from SiH_4,[2] and adjusted slightly to give best agreement. The other five force constants were then calculated and are listed in Table III.

TABLE III

FORCE CONSTANTS AND CALCULATED FREQUENCIES

Force constant $\times 10^5$	Frequency Calcd.	Obsd.[2]	This work liquid	Deviation, % From ref. 2	From this work
		Chloroform			
f_d	3.38[a]	3034	3033	3032	+0.03	+0.06
f_D	5.04[a]	664	667	668	−0.35	−0.60
f_α	0.59	366	364	..	+0.55	....
f_β	0.21	263	260	..	+1.26	....
$f_{d\alpha}$	0.36	758	760	759	−0.27	−0.13
$f_{d\beta}$	0.48	1207	1205	1218	+0.16	−0.91
		Trichlorosilane[7]			
f_d	2.92[b]	2256	2258	2258	−0.01	0.0
f_D	4.43	486	489	..	−0.6	....
f_α	0.43	253	250	..	+1.2	....
f_β	0.11	802	799	798	+0.38	+0.48
$f_{d\alpha}$	0.67	583	587	..	−0.69	....
$f_{d\beta}$	0.35	181	179	..	+1.1	....

[a] Transferred from ref. 14.   [b] Transferred from ref. 2.

The agreement between calculated frequencies from the above force constants and the experimental values is within 1.5%. It should be

pointed out that these force constant calculations were based upon the published values of fundamental frequencies obtained by Raman spectroscopy for $SiHCl_3$ and by infrared spectroscopy for $CHCl_3$. This was necessary to ensure a consistent set of values, since for $SiHCl_3$ only two of the six fundamentals are in the 1–15 μ range of our spectrometer, and for $CHCl_3$ only four fundamentals were determinable.

The value of the stretching constant $f_{Si-H} = 2.93$ compares well with the 2.84 value in SiH_4 quoted by Herzberg.[2] Our Si–Cl stretching constant $f_{Si-Cl} = 4.43$ falls between the $SiCl_4$ value of 3.75 of Herzberg[2] and the value of 5.10 obtained by Linnett.[16]

The bending and interaction constants for $SiHCl_3$ agree in relative magnitude with those calculated for $CHCl_3$, but due to the lack of data no further comparison can be made at this time.

(16) D. F. Heath and J. W. Linnett, Trans. Faraday Soc., 44, 561 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Copolymerization of 2-Chloroallyl Linoleate with Styrene[1]

BY ELIZABETH DYER AND WILLIAM C. MEISENHELDER[2]

Studies have been made of the composition, properties and structure of copolymers of 2-chloroallyl linoleate and styrene. These were prepared by bulk polymerization with benzoyl peroxide at 80°, with stannic chloride at room temperature and by emulsion polymerization in the presence of potassium persulfate at 50°. The ester content of the copolymer was dependent on the monomer ratio, the amount of catalyst, and the type of polymerization. Self-polymerization did not occur with benzoyl peroxide as catalyst.

As the ester content of the polymers was increased to 27% (one ester per nine styrene units), the softening temperatures and intrinsic viscosities were lowered. Polymers containing a higher proportion of ester were infusible and largely insoluble.

By analysis of the copolymers after saponification it was shown that approximately 83% of the ester polymerized with styrene through chloroallyl double bonds, and 17% through linoleic double bonds. In the infusible polymers cross-linking had occurred through linoleic side-chains.

There have been several recent papers[3] on the polymerization of vinyl and allyl esters of various fatty acids. In the case of the oleates, Swern, Billen and Knight[3b] showed that the 2-chloroallyl ester had a greater tendency to polymerize than the allyl, methallyl or 3-butene-2-yl esters. It was thought of interest to prepare 2-chloroallyl linoleate and study its copolymerization with styrene.

The 2-chloroallyl ester of linoleic acid is not mentioned in the literature except in a patent by Coleman and Hadler,[4] in which the actual preparation and properties are not described. In the

(1) From the Ph.D. Thesis of William C. Meisenhelder, University of Delaware, 1950.

(2) Armstrong Cork Company Research Fellow.

(3) (a) P. O. Powers, Ind. Eng. Chem., 38, 837 (1946); (b) D. Swern, G. N. Billen and H. B. Knight, THIS JOURNAL, 69, 2439 (1947); (c) D. Swern and E. F. Jordan, ibid., 70, 2334 (1948); (d) E. F. Jordan and D. Swern, ibid., 71, 2377 (1949); (e) P. D. Bartlett and R. Altschul, ibid., 67, 816 (1945); (f) E. Dyer, T. G. Custer and W. C. Meisenhelder, ibid., 71, 2728 (1949); (g) S. A. Harrison and D. H. Wheeler, ibid., 73, 839 (1951).

(4) C. H. Coleman and B. C. Hadler, U. S. Patent 2,127,660 (1938).

present work the ester was obtained by the acid-catalyzed reaction of 2-chloroallyl alcohol with linoleic acid.

Unlike 2-chloroallyl oleate[3b] and allyl acetate[3e] this ester did not polymerize when heated with benzoyl peroxide (1 or 2% of the quantity of the ester) at 80° for 40 hours under nitrogen.

Copolymers of the ester with styrene were formed by peroxide and stannic chloride-catalyzed reactions in bulk and by emulsion polymerization with a persulfate catalyst. The composition and properties of the copolymers are given in Table I. The unreacted ester recovered from the copolymerization mixtures was practically unchanged in unsaturation except in the case of the stannic chloride reactions, when some evidence of dimer formation was obtained.

It was found that the ester content of the copolymers was increased by increasing the proportion of ester in the monomer mixtures, although this was at the expense of the yield of polymer. This

TABLE I

POLYMERIZATION OF 2-CHLOROALLYL LINOLEATE WITH STYRENE

Catalyst[a]	Catalyst,[b] %	Ester:styr. ratio in monomers, moles	Yield[b] of polymer, %	Ester recov., %	Chlorine[c] in polymer, %	Ester:styr. ratio in polymers, moles	Softening point of polymer, °C.	Sol.[i] of polymers in C6H6, %	[η] of soluble polymer[g]	Approx. molec. weight	No. of ester units per chain
Bz2O2	1	0:1	94	..	..	....	140–145	100	0.423	60,000	..
Bz2O2	1	1:0	0	88	..	....	.....	...	....	....	..
Bz2O2	1	1:5	52	76	1.34	1:22	110–115	100	.225[h]	27,000	10
Bz2O2	1	1:2	32	..	2.19	1:12	85–88	100	....	....	..
Bz2O2	1	1:1.33	14	68	2.77	1:9.1	75–80	100	.148	16,000	12
Bz2O2	1	1:1	11	81	3.16	1:7.4	Infus.[e]	PS[f]	....	....	..
Bz2O2	1	1:1	14	..	4.01	1:5.1	Infus.[e]	5.1	.059	5,100	6
Bz2O2	0.25	1:2	13	64	2.29	1:11	78–83	98.7	.228	28,000	17
Bz2O2	1	1:2	31	53	2.82	1:8.8	75–80	PS	....	....	..
Bz2O2	2	1:2	32	58	3.10	1:7.6	Infus.[e]	20.1	.100	9,900	9
Bz2O2	4	1:2	8[d]	40	3.05	1:7.8	Infus.[e]	PS	....	....	..
Bz2O2	4	1:2	37	..	3.59	1:6.1	Infus.[e]	13.5	.075	6,800	7
SnCl4	1	0:1	30	..	..	....	110–115	100	....	....	..
SnCl4	2	1:5	27	91	0.45	1:72	95–100	100	....	....	..
SnCl4	2	1:2	10	79	1.13	1:27	75–80	100	.044	3,400	1
K2S2O8	0.6	1:5	45	41	0.46	1:71	115–120	100	....	....	..
K2S2O8	0.6	1:2	14[d]	36	1.19	1:25	85–90	100	....	....	..
K2S2O8	0.6	1:1.33	14[d]	52	1.99	1:13.7	75–80	PS	....	....	..
K2S2O8	0.6	1:1	7[d]	32	2.02	1:13.5	70–75	PS	....	....	..

[a] Peroxide-catalyzed reactions at 80° for 40 hr., SnCl4 reactions at room temp. for 55 hr., emulsion runs at 50° for 40 hr. [b] Based on total weight of monomers. [c] Each value is the average of duplicate samples. [d] Some of polymer was lost. [e] No fusion up to 220°, but discoloration usually above 170°. [f] PS means partially soluble. [g] Determined in benzene at 25°. [h] Found by the single value method of Smith (ref. 13). [i] Expressed as the % of a 0.5-g. sample soluble in 50 ml. of benzene.

effect was observed in the three types of polymerization studied. With the same monomer mixtures, the benzoyl peroxide-catalyzed reactions gave polymers containing more ester than the stannic chloride or persulfate-catalyzed experiments. In the case of the peroxide polymerizations, the ester content of the copolymers was also increased by increasing the catalyst concentration from 0.25 to 4%.
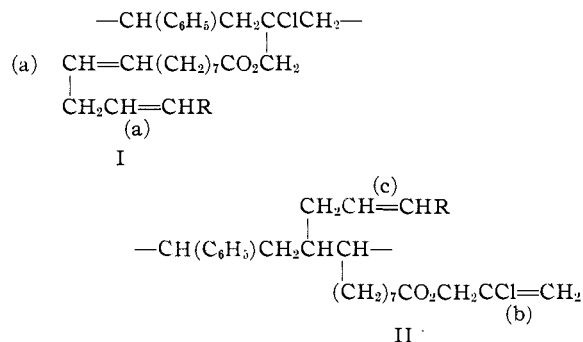
The softening points of the copolymers were found to decrease with increasing ester content, indicating a decrease in molecular weight. Viscosity measurements in benzene corroborated this. In the case of the polymer obtained from the stannic chloride-catalyzed reaction of a 1:2 monomer ratio, the approximate molecular weight obtained from viscosity measurements was close to the molecular weight of the repeating unit (calculated from the composition of the polymer). This indicates that the 2-chloroallyl linoleate acted as a chain terminator under these conditions. In all of the other cases investigated, however, there were several ester units per chain.

Products of higher ester content than the 1:9.1 copolymer were infusible and at least partially insoluble in benzene. This was presumably due to cross-linking through the linoleic chain, since the solubility decreased as the ester content of the polymers increased. The 1:9.1 copolymer and others completely soluble in benzene were convertible by heating in air to insoluble gels. This might be assumed to be due to oxidation and polymerization through the linoleic groups.

Some evidence as to which of the double bonds were involved in copolymerization and in cross-linking was obtained by saponification of certain of the polymers. The hydrolyzed products were isolated and analyzed for free carboxyl groups.

The data of Table II show that the milliequivalents of carboxyl per gram of saponified polymer generally increased with increasing ester content. However, the per cent. of the carboxyl was essentially constant (average value 28) for those polymers giving some indication of cross-linking. The polymer containing a 1:9.1 ester to styrene ratio was completely soluble, thus apparently without cross-linking, and showed a significantly lower per cent. carboxyl in the saponified polymer.

The chloroallyl linoleate could copolymerize with styrene through the chloroallyl unsaturation (I) or through the linoleic double bonds (II).

$$-CH(C_6H_5)CH_2CClCH_2-$$

(a) $CH=CH(CH_2)_7CO_2CH_2$

        $CH_2CH=CHR$

        (a)

        I

                    (c)
              $CH_2CH=CHR$

$-CH(C_6H_5)CH_2CHCH-$

              $(CH_2)_7CO_2CH_2CCl=CH_2$
              (b)

              II

The saponified copolymer would contain carboxyl if linked as in II, but not if as in I. The data show that at least 72% of the ester was combined as in I, since only 28% of the carboxyl remained after saponification. This is not surprising, as the reactivity of the chloroallyl double bond would be expected to be greater than that of the linoleic double bonds. The polymer which showed no evidence of cross-linking contained only 17% of carboxyl after saponification, and hence

had an even greater portion of the ester (83%) combined as in I.

Since the ester was combined with styrene in both possible ways, cross-linking could occur in three ways (a, b, c). However, only when cross-linking took place through (a) could the carboxyl content of the saponified polymer be greater than that of a saponified non-cross-linked polymer of approximately the same initial ester content. This was found to be the case by a comparison of the carboxyl content after saponification of the soluble 1:9.1 copolymer and the other four partially soluble copolymers, of which one was a 1:8.8 copolymer. The difference of about 11% (28-17) suggests that cross-linking has occurred according to (a) in these four polymers. Hence the evidence available indicates that approximately 83% of the ester copolymerized as in I and 17% as in II with 13% of the side-chain linoleic groups (Ia) forming cross-links.

Experimental

2-Chloroallyl Linoleate.—A mixture of 50 g. (0.18 mole) of linoleic acid (Hormel, containing 0.204% conjugated polyunsaturated material), 23.2 g. (0.25 mole) of freshly distilled 2-chloroallyl alcohol[5] (b.p. 133–134°), 200 ml. of benzene and 1.7 g. (0.04 molecular equivalent) of p-toluenesulfonic acid was stirred at 95–110° for 6 hours in the presence of carbon dioxide with arrangement for the azeotropic removal of water.[4] The resulting solution was freed from acids by washing with water, salt solution, 2.5% sodium carbonate, and then water until neutral. The solvent was removed from the dried solution, and the ester distilled in the absence of air. The product, obtained in yields of 73–84%, boiled at 184–189° at 0.5–1.0 mm. and had an acid number varying from 2–6. The redistilled ester boiled at 184–185° at 1.9 mm.; d^{25}_4 0.9455; n^{25}D 1.4725. It was stored under carbon dioxide.

Anal. Calcd. for $C_{21}H_{35}O_2Cl$: C, 71.05; H, 9.94; Cl, 9.99; acid no.,[6] 0; molecular refraction, 104.3. Found: C, 70.88, 70.80; H, 10.19, 10.12; Cl, 10.03, 9.90; acid no., 0.11, 0.51; molecular refraction, 105.2.

Polymerization. A. Bulk, Peroxide-Catalyzed.—Mixtures of 2-chloroallyl linoleate, styrene (washed with alkali and freshly distilled), and benzoyl peroxide (recrystallized from chloroform–methanol) were heated for 40 hours at 80° in sealed tubes under an atmosphere of purified[7] nitrogen. The monomer ratios, based on 4 to 5 g. of styrene, and the quantities of catalyst used are shown in Table I. The polymers were isolated by dissolving in benzene, washing with 5% sodium carbonate and then water, and precipitating by slow addition of the benzene solution to methanol, followed by soaking of the precipitate in fresh non-solvent. The products were purified by two additional reprecipitations (or in one case by successive leachings until no unchanged ester was found in the filtrate). The unreacted ester recovered from the filtrates by vacuum distillation of solvents was shown by comparative iodine values to contain only slightly less unsaturation than the original.

Two separate attempts to polymerize 2-chloroallyl linoleate alone by heating with 1 and 2% of its weight of benzoyl peroxide at 80° for 40 hours were unsuccessful.

B. Bulk, Cationic.—Mixtures of 2-chloroallyl linoleate, styrene and stannic chloride (1% of the total monomer weight) were allowed to stand at room temperature in the presence of nitrogen. Although the control containing styrene alone showed immediate polymerization, no visible change had occurred in the others after 19 hours. An additional 1% of catalyst was then added. Heat was evolved and the material rapidly became more viscous. After a total of 55 hours the contents of the tubes were dissolved in benzene, the solution washed with nearly saturated sodium sulfate solution and water to remove stannic chloride, and

the products isolated by precipitation as in the peroxide-catalyzed experiments.

The ester recovered from the filtrates showed an appreciable decrease in unsaturation (iodine value 78.7 in one case as compared to 143 for the original ester). Cryoscopic molecular weight determinations in purified cyclohexane gave values of 486 and 414 for the recovered ester from 1:5 and 1:2 monomer mixtures. Calculations based on the assumption that only monomer and dimer were present indicated that this material contained 37 and 17% dimer, respectively.

C. Emulsion.—Emulsions of styrene (4 g. usually), 2-chloroallyl linoleate, potassium persulfate, S.F. flakes and water (the last three 0.6, 5 and 1.5%, respectively, of the total monomer weight) were agitated at 50° in tubes filled with nitrogen before sealing. After 40 hours the contents of each tube were treated with 1 ml. of 1% hydroquinone solution, and poured into 200 ml. of absolute methanol containing 0.5 ml. of concd. sulfuric acid. The precipitated polymers were soaked in methanol, ground, and freed from unchanged ester by repeated leaching with methanol. The ester isolated from the initial acid–methanol filtrate showed no decrease in unsaturation. A styrene control polymerized normally.

Methods of Analysis.—The most successful method of determining chlorine in the monomeric ester was by the sodium–liquid ammonia procedure[8] followed by Volhard titration. The polymers were analyzed for chlorine by use of the Parr bomb and the Volhard method.

A quantitative determination of unsaturation by means of iodine values could not be obtained, since 2-chloroallyl linoleate did not react completely with iodine bromide or iodine chloride, even after prolonged periods. This is in agreement with the observation of Lee, Kolthoff and Mairs,[9] who noted the very slow addition of iodine monochloride to a polymer containing halogen on the carbon of the double bond. Although the halogen addition was not quantitative, low but reproducible iodine values (141–145 when the theoretical is 215) were obtained from pure 2-chloroallyl linoleate by the Wijs 3-minute catalytic method.[10] Consequently this procedure was used on a comparative basis to detect changes in the unsaturation of the recovered ester. Since the theoretical iodine value for the absorption of only two moles of iodine by the ester is 143, it is possible that the chloroallyl double bond did not react at all under these conditions. However, 2-chloroallyl alcohol gave poorly reproducible iodine values which were about 0.4 of the theoretical.

Intrinsic viscosities were determined in benzene at 25° with an Ostwald viscosimeter. In the case of the completely soluble polymers $[\eta]$ was found[11] by extrapolating to zero concentration a graph of ln $\eta r/c$ versus c (where c is in g. per 100 ml.). For the partially soluble polymers the method of Marvel, Inskeep and Deanin[12] was used to determine the per cent. soluble and the $[\eta]$ of the soluble portion. Approximate viscosity average molecular weights were calculated from Ewart's equation[13] for oil-phase polystyrene.

Heat Convertibility of Polymers.—Small samples of the polymers having 1:25, 1:13.7 and 1:9.1 ester to styrene ratios, respectively, were heated for 24 hours at 80° in air. Before heat treatment the first and third were completely soluble in benzene, the second almost completely soluble. After heating the first, largely polystyrene, gave a slight gel and the second and third became almost completely insoluble.

Saponification of Polymers and Analysis of Products for Carboxyl.—A sample of polymer weighing 0.6 to 1.0 g. was refluxed for 5 hours with 25 to 30 ml. of a reagent made from 10 g. of potassium hydroxide, 90 ml. of benzyl alcohol, 10 ml. of methanol and 5 ml. of water. During saponification the polymers dissolved. The reaction mixture was poured into a solution of 200 ml. of methanol, 50 ml. of water and 2

(5) Obtained through the courtesy of the Shell Development Company.

(6) Calculated as mg. of NaOH to neutralize 1.0 g. of substance. C, H, Cl analyses by Carl Tiedcke.

(7) L. F. Fieser. THIS JOURNAL, **46**, 2639 (1924).

(8) T. H. Vaughn and J. A. Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(9) T. S. Lee, I. M. Kolthoff and M. A. Mairs. *J. Polymer Sci.*, **3**, 77 (1948).

(10) H. D. Hoffman and C. E. Green, *Oil and Soap*, **16**, 239 (1939).

(11) With one exception as noted in Table I.

(12) C. S. Marvel, G. E. Inskeep and R. Deanin, *Ind. Eng. Chem.*, **39**, 1488 (1947).

(13) W. V. Smith, THIS JOURNAL, **68**, 2061 (1946).

TABLE II

ANALYSIS OF SAPONIFIED POLYMERS FOR CARBOXYL

Ester:styr. ratio in polymer, moles	Sol. of polymer in C₆H₆, %	Softening point of original polymer, °C.	M. e. of –COOH/g. of sapon. polymer	Max. m. e. of –COOH possible[a]	-COOH in sapon. poly- mer, %[b]
Polystyrene	100	140–145	0.00813[c]		
1:9.1	100	75–80	.141	0.781	17.0
1:8.8	PS[d]	74–77	.233, 0.225	.784	27.7
1:7.6	20.1	Infus.	.303, 0.250	.873	30.8
1:6.1	13.5	Infus.	.365, 0.294	1.01	28.2
1:6.1[e]	13.5	Infus.	.257, 0.253	1.01	24.4
1:5.1	5.1	Infus.	.313, 0.320	1.13	27.6

[a] Calculated from composition of unsaponified polymer on assumption that all the linoleic acid was bound to the chain through linoleic double bonds. [b] Found from 100 x column 4/column 5. [c] This was deducted from the values below in calculating column 6. [d] Partially soluble. [e] Heated with base 10 hours to saponify, others 5 hours.

ml. of concd. sulfuric acid to precipitate the hydrolyzed polymer. The product was filtered, washed on the filter with methanol and water, and then washed by successive agitations on a mechanical shaker for several hours with slightly acidulated 3:1 methanol–water, pure water and absolute methanol.

The dried product was analyzed for carboxyl by titration in benzyl alcohol solution, using phenolphthalein and 0.05 N potassium hydroxide dissolved in 10% methanol–90% benzyl alcohol.[14] The results obtained are shown in Table II. That the time for the saponification of the original polymer was long enough was shown by the fact that the carboxyl content of the saponified polymer was not increased by doubling the heating period.
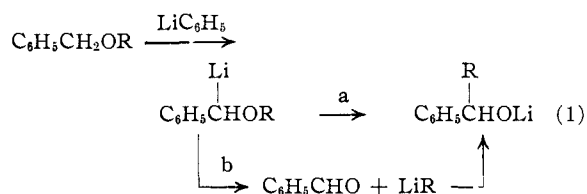

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rearrangement of Benzyl Ethers to Carbinols by Potassium Amide. Mechanism of Isomerization of Carbanions Involving 1,2-Shifts[1,2,3]

BY CHARLES R. HAUSER AND SIMON W. KANTOR

The objective of this investigation was to establish the mechanism of intramolecular isomerizations of carbanions involving 1,2-shifts of alkyl groups without their bonding pair of electrons. These isomerizations, which include the Stevens rearrangement of quaternary ammonium and sulfonium ions by bases and the Wittig rearrangement of benzyl ethers by lithium phenyl, are to be distinguished from the common rearrangements of carbonium ions in which alkyl groups shift with their bonding pair of electrons. The work of Wittig was extended using lithium butyl and particularly potassium amide with which there can be no doubt that carbanions are actually the intermediates. The relative ease of isomerization of the carbanions of several ethers was established. The carbanion of dibenzyl ether not only isomerized to form the anion of benzylphenyl-carbinol but also underwent partly β-elimination to form benzaldehyde and benzyl ion—a type of reaction that predominated with the carbanion of dibenzohydryl ether. These isomerizations as well as those reported previously are in agreement with an internal displacement mechanism.

Wittig and co-workers[4] showed that dibenzyl ether, benzyl methyl ether and certain related ethers are converted to carbinols by lithium phenyl. They considered that the ether is first metalated at an α-hydrogen and that the resulting lithium derivative undergoes intramolecular isomeriza-tion,[5] course a in eq. (1). They rejected course b in (1), involving β-elimination followed by recom-bination, because lithium phenyl converted benzyl methyl ether to phenylmethylcarbinol without forming a detectable amount of benzohydrol, some

$$C_6H_5CH_2OR \xrightarrow{LiC_6H_5}$$

$$C_6H_5\overset{\underset{|}{Li}}{C}HOR \xrightarrow{a} C_6H_5\overset{\underset{|}{R}}{C}HOLi \quad (1)$$

$$\overset{b}{\longrightarrow} C_6H_5CHO + LiR$$

(1) Paper I on Isomerizations of Carbanions.

(2) This work was carried out under Contract N7onr-455 with the Office of Naval Research.

(3) Presented at the Atlantic City Meeting of the American Chemical Society, September, 1949.

(4) (a) Wittig and Lohman, *Ann.*, **550**, 260 (1942); (b) Wittig and Happe, *ibid.*, **557**, 205 (1947).

(5) For evidence for the intermediate formation of the lithium deriva-tive of 9-fluorenylmethyl ether, see ref. 4b. Although the lithium–carbon bond may be largely covalent (see Rogers and Young, THIS JOURNAL, **68**, 2748 (1946)), the isomerization may be considered to take place within the carbanion which is potentially present.

of which might have been expected had benzal-dehyde been an intermediate.

As further evidence against course b, we have found that lithium butyl converts dibenzyl ether to benzylphenylcarbinol without forming an isolable amount of benzylbutylcarbinol. Judging from an experiment with benzaldehyde and a mixture of lithium butyl and lithium benzyl, both carbinols would have been produced in equal yield if ben-zaldehyde were an intermediate.

The present investigation was concerned mainly with the study of the reactions of benzyl ethers and related ethers with potassium amide which is a better ionizing agent than the lithium reagents. In general, the benzyl ethers in diethyl ether were added to two molecular equivalents of potassium amide in liquid ammonia, the ammonia replaced by diethyl ether and the mixture refluxed (Table I). The reaction mixtures were colored indicating the presence of the carbanions. With dibenzyl ether there were obtained benzylphenylcarbinol (61–67%),[6] toluene (16%) and benzamide (14%, isolated as benzoic acid). The benzamide was

(6) Although sodium amide produced a similar red colored mixture, no benzylphenylcarbinol was obtained when the diethyl ether suspen-sion was refluxed for several hours, 87% of the dibenzyl ether being recovered. Neither was the carbinol obtained when dibenzyl ether was refluxed with diethylaminomagnesium bromide in diethyl ether for several hours; in this case, 88% of the dibenzyl ether was recov-ered.