ethers $C_6H_5OC_5H_{11}$ and $C_6H_5OC_5H_9$, obtained from the interaction of $C_6H_5O(CH_2)_5Cl$ with isopropylmagnesium bromide and cobaltous bromide, boiled at 97-99°/8 mm. $(n_p^{20} \ 1.5001)$. Ozonolysis and hydrogenation indicated that the mixture contained 30% of the unsaturated ether $C_6H_5O(CH_2)_3CH=CH_2$.

Anal. Calc'd for a mixture containing 30% $C_6H_5OC_5H_9$ and 70% $C_6H_5OC_6H_{11}$: C, 80.7; H, 9.5.

Found: C, 80.8; H, 9.56.

Hydrogenation of the mixture of these ethers $(n_{P}^{20} \ 1.5001)$ gave a material which had an index of refraction at 20° of 1.4949. The literature value for the index of refraction at 20° for the ether $C_6H_5O(CH_2)_4CH_3$ is 1.4947.

After removal of the ethers $C_6H_5OC_5H_{11}$ and $C_6H_5OC_5H_9$ a small amount of residue (1 g.) was obtained. This was crystallized twice from methanol. It melted at 81-82°. The compound is presumably $C_6H_5O(CH_2)_{19}OC_5H_5$.

5. The mixture of the two ethers $C_6H_5OC_6H_{13}$ and $C_6H_5OC_6H_{11}$, obtained from the interaction of $C_6H_5O(CH_2)_6Br$ with ethylmagnesium bromide, boiled at 112–113°/8 mm. $(n_p^{20}$ 1.4951). Hydrogenation and ozonolysis indicated that the ether contained 12% of the unsaturated ether.

Anal. Calc'd for a mixture of $C_6H_5OC_6H_{13}$ (90%) and $C_6H_5OC_6H_{11}$ (10%): C, 80.93; H, 10.08.

Found: C, 80.94; H, 10.04.

Hydrogenation of the mixture $(n_{\rm p}^{20} \ 1.4951)$ of saturated and unsaturated ethers gave a saturated ether $n_{\rm p}^{20} \ 1.4929$. The literature gives $n_{\rm p}^{20} \ 1.4920$ for $C_6H_8O(CH_2)_5CH_3$.

The residue remaining after removal of the saturated and unsaturated ethers solidified upon standing. It was crystallized twice from methanol (m.p. 85-86°). The yield of this material was 25%, based on the amount of the starting material $[C_6H_5O(CH_2)_6Br]$. The compound is presumably $C_6H_5O(CH_2)_{12}OC_6H_5$.

Anal. Calc'd for C24H34O2: C, 81.2; H, 9.7; Mol. wt., 354.

Found: C, 81.0; H, 9.4; Mol. wt., 354.

Ozonolysis. Five millimoles of the mixture of saturated and unsaturated ethers $[C_{\theta}H_{\delta}O(CH_2)_n +_H$ and $C_{\delta}H_{\delta}O(CH_2)_{n-H}]$ were dissolved in ethyl acetate and ozonized at -80° , and the ozone consumed noted. The solvent was removed and the ozonides were dissolved in absolute alcohol and hydrogenated in the presence of palladium oxide on calcium carbonate. Nitrogen was then passed through the solution and the volatile aldehydes were collected in a saturated solution of dimedone in water. With the mixture of ethers n = 4 and 5 only the dimedone of formaldehyde was obtained (m.p. 189–190°). The mixture of the ethers n = 6 the dimedone derivative did not melt sharply. The mixture of the saturated and unsaturated ethers was therefore ozonized in CCl_4 at 0°, and the volatile aldehydes were absorbed in water. This solution was then added to a saturated solution of dimedone in water. The precipitate which separated within 15 minutes was collected. It melted, upon crystallization from ethanol, at 187°, and did not depress the melting point of an authentic sample of the dimedone derivative of formaldehyde. From the fitrate, after several hours standing, a second precipitate separated. It melted at 137° and it did not depress the melting point of an authentic sample of the dimedone derivative of acetaldehyde.

Reaction of n-hexyl bromide with isopropylmagnesium bromide in the presence of cobaltous bromide. In connection with the formation of the compound $C_6H_5O(CH_2)_{12}OC_6H_5$ from isopropylmagnesium bromide and $C_6H_5O(CH_2)_6Br$ in the presence of cobaltous bromide, it was of interest to learn whether n-hexyl bromide would behave in a manner similar to that of the ether $C_6H_5O(CH_2)_6Br$. Accordingly, n-hexyl bromide (0.12 mole) was added to isopropylmagnesium bromide (0.32 mole) containing 3 mole-% of cobaltous bromide. The rate of addition of the reagent and the temperature were the same as used in the case of the ether $C_6H_5O(CH_2)_6Br$.

In this case, however, the reaction product consisted mainly of hexane and hexene. A

small fraction (1 g.) (b.p. $40^{\circ}/16$ mm.) of a high-boiling material (mol. wt., 121, probably a nonane formed by a normal Grignard condensation) was obtained. No higher-boiling material was present, indicating the absence of any of the C₁₂H₂₆ hydrocarbon.

Reaction of methylmagnesium bromide with methyl bromide and dodecanal in the presence of cobaltous bromide. In a previous publication (4) it was shown that n-hexylmagnesium bromide in diethyl ether when treated with methyl bromide does not yield any octanol-2, a product which would result if the free radical derived by abstraction of a hydrogen atom from the diethyl ether broke down to acetaldehyde and a free ethyl radical.

 $CH_{3}CHOC_{2}H_{5} \rightarrow C_{2}H_{5} + CH_{3}CHO$

One might argue, however, that the free radical reaction of the Grignard reagent with the methyl bromide and cobaltous bromide is faster than the addition reaction of the Grignard reagent to the aldehyde. It was, therefore, considered desirable to determine whether addition of a Grignard reagent to an aldehyde would take place if methyl bromide and cobaltous bromide are present in the reaction mixture. The experiment was performed as follows: To a cooled solution of methylmagnesium bromide in diethyl ether cobaltous bromide was added and methyl bromide was passed into the reaction mixture. A vigorous gas evolution took place. When the gas evolution was well sustained, dodecanal dissolved in ethyl ether was added very slowly. The rate of the gas evolution decreased somewhat and the addition of the aldehyde was stopped when the gas evolution ceased. The reaction mixture was worked up in the usual way. From 16 g. of dodecanal only 2 g. was recovered. The rest of the reaction mixture consisted of 10 g. of $CH_3(CH_2)_{10}CHOHCH_3$ (b.p. 95-96°/0.5 mm.).

Anal. Calc'd for C₁₂H₂₈O: C, 78.0; H, 14.1.

Found: C, 78.04; H, 14.27.

The phthalic acid half ester of the alcohol [CH₃(CH₂)₁₀CHOHCH₃] here obtained melted, after crystallization from dilute alcohol, at 54-56°. This compound is probably a hydrate. Anal. Calc'd for C₂₇H₃₂O₄·H₂O: C, 69.0; H, 9.3.

nal. Calc d for $C_{27}\Pi_{32}O_4 \cdot \Pi_2O$: C, 09.0; Π

Found: C, 69.0; H, 9.09.

The gas consisted of a mixture of 78% methane, 15% ethylene, and 7% ethane and 3-4 g. of a heavy brown oil.

SUMMARY

1. The reaction of haloalkyl phenyl ethers $C_6H_5O(CH_2)_nBr$ or $C_6H_5O(CH_2)_nCl$ with Grignard reagents (in ethyl ether) in the presence of cobaltous bromide gave the following results: (a) n = 2. Phenol (58–90%), ethylene and $C_6H_5O(CH)_2H$ (3–4%); (b) n = 3. Phenol (59–70%) and cyclopropane (70%) containing about 5–10% of propylene, and a trace of $C_6H_5O(CH_2)_6OC_6H_5$ and $C_6H_5O(CH_2)_8H$ (17–27%); (c) n = 4. Phenol (up to 8%), a mixture (74–85%) of $C_6H_5O(CH_2)_4 + H$ and $C_6H_5O(CH_2)_4 - H$ (11% of unsaturated ether in the case of the bromoalkyl phenyl ether and 26% of the unsaturated ether in the case of chloroalkyl phenyl ether) and a trace of the ether $C_8H_5O(CH_2)_8OC_6H_5$; (d) n = 5. Traces of phenol, a mixture (87%) of $C_6H_5O(CH_2)_5 + H$ and $C_6H_5O(CH_2)_5 - H$ (30% of the unsaturated ether $C_6H_5O(CH_2)_5 - H$) and a trace of the ether $C_6H_5O(CH_2)_{10}OC_6H_5$; (e) n = 6. Phenol (7%), a mixture (70%) of $C_6H_5O(CH_2)_6 + H$ and $C_6H_5O(CH_2)_6 - H$ (12% of the unsaturated ether), and 25% of the ether $C_6H_5O(CH_2)_{12}OC_6H_5$.

2. It was established that *n*-hexylmagnesium bromide (in ethyl ether) reacts with methyl bromide in the presence of cobaltous bromide to give hexane and hexene and a small amount of a nonane. A careful but unsuccessful search for the hydrocarbon $C_{12}H_{26}$ was made.

3. Methylmagnesium bromide in ethyl ether reacts with methyl bromide and dodecanal, in the presence of cobaltous bromide, to give $CH_3(CH_2)_{10}CHOHCH_3$, a small amount of unidentified oil, and a gas. The composition of the gas was 78% methane, 15% ethylene, and 7% ethane.

CHICAGO 37, ILLINOIS

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