Muskat apparatus at a reaction temperature of 84–88°. Rates of flow were adjusted so that the ratio of $CF_3CHClCH_3$ to chlorine was always greater than 3:1. The product contained 72% $CF_3CCl_2CH_3$ and 28% $CF_3CHClCH_2Cl$.

Acknowledgment.—The authors wish to acknowledge the financial assistance of Mallinckrodt Chemical works which made this research possible.

Summary

1. The preparation of $CF_3CH_2CH_3$ and $CClF_2CH_2CH_3$ has been accomplished in excellent yields.

2. Both photochemical and thermal chlorination of $CClF_2CH_2CH_3$ have yielded several new chlorofluoropropanes.

3. Several new fluorine-containing propanes have been prepared by the fluorination of certain chloro- and chlorofluoropropenes with mercury(II) oxide and hydrogen fluoride. Some bromofluoropropanes also were synthesized by fluorination of the corresponding bromides.

LAFAYETTE, INDIANA RECEIVED[17] JANUARY 2, 1947

---

[17] Original manuscript received February 25, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

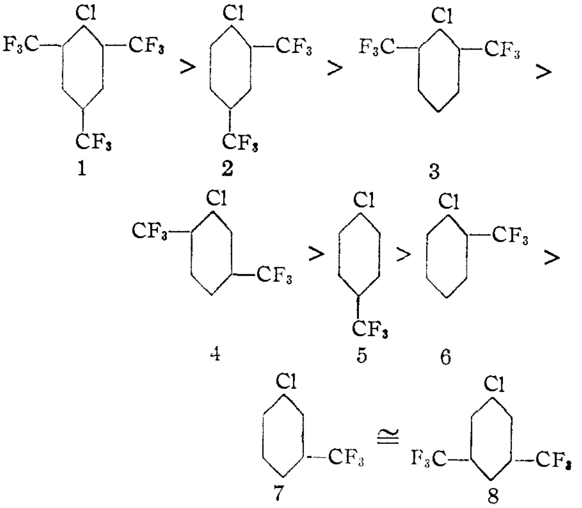
The Preparation of Certain Ethers of Trifluoromethyl-substituted Phenols[1,2]

BY EARL T. MCBEE, ROBERT O. BOLT,[3] PETER J. GRAHAM AND ROBERT F. TEBBE[4]

Certain alkoxy-(trifluoromethyl)-benzenes and alkoxy- and aryloxy-bis-(trifluoromethyl)-benzenes have been synthesized. The preparation of these compounds involves the action of a sodium or potassium alkoxide on a trifluoromethyl-substituted chloro- or bromobenzene. Such ethers are of interest as possible heat-transfer fluids since they exhibit a tendency toward non-flammability, a wide liquid range, and an enhanced stability to heat and the action of metals. Further, it would seem desirable for a heat transfer agent to possess an electron donor center, such as an oxygen atom, in the molecular structure. Dative bond formation between this electron donor and the metallic atoms of a heat transfer wall should effect more efficient transfer of heat. Other interesting possibilities for these ethers might include use as dielectric media, and as materials to improve the lubricating properties of oils.

The new compounds prepared, together with their physical properties, are listed in Table I. Of the compounds synthesized, only 3-methoxy-(trifluoromethyl)-benzene has been mentioned previously in the literature.[5] However, the method of preparation of this compound was not disclosed.

During the present study it was observed that, in the preparation of methyl ethers from trifluoromethyl-substituted chlorobenzenes, the temperature required for a particular synthesis was dependent upon the relative reactivity of the chlorine atom in the benzene derivative. Analogous to the behavior of the nitro-substituted chlorobenzenes, this reactivity appears to be a function of the position of the chlorine atom relative to the meta-directing group or groups. For the compounds investigated the order of reactivity was found to be



Experimental

Preparation of Starting Materials

2- and 4-Chloro-(trifluoromethyl)-benzenes.—These compounds were prepared by the fluorination of commercially available 2- and 4-chloro-(trichloromethyl)-benzenes. The fluorination was carried out at room temperature in iron equipment using anhydrous hydrogen fluoride in the presence of a small quantity of antimony(V) chloride as the fluorinating agent. 2-Chloro-(trifluoromethyl)-benzene (b. p. 148–150° (745)) was obtained in 85% yield; 4-chloro-(trifluoromethyl)-benzene (b. p. 135–136° (745)) was obtained in 91% yield.

3-Chloro-(trifluoromethyl)-benzene.—This compound (b. p. 135–136° (745)) was prepared according to the method of Holt and Daudt[6] by the chlorination, in glass

---

[1] Presented as a part of the Meeting-in-Miniature, Purdue University, November 17, 1945. Abstracted in part from a thesis submitted (October, 1945) by R. F. Tebbe and a thesis to be submitted (1947) by P. J. Graham to the faculty of Purdue University in partial fulfilment of the requirements for the degree of doctor of philosophy.

[2] Acknowledgment is gratefully made to the Ethyl Corporation for sponsoring the research fellowship on which this work was accomplished.

[3] Present address: California Research Corporation, a subsidiary of the Standard Oil Company for California, Richmond, California.

[4] Present address: University of Maine, Orono, Maine.

[5] Zitscher and Kehlen (to General Aniline), U. S. Patent 2,141,893, Dec. 27, 1938.

[6] Holt and Daudt (to du Pont), U. S. Patent 2,174,513, Oct. 3, 1939.

apparatus, of trifluoromethylbenzene in the presence of iron(III) chloride.

3-Bromo-(trifluoromethyl)-benzene.—Trifluoromethylbenzene was brominated with the aid of an iron(III) chloride catalyst at 60° to prepare the bromo derivative[7] (b. p. 153–154° (745)).

4-Chloro-1,3-bis-(trifluoromethyl)-benzene.—Technical 1,3-dimethylbenzene was purified according to the method of Clarke and Taylor[8] and the purified 1,3-dimethylbenzene was chlorinated at 40 to 50° in the presence of iron(III) chloride catalyst.[9] The 4-chloro-1,3-dimethylbenzene (b. p. 89–90° (24)) thus obtained was chlorinated photochemically at temperatures ranging from 30°, at the beginning of the reaction, to 150°, at the end. The fraction of this product boiling at 170 to 180° at 8 mm. was 4-chloro-1,3-bis-(trichloromethyl)-benzene.

Anal. Calcd. for $C_6H_3Cl(CCl_3)_2$: Cl, 71.6. Found: Cl, 72.0.

The 4-chloro-1,3-bis-(trichloromethyl)-benzene was converted to 4-chloro-1,3-bis-(trifluoromethyl)-benzene by treatment with hydrogen fluoride in the presence of a small quantity of antimony(V) chloride. The reaction was carried out in a nickel vessel at 70 to 80°. The yield of 4-chloro-1,3-bis-(trifluoromethyl)-benzene (b. p. 148°) was 41.5%.

Anal. Calcd. for $C_6H_3Cl(CF_3)_2$: Cl, 14.3; F, 45.8; mol. wt., 248.5. Found: Cl, 14.7; F, 46.1; mol. wt., 251.0.

5-Chloro-1,3-bis-(trifluoromethyl)-benzene.—This material (b. p. 138–139° (745)) was furnished by M. R. Frederick of Purdue University. The method of preparation will be published at a later date.

Anal. Calcd. for $C_6H_3Cl(CF_3)_2$: Cl, 14.3; F, 45.8; mol. wt., 248.5. Found: Cl, 14.1; F, 45.6; mol. wt., 250.

2-Chloro-1,3-bis-(trifluoromethyl)-benzene.—The directions of Kalischer and Frister[10] were followed for the preparation of 2-chloro-1,3-dimethylbenzene. This material was chlorinated and fluorinated in the usual manner. A 27.8% yield and conversion to 2-chloro-1,3-bis-(trifluoromethyl)-benzene (b. p. 154–158° (745)) was obtained. A sizable fraction boiling at about 147° was also isolated which is presumably 4-chloro-1,3-bis-(trifluoromethyl)-benzene, a possible isomer in the synthesis.

2-Chloro-1,4-bis-(trifluoromethyl)-benzene.—This compound was synthesized from 1,4-dimethylbenzene in a manner similar to that outlined for the preparation of 4-chloro-1,3-bis-(trifluoromethyl)-benzene. The yield of 2-chloro-1,4-bis-(trifluoromethyl)-benzene (b. p. 147°) was 60%.

Anal. Calcd. for $C_6H_3Cl(CF_3)_2$: Cl, 14.3; F, 45.8; mol. wt., 248.5. Found: Cl, 14.1; F, 46.1; mol. wt., 247.0.

Though 4-chloro- and 5-chloro-1,3-bis-(trifluoromethyl)-benzene and 2-chloro-1,4-bis-(trifluoromethyl)-benzene have been anticipated in the patent literature,[11] the physical properties of these compounds (see Table I) have not been reported.

3-Trifluoromethylphenol.—This material (b. p. 68–69° (12)) was synthesized in small quantities by the method of Swarts[12] which involves the hydrolysis of 3-trifluoromethylbenzenediazonium sulfate. The latter compound was derived from trifluoromethylbenzene by nitration,[13] reduction[13] and diazotization.[12]

Metallic Alkoxides and Aryloxides.—The sodium methoxide was commercial material of 95% purity. In general, other alkanol derivatives were made either by treating an excess of alkanol with sodium (U. S. P.), sodium hydroxide (C. P.) or potassium hydroxide (C. P.). The resulting solutions were then used directly in the appropriate procedures. Sodium phenoxide was prepared by treating an excess of phenol (U. S. P.) with sodium in anhydrous ether solution. The solid phenoxide which precipitated was filtered from the solution for the syntheses. The alkanols were of commercial grade and the 3,6,9-trioxahendecane was diethyl carbitol solvent.

Syntheses of Ethers of Trifluoromethyl-substituted Phenols

The several procedures which were used are described generally in the following paragraphs. Table I lists the compounds and the methods used in their syntheses together with results.

Procedure A-1.—A mixture of one mole of a trifluoromethyl-substituted chlorobenzene, 2.5 moles of a sodium alkoxide and 300 ml. of the corresponding alkanol was refluxed at atmospheric pressure for a period of twelve hours. At the end of this time the volatile reaction product was steam-distilled. The lower layer of the distillate was separated and dried over calcium sulfate. The aqueous layer of the distillate was extracted three times with 100-ml. portions of chloroform and the extracts mixed with the original organic layer and drying agent. This mixture was then rectified.

Procedure A-2.—This is identical with Procedure A-1 except that 3,6,9-trioxahendecane was used in place of the alkanol. The reaction temperature realized with this method depends on the boiling point of the halohydrocarbon used and/or on the boiling points of the products obtained.

Procedure A-3.—This method is similar to Procedure A-1 except that an equimolar mixture of potassium hydroxide and the alkanol was used in place of the anhydrous sodium alkoxide.

Procedure B-1.—One mole of a trifluoromethyl-substituted chlorobenzene, 2.5 moles of a sodium alkoxide or aryloxide, and 300 ml. of the corresponding alkanol were placed in an iron autoclave (constructed to withstand 40 atm. at 200°) of one-liter capacity fitted into an electric heater mounted on a mechanical rocker. The vessel was heated to 160° in four hours, after which it was allowed to cool to 85° in four and one-half hours. The reaction product was removed from the autoclave at about room temperature and treated as in Procedure A-1 prior to rectification.

Procedure B-2.—This method is similar to Procedure B-1 except that an equimolar mixture of sodium hydroxide and the alkanol or phenol was used in place of the anhydrous sodium alkoxide or aryloxide.

Procedure C-1.—One mole of a trifluoromethyl-substituted phenol was dissolved in one mole of sodium hydroxide in 415 ml. of water. The solution was cooled with agitation to 0° and one mole of a dialkyl sulfate added dropwise. After one hour, the mixture was heated at reflux temperature for about three hours. The resulting ether was recovered by the method described in Procedure A-1.

Discussion

In the general procedures described for the preparation of the ethers, the only basic differences are those in temperature, exposure time, and the amount of water present. The position of the halogen atom to be replaced in the benzene nucleus and the complexity of the carbon chain of the alkoxide or aryloxide determine the procedure necessary. These factors fix the threshold temperature required for a finite reaction rate and determine the amount of hydrolysis product. Once the threshold has been surpassed, the

---

(7) Simons and Ramler, This Journal, **65**, 389–392 (1943).

(8) Clarke and Taylor, *ibid.*, **45**, 830–833 (1923).

(9) P. Jacobson, *Ber.*, **18**, 1760–1762 (1885).

(10) Kalischer and Frister (to General Aniline), U. S. Patent 1,796,108, March 10, 1931.

(11) Holt and Mattison (to Kinetic Chemicals, Inc.), U. S. Patent 1,967,244, July 24, 1934.

(12) Swarts, *Bull. acad. roy. Belg.*, 241–278 (1913).

(13) Swarts, *ibid.*, [3] **35**, 375–420 (1898).

TABLE I

ETHERS OF TRIFLUOROMETHYL-SUBSTITUTED PHENOLS AND CHLOROBIS(TRIFLUOROMETHYL)-BENZENES

Ether	Procedure,[a] used	Conversion,[b] %	Yield,[b] %	B. p.,[c,d] °C. (754)	M. p.,[d] °C.	n^{20}_D	d^{20}_4	Fluorine, %		Mol. wt.	
								Calcd.	Obs.	Calcd.	Obs.
2-$CF_3C_6H_4OCH_3$	B-1[e]	36.4	57.5	173.7	−14.1 to −14.3	1.4524	1.2616	32.4	32.9	176	174
	B-2[f]	29.5	27.2								
2-$CF_3C_6H_4OC_2H_5$	B-2[g]	40.0	62.0	184.5	− 2.4 to − 2.8	1.4470	1.1970	30.0	30.3	190	190
2-$CF_3C_6H_4OCH(CH_3)_2$	B-2[h]	26.4	45.2	202.9	−29.7 to −30.3	1.4488	1.1624	27.9	28.1	204	204
3-$CF_3C_6H_4OCH_3$	B-1	28.4	54.5	159.5	−65.0	1.4435	1.2426	32.4	32.7	176	181
	A-2[i]	7.9	20.5								
	B-1[j]	23.3	31.2								
	B-1[k]	8.0	31.0								
	C-1	55.5	55.5								
3-$CF_3C_6H_4OC_2H_5$	C-1	37.6	37.6	173.0	−16.0	1.4428	1.1903	30.0	30.2	190	192
4-$CF_3C_6H_4OCH_3$	A-2[l]	8.5	29.3	168.6	− 9.1	1.4455	1.2445	32.4	33.0	176	175
	B-1[m]	56.8	75.2								
	B-2[n]	52.4	66.0								
4-$CF_3C_6H_4OC_2H_5$	B-2	49.8	67.8	182.6	9.3	1.4451	1.1912	30.0	30.6	190	190
4-$CF_3C_6H_4OCH(CH_3)_2$	B-2[o]	77.5	77.5	200.0	3.0	1.4458	1.1524	27.9	28.4	204	203
1,3-$(CF_3)_2C_6H_4$-4-OCH_3	A-3	43.8	56.2	176.0	+17.5 to 18.0	1.4149	1.4330	46.7	47.2	244	249
	B-1	52.5	64.0								
1,3-$(CF_3)_2C_6H_3$-4-OC_2H_5	A-3	41.6	64.5	185.0	26.0 to 26.5	1.4130	1.3559	44.2	44.6	258	257
1,3-$(CF_3)_2C_6H_3$-4-OC_3H_7	B-1	41.2	48.5	200.0	−15.0 to −16.0	1.4162	1.3101	42.0	41.8	272	270
	B-2[p]	34.8	50.0								
1,3-$(CF_3)_2C_6H_3$-4-$OCH(CH_3)_2$	B-1	35.3	43.6	192.0	Sets to a glass	1.4128	1.2958	42.0	41.9	272	270
1,3-$(CF_3)_2C_6H_3$-4-$OCH_2C_6H_4$	A-1	48.5	58.5	275.0–277.0	Sets to a glass	1.4887	1.3454	35.6	34.6	...	...
1,3-$(CF_3)_2C_6H_3$-4-O-octyl	B-1	48.8	48.8	278.0	− 8.5 to − 9.5	1.4304	1.1705	33.3	33.5	...	...
1,3-$(CF_3)_2C_6H_3$-4-OC_6H_5	B-1[q]	27.1	27.1	244.0	Sets to a glass	1.4756	1.3777	37.3	37.8	306	302
1,4-$(CF_3)_2C_6H_3$-2-OCH_3	B-1	22.9	22.9	163.0	26.5 to 27.5	1.4221	1.4110	46.7	46.9	244	239
1,3-$(CF_3)_2C_6H_3$-5-OCH_3	B-1[r]	48.0	76.0	160.5	2.0 to 3.0	1.4084	1.4192	46.7	46.6	244	240
1,3-$(CF_3)_2C_6H_3$-2-OCH_3	A-3	31.2	44.5	173.0	4.0 to 5.0	1.4170	1.4507	46.7	46.6	244	243
1,4-$(CF_3)_2C_6H_3$-2-OCH_3				163.5	26.5 to 27.5	1.4150	1.4110	46.7	46.9	244	239
1,3-$(CF_3)_2C_6H_3$-4-Cl				148.0	−58.0 to −59.0	1.4150	1.5201	45.8	45.9[s]	248.5	254
1,3-$(CF_3)_2C_6H_3$-5-Cl				137.5	−29.5 to −30.0	1.3611	1.4942	45.8	45.6[t]	248.5	250
1,4-$(CF_3)_2C_6H_3$-2-Cl				147	−12.0 to −13.0	1.4135	1.5112	45.8	46.1[u]	248.5	237

[a] See text for explanation of procedures. [b] Calculations based on the halohydrocarbons. [c] Determined by Siwoloboff micromethod (Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., 1940, p. 93). [d] Absolute values accurate to ±0.2°. [e] 7.2% conversion to 2-$HOC_6H_4CO_2H$. [f] 24% conversion to 2-$HOC_6H_4CO_2H$. [g] 3% conversion to 2-$HOC_6H_4CO_2H$. [h] Six hours to 200°. [i] 3-$CF_3C_6H_4Br$ used; four hours at 130°. [j] 3-$CF_3C_6H_4Br$ used; 21.2% conversion to $CF_3C_6H_5$. [k] Three hours to 140°; 5.4% conversion to $CF_3C_6H_5$. [l] A.1 yields no ether; twenty-four hours at 110°. [m] 6.5% conversion to 4-$HOC_6H_4CO_2H$. [n] 17.7% conversion to 4-$HOC_6H_4CO_2H$. [o] Six hours to 200°. [p] Potassium hydroxide and 150° used. [q] Seven and one-half hours to 225°, 1 g. copper catalyst used. [r] Five hours to 180°. [s] 14.3% Cl calcd., 14.5% obs. [t] 14.3% Cl calcd., 14.1% obs. [u] 14.3% Cl calcd., 14.1% obs.

chosen procedure is one involving a temperature which will produce a convenient reaction rate. The hydrolysis product occurs to an appreciable extent only in the preparation of the methoxy-(trifluoromethyl)-benzenes, where hydroxybenzoic acids were isolated. Thus, in the case of the synthesis of 4-methoxy-(trifluoromethyl)-benzene, Procedure A-1 gives no ether, Procedure A-2 gives product after a long reaction period, Procedure B-2 gives an appreciable amount of hydrolysis, and Procedure B-1 is satisfactory. Consideration of the data in Table I and the indicated relative reactivities of the halohydrocarbons and the alkoxides and aryloxides makes possible the selection of a suitable procedure for the synthesis of a particular ether.

The optimum ratio of alkoxide to halohydrocarbon in the syntheses was determined to enable most complete utilization of the latter material. Conversions to the ethers increased with increasing mole ratios up to 2.5 to 3.0, with no significant improvement in efficiency being obtained at higher ratios. A powdered copper catalyst when used in Procedure B-2 only increased the amount of hydrolysis product obtained and did not promote formation of a methyl ether. However, the catalyst was found to improve conversion and yield of a phenyl ether in Procedure B-1.

The difficulty of obtaining the trifluoromethyl-substituted bromobenzenes limits the utility of these compounds in the ether syntheses. Furthermore, experiments with 3-bromo-(trifluoromethyl)-benzene indicate that this material is inferior to the corresponding chloro compound. The low yields obtained testify to the multiplicity of reactions, including reduction and coupling, attendant upon the employment of 3-bromo-(trifluoromethyl)-benzene. In addition to the limited availability of the trifluoromethyl-substituted phenols, which at present restricts the scope of Procedure C-1, the method also appears economically inferior to the others described.

Summary

Various ethers of trifluoromethyl-substituted phenols have been synthesized and physical properties reported. These compounds were prepared by the action of a sodium or potassium alkoxide or aryloxide on a trifluoromethyl-substituted chloro- or bromobenzene. The position on

the benzene ring of the halogen atom to be replaced and the complexity of the carbon chain of the alkoxide or aryloxide determined the procedure used in each synthesis. Variations in the general procedure involved reaction temperature, exposure time and amount of water present.

LAFAYETTE, INDIANA RECEIVED[14] JANUARY 2, 1947

---

[14] Original manuscript received July 15, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. VI. The Alfin Catalysts[1a]

BY AVERY A. MORTON, EUGENE E. MAGAT[1b] AND ROBERT L. LETSINGER[1c]

The sodium salt of a methyl *n*-alkyl carbinol and the sodium salt of an olefin, for example propylene, form a complex that causes the catalytic polymerization of butadiene and isoprene. Agents of this type are called Alfin catalysts because an *al*cohol and an ole*fin* are involved in their preparation. This paper (1) gives an account of the discovery of these catalysts, (2) lists the types of compounds that will form such agents, (3) describes the methods used for testing the catalysts (4) shows the unique features that mark the polymerization, induced by these agents, to be distinctly different from that caused by other polymerizing agents, (5) lists the general characteristics of Alfin polymerization, (6) shows some variations that are possible with different Alfin catalysts and (7) suggests a possible formula for the active catalyst complex.

Discovery of the Catalyst

The catalyst was discovered by accident in the course of our study[2] of the addition of organosodium compounds to dienes. The effect of diisopropyl ether was being tested in the same way as the effect of a tertiary amine on the addition of amylsodium to butadiene had previously been tested.[2] The reaction took, however, an entirely different course and high polymers resulted in spite of the fact that the diene was added drop by drop to a very large excess of the organoalkali metal reagent. A similar result was obtained with isoprene, although the polymer was stickier than that obtained from butadiene.

The explanation for this unusual effect on the two dienes lay in the formation of two products, sodium isopropoxide and allylsodium, derived from the ether and amylsodium, according to the equations

$$C_5H_{11}Na + (CH_3)_2CHOCH(CH_3)_2 \longrightarrow (CH_3)_2CHONa + C_5H_{12} + CH_2{=}CHCH_3 \quad (1)$$

$$C_5H_{11}Na + CH_2{=}CHCH_3 \longrightarrow CHCH_2Na + C_5H_{12} \quad (2)$$

This conclusion was drawn after a series of experiments, shown in Table I. A rubber-like polymer was obtained only when sodium isopropoxide and allylsodium were both present and no polymer was obtained if either one was absent (experiments 7 and 8). Amylsodium or the ether could be absent without destroying the catalytic effect (experiments 4 or 1 and 2, respectively). Only a trace of reaction with the ether was needed in order to furnish enough of the two pertinent salts (experiments 3 and 5), although the amount could fall too low, as it did in experiment 6. The catalytic action was not induced by any energy or free radical liberated from the reaction of amylsodium with the ether because in experiments 2 and 4 the catalytic activity was present long after ether cleavage was concluded. The preparation of the catalyst from other reagents besides the ether confirmed this point (experiment 9). This series of studies was concluded by a successful test with a catalyst made by mixing a preparation of the alkoxide with an independent preparation of allylsodium obtained from the reaction of amylsodium with propylene. The unusual effect on dienes is clearly a consequence of the simultaneous presence of two particular alkali metal salts.

The Class of Compound

Allylsodium and sodium isopropoxide form one of a class, the components of which, as shown in Table II, are specific. Only alkoxides from methyl *n*-alkyl carbinols have so far proven effective. Only mono olefins that have at least one alkyl group attached to a carbon atom of the vinyl group or two alkyl groups attached, one to each of the carbon atoms, have so far been suitable.

The mercaptide $(CH_3)_2CHSNa$, and the amide $(CH_3)_2CHNHNa$, corresponding to the alkoxide, could not replace the isopropoxide in combination with 2-butene as the olefin.

The metalation product of diallyl in the presence of isopropoxide proved unsuitable, although one of the products of such a reaction was a propenyl substituted allylsodium,[3] $CH_2{=}CHCH(R)Na$ (where $R{=}CH_2CH{=}CH_2$). The addition product of amylsodium with butadiene likewise failed as a component of the catalyst, although the product[2] of such addition is a hexylallylsodium, either $Na(R)CHCH{=}CH_2$ or $RCH{=}CHCH_2Na$ ($R = C_6H_{13}$) depending on whether the addition occurs 1,2- or 1,4. Both failures are important because

---

[1a] The authors are indebted to the Research Corporation and to the Rubber Reserve for financial support of this investigation.

[1b] Present address: Experiment Station, E. I. du Pont de Nemours & Co., Wilmington, Del.

[1c] Present address: Chemistry Department, Northwestern University, Evanston, Ill.

[2] Morton, Brown and Magat, THIS JOURNAL, **69**, 161 (1947).

[3] Morton and Brown, THIS JOURNAL, **69**, 160 (1947), and unpublished research.