Radioactive DL-4-(4-Hydroxy-3,5-dibromophenyl)-3-acetaminobutanone-2.—Radioactive pyridine perbromide·HBr was prepared by the distillation of labeled Br_2 from 125 mg. of pile bombarded NH_4Br into 90 mg. of pyridine·HBr in 0.3 ml. of glacial acetic acid. The acetic acid solution was warmed to dissolve the precipitate, cooled, the crystalline radioactive perbromide centrifuged off, washed with ligroin and dried. Unbrominated ketone equal to one-third the weight of the radioactive perbromide was dissolved in 0.2 ml. of pyridine and the perbromide added slowly, allowing time for decolorization between each addition. The solution obtained was evaporated *in vacuo* to dryness and the residue purified in a manner similar to the other radioactive derivatives; m.p. 133–134°.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

High Molecular Weight Polymethylene

BY SIMON W. KANTOR AND ROBERT C. OSTHOFF

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A polymethylene of molecular weight of 3.3 million was prepared by the catalytic decomposition of diazomethane. This polymer is highly crystalline and has a crystal melting point of 132°. This temperature is close to the convergence temperature for straight-chain paraffins. Some of the physical properties of the polymethylene are described and a mechanism of the polymerization is presented.

There has been considerable theoretical interest in ascertaining the physical properties of a very high molecular weight straight-chain hydrocarbon.[1,2] We have succeeded in preparing a polymethylene of *ca.* three million molecular weight by the catalytic decomposition of diazomethane in ether solution and we have determined some of its properties.

In a typical experiment, a 500-ml. solution of 10–11 g. of diazomethane in diethyl ether, prepared from N-nitrosomethylurea,[3] was treated with about 0.1 ml. of diethyl ether–boron trifluoride complex at 0°. Immediately the violent exothermic reaction liberated nitrogen and precipitated 3.7 g. of a white waxy polymeric solid.

Anal. Calcd. for $(CH_2)_x$: C, 85.7; H, 14.3; N, 0.0. Found: C, 85.5; H, 14.4; N, 0.26.

This polymer could be dissolved in boiling benzene, toluene and xylene. The nitrogen content of a sample of the material reprecipitated from xylol solution was *ca.* 0.1%.

The molecular weight of this polymer was determined by measuring the intrinsic viscosity in xylol solution at 132°. The data are summarized in Table I.

TABLE I

VISCOSITY OF XYLOL SOLUTIONS OF POLYMETHYLENE

C(g./l.)	η_{rel}	η_{sp}/C
0.25	1.469	1.875
0.50	2.220	2.440
1.0	3.002	3.002
1.25	5.03	3.22
		$[\eta] = 1.7 \pm 0.1$

The value of the intrinsic viscosity $\lim_{c \to 0} \eta_{sp}/C$ was obtained by a linear extrapolation of the graph of η_{sp}/C against C in the usual fashion. From the intrinsic viscosity (1.7 ± 0.1) and the Staudinger constants reported by Harris,[4] we obtained a molecular weight of $3.3 \times 10^6 \pm 0.4 \times 10^6$. This value is 100 to 1,000 times greater than that of the polymethylene previously obtained from diazomethane (reported molecular weights: 22,000,[4] 1,800–2,000,[5] *ca.* 20,000[6]).

In order to obtain the melting point of the polymer, thermal analyses in the temperature range of 25–213° were carried out with a copper–constantan thermocouple and a recording potentiometer. The results indicated a crystal melting point of 132° (rate of warming, 0.5°/min.) and a freezing point of 124° (rate of cooling, 0.5°/min.). The lower freezing point is not too surprising since polymer melts tend to supercool. Examination of the polymer under crossed Nicols indicated that the crystallites began to disappear at about the same temperature. However, the bulk viscosity remained very high until a temperature of *ca.* 200° was attained. A sample of the polymer maintained at 150° in an air oven for 165 hours did not flow under its own weight in spite of considerable discoloration and degradation.

We feel that the melting point of 132° is close to the convergence temperature for straight-chain paraffins considering the very high molecular weight of this polymethylene. This temperature compares favorably with the frequently quoted convergence temperature of 137°[2] which was derived from thermodynamic data.

An X-ray investigation of strips of the polymer indicated essentially the same crystal structure as commercial polyethylene but showed possibly an even higher degree of crystallinity than that found in previously reported cases.

Samples of the polymer were pressed into thin sheets at 230° and 10,000 lb./in.² pressure. Strips of this sheet had a tensile strength of 4,900 lb./in.² and an elongation at break of 500%. This value is about 2,000 pounds greater than that obtained with the commercially available polyethylenes[7] and is indicative of the greater molecular weight and lower degree of branching of the polymer prepared by the authors.

The electrical properties of this polymethylene are listed in Table II in which ϵ represents the dielectric constant and $\tan \delta$ represents the power factor.

TABLE II

Frequency	$\tan \delta$	ϵ
60	0.0008	2.38
300	.0003	2.38
1000	.0001	2.38

The breakdown voltage was found to be *ca.* 2,760 volts/mil for a sheet 0.015 in. in thickness. All these dielectric properties are comparable to those of commercial polyethylenes.[7]

Mechanism of the Polymerization.—The polymerization of diazomethane could simply be represented as the combination of methylene diradicals, $\cdot CH_2 \cdot$ formed by loss of nitrogen from CH_2N_2. The growing diradical chain could then

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[1] K. H. Meyer and A. van der Wyk, *Helv. Chim. Acta*, **20**, 1313 (1937).

[2] H. Mark, *J. Applied Phys.*, **12**, 41 (1941).

[3] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

[4] I. Harris, *J. Polymer Science*, **8**, 353 (1952).

[5] H. Meerwein, *Angew. Chem.*, **60**, 78 (1948).

[6] G. D. Buckley, L. H. Cross and N. H. Ray, *J. Chem. Soc.*, 2714 (1950).

[7] C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, pp. 512, *et seq.*

terminate in the usual manner by chain transfer, cyclization or reaction with the solvent. We believe, however, that the polymerization does not take place through a radical mechanism but rather through an ionic mechanism. This conclusion is based upon the consideration that the catalyst and solvent are promoters of ionic reactions. Indeed, in the large excess of ether, one might expect a radical mechanism to lead to low molecular weight polymer chains terminated by $CH_3\underset{|}{C}H\text{-}OC_2H_5$ groups.

In the following discussion, we present what we believe to be a reasonable ionic mechanism. It has been conveniently divided into initiation, propagation and termination steps.

(A). **Initiation.**—The initiation step of the ionic mechanism involves a resonance form of diazomethane which makes it a potential carbanion (electron donor).

$$BF_3 + :\overset{(-)}{C}H_2—\overset{(+)}{N}{\equiv}N \longrightarrow F_3\overset{(-)}{B}—CH_2—\overset{(+)}{N}{\equiv}N$$

$$F_3\overset{(-)}{B}—CH_2—\overset{(+)}{N}{\equiv}N \longrightarrow F_3\overset{(-)}{B}—\overset{(+)}{C}H_2 + N_2$$

On the other hand, coördination of BF_3 with the terminal nitrogen of diazomethane would give $F_3\overset{(-)}{B}—N{=}N—\overset{(+)}{C}H_2$, which would lead to a polymer containing nitrogen.

(B). **Propagation.**—The boron trifluoride–methylene complex has a carbonium ion end which can grow by adding diazomethane in the manner:

$$F_3\overset{(-)}{B}—\overset{(+)}{C}H_2 + :\overset{(-)}{C}H_2—\overset{(+)}{N}{\equiv}N \longrightarrow F_3\overset{(-)}{B}—CH_2—CH_2—\overset{(+)}{N}{\equiv}N$$

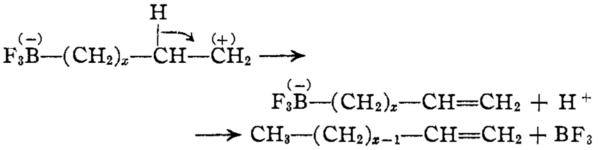
$$F_3\overset{(-)}{B}—CH_2—CH_2—\overset{(+)}{N}{\equiv}N \longrightarrow F_3\overset{(-)}{B}—CH_2—\overset{(+)}{C}H_2 + N_2$$

Alternatively, attack of the terminal nitrogen of diazomethane on the growing carbonium ion would give an ion of the type

$$F_2\overset{(-)}{B}—CH_2—N{=}N—\overset{(+)}{C}H_2$$

which would again result in a polymer containing nitrogen.

(C). **Termination.**—There are several possible ways in which the chain might terminate. It could, for example, lose a β-hydrogen and BF_3 to give an olefin thus



$$F_3\overset{(-)}{B}—(CH_2)_x—\overset{H}{C}H—\overset{(+)}{C}H_2 \longrightarrow F_3\overset{(-)}{B}—(CH_2)_x—CH{=}CH_2 + H^+ \longrightarrow CH_3—(CH_2)_{x-1}—CH{=}CH_2 + BF_3$$

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SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Some Reactions of Fluoroethanes with Sodium Ethoxide[1]

BY PAUL TARRANT AND JOHN A. YOUNG

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Evidence is offered that the formation of fluoroethers by the reaction of a saturated fluorohalo compound with sodium ethoxide is not due to a simple displacement reaction of the Williamson type in most instances. The products formed in a number of reactions can be accounted for only by assuming that the saturated compounds are converted to fluoroölefins which then add alcohol to give the fluoroether.

The two most common procedures in use today for the preparation of fluoroethers involve the base-catalyzed addition of alcohols to fluoroölefins[2-4] and reaction of a saturated fluorohalo compound with alkoxide or aryloxide.[5,6] The latter method seems to be the common Williamson method for preparing ethers. Representative equations for the two methods, both of which give good yields of ethers, are

$$\text{(I)}\quad CCl_2{=}CF_2 + HOR \xrightarrow{^-OR} CHCl_2CF_2OR$$

$$\text{(II)}\quad CHCl_2CF_2Cl + {}^-OR \xrightarrow{HOR} CHCl_2CF_2OR + Cl^-$$

McBee and Bolt[5] made a study of the reaction of 1,2,2-trichloro-1,1-difluoroethane with several aryloxides in which compounds of the type $CHCl_2\text{-}CF_2OAr$ were formed, and concluded that the chlorine atom of the $-CF_2Cl$ group possessed unusual activity since it was the apparent point of attack by the aryloxide. It has been suggested[7] that the $-OAr$ removes a proton from the saturated fluorochloro compound to yield an olefin which then adds a molecule of ArOH to give the aryl ether.

In reactions with a number of saturated compounds such as 1,2,2-trichloro-1,1-difluoroethane, 1,2-dichloro-1,1-difluoroethane, etc., it is not possible to draw conclusions as to the mechanism by which the fluoroethers are formed since both the displacement and the olefin–alcohol addition method yield the same product. However, by judicious choice of other starting materials, the two routes can be made to give different results and the predominance of one mechanism over the other determined by the nature of the products.

A study of the reactions of the isomeric chloro-1,1-difluoroethanes with sodium ethoxide in ethanol would offer some indication of the course of the

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[1] Presented at the Diamond Jubilee Meeting of the American Chemical Society, New York City, September, 1951.

[2] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (1946).

[3] J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, THIS JOURNAL, **70**, 1550 (1948).

[4] Paul Tarrant and H. C. Brown, *ibid.*, **73**, 1781 (1951).

[5] E. T. McBee and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

[6] F. Swarts, *Bull. acad. roy. Belg.*, 383 (1901); *Mem. ocur. acad. roy. Belg.*, 61 (1901).

[7] Paul Tarrant and H. C. Brown, THIS JOURNAL, **73**, 5831 (1951).