β-keto ester XXVIII with aqueous hydrochloric acid–acetic acid gave 1.7 g. (80%) of the liquid spiranone XXIX, b.p. 145–146° (2 mm.).

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.79; H, 8.59.

The semicarbazone of XXIX formed colorless needles from ethanol; m.p. 129–130°.

Anal. Calcd. for $C_{16}H_{21}ON_3$: N, 15.49. Found: N, 15.38.

The 2,4-dinitrophenylhydrazone of XXIX formed orange plates from ethanol; m.p. 85–86°.

Anal. Calcd. for $C_{21}H_{22}O_4N_4$: N, 14.21. Found: N, 14.17.

The oxime of XXIX formed colorless crystals from ethanol; m.p. 104–105°.

Anal. Calcd. for $C_{15}H_{19}ON$: N, 6.11. Found: N, 6.05.

Clemmensen Reduction of the Spiranones.—Clemmensen reduction of the spiranone XXI was carried out in the usual manner.[14] The resulting spiran II was a nearly colorless liquid, b.p. 121–123° (5 mm.); $n^{20}D$ 1.5429 (reported[4] b.p. 122–125° (5 mm.)).

Clemmensen reduction of the spiranones XVII, XXVI or XXIX gave the spiran I in 30–40% yield, b.p. 122–124° (4 mm.); $n^{20}D$ 1.5476 (reported[4] b.p. 115–117° (3 mm.); $n^{20}D$ 1.5431).

BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, WEIZMANN INSTITUTE OF SCIENCE]

Reduction and Benzylation by Means of Benzyl Alcohol. I. Carbon Benzylation. The Preparation of 9-Benzylfluorenes

BY YAÏR SPRINZAK

RECEIVED JULY 25, 1955

Fluorene is readily transformed into 9-benzylfluorene by heating with benzyl alcohol in the presence of potassium hydroxide. The reaction is shown to involve condensation with benzaldehyde to form benzalfluorene, followed by reduction of the latter. The reaction has been extended to fluorene derivatives, including 2-methyl-, 2-bromo-, 2,7-dibromo-, 2-amino-, 2-hydroxy-, 4-carboxy- and 1,2,3,4-dibenzofluorene, on the one hand, and to *p*-tolylcarbinol and *p*-anisyl alcohol, on the other hand.

The reducing properties of hot benzyl alcoholic solutions of potassium hydroxide have been noted by Palfray and Sabetay[1] during their attempts to devise a method for the determination of aldehydes by means of the Canizzaro reaction. Using benzyl alcohol as a medium for this reaction, they observed that, with aromatic aldehydes[1a] such as *p*-methoxybenzaldehyde, hydrogen transfer from alcohol to aldehyde took place, as indicated by the isolation of benzoic acid instead of the expected *p*-methoxybenzoic acid

$$p\text{-}CH_3OC_6H_4CHO + PhCH_2OH \xrightarrow{KOH} p\text{-}CH_3OC_6H_4CH_2OH + PhCHO$$

$$2PhCHO + KOH \longrightarrow PRCH_2OH + PhCO_2K$$

Mastagli[2] later studied the action of the reagent in question on other types of aldehydes, as well as on ketones and α,β-unsaturated alcohols, and obtained a variety of products the formation of which could be explained readily in terms of reduction and condensation reactions, as may be illustrated by the case of β-phenylpropionaldehyde

$$PhCH_2CH_2CHO + PhCH_2OH \xrightarrow{KOH} PhCH_2CH_2CH_2OH + PhCHO$$

$$PhCH_2CH_2CHO + PhCHO \xrightarrow{KOH} PhCH{=}C(CH_2Ph)CHO \xrightarrow[KOH]{PhCH_2OH} PhCH{=}C(CH_2Ph)CH_2OH \xrightarrow[KOH]{PhCH_2OH} (PhCH_2)_2CHCH_2OH$$

It has now been found[3] that benzyl alcoholic potassium hydroxide may be used advantageously for the preparation of 9-benzylfluorene (III) and related compounds. The various methods available in the literature for the preparation of 9-benzylfluorene employ derivatives obtained from fluorene (I) by substitution in the 9-position, for example, 9-formylfluorene[4] and 9-carbethoxyfluorene,[5] which may be alkylated by benzyl chloride, with subsequent elimination of the formyl and carboxyl groups, respectively. Likewise, 9-benzylfluorene has been obtained by reduction of benzalfluorene (II), either with aluminum amalgam[6] or catalytically, in the presence of a palladium catalyst.[7] A more direct method of benzylation could, perhaps, be achieved by the interaction of benzyl chloride and 9-fluorenyllithium, obtained from fluorene and phenyllithium.[8]

In the present method, benzylation is accomplished easily by heating fluorene and benzyl alcohol in the presence of a small amount of potassium hydroxide and traces of benzaldehyde. Addition of the latter is not necessary, as it is gradually formed from benzyl alcohol by oxidation or dehydrogenation[9] under the alkaline conditions used. Although the reaction may be carried to completion by refluxing the mixture, removal of the water formed accelerates it considerably, presumably owing to the higher temperature achieved.

The conversion of fluorene to 9-benzylfluorene is considered to be the result of two consecutive reactions. In the first, fluorene condenses with benzaldehyde to yield benzalfluorene; in the second, the latter is reduced by benzyl alcohol (or potassium benzylate) to 9-benzylfluorene, the benzaldehyde

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[1] L. Palfray and S. Sabetay, *Compt. rend.*, **200**, 404 (1935).

[1a] L. Palfray, S. Sabetay and P. Mastagli, *ibid.*, **203**, 1523 (1936) and reference 2.

[2] P. Mastagli, *Ann. chim.*, [11] **10**, 281 (1938).

[3] A note has been published: *Bull. Research Council Israel*, **3**, No. 1/2, 104 (1953).

[4] W. G. Brown and B. A. Bluestein, THIS JOURNAL, **65**, 1082 (1943).

[5] W. Wislicenus and W. Mocker, *Ber.*, **46**, 2772 (1913).

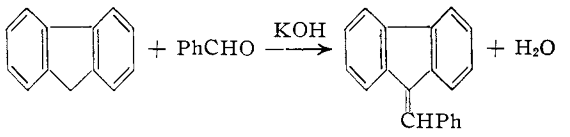
[6] J. Thiele and F. Henle, *Ann.*, **347**, 290 (1906).

[7] E. D. Bergmann, *Ber.*, **63**, 1617 (1930).

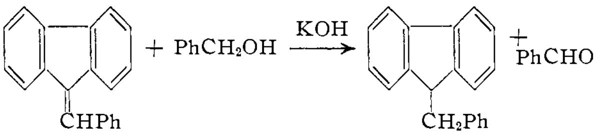
[8] G. Wittig, P. Davis and G. Koenig, *ibid.*, **84**, 627 (1951).

[9] See *e.g.*, M. Guerbet, *Bull. soc. chim. France*, [4] **3**, 500 (1908).

reformed in the reduction thus becoming available for further reaction.



I II

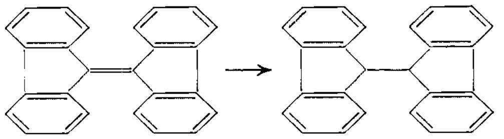


III

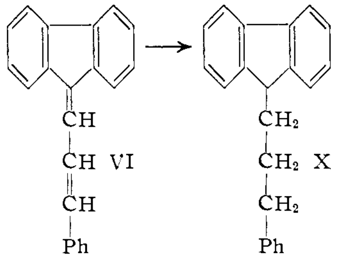
This assumption is borne out by the following observations: (1) The reaction is accelerated by the addition of benzaldehyde. In fact, fluorene was recovered unchanged when treated with benzaldehyde-free benzyl alcohol and potassium hydroxide in an atmosphere of nitrogen under procedure conditions which led to its complete benzylation when a little benzaldehyde was added to the reaction mixture. (2) Fluorene readily condenses with benzaldehyde in benzyl alcohol solution containing potassium hydroxide to form benzalfluorene, which can be isolated in a good yield when the reaction is carried out at a temperature low enough to prevent its reduction. (3) Benzalfluorene is rapidly and quantitatively reduced to the 9-benzyl compound when heated with benzyl alcohol and potassium hydroxide in excess of the amount necessary for the Cannizzaro reaction of the benzaldehyde formed in the reduction. In accordance with the theory, one half mole of potassium benzoate is produced per mole of benzalfluorene.

Response of a double-bond to the reducing action of potassium benzylate appears to be associated with its polar character. This may be inherent, as in the case of the carbonyl group, or induced, as in the allyl alcohol system. As for the easy reducibility of benzalfluorene, it should be remembered that this hydrocarbon is a dibenzofulvene derivative, and that members of this class of compounds, including benzalfluorene, have been shown to be attacked at the semi-cyclic double-bond by reagents that do not ordinarily affect isolated carbon–carbon double bonds. Such reactions are, for example, the reduction of benzalfluorene with aluminum amalgam[6] or lithium aluminum hydride,[10] and its addition reactions with phenyllithium[11] and with fluorene in the presence of potassium hydroxide.[12] Furthermore, it has been shown recently,[13] in confirmation of predictions made by Pullman, Coulson and others on theoretical grounds, that fulvenes, including benzalfluorene, possess a finite dipole moment.

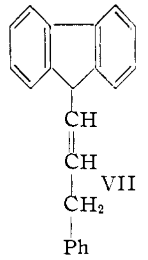
As might be expected, dibiphenylene-ethylene (IV) also is readily reduced by potassium benzylate to yield dibiphenylene-ethane (V). Another hydrocarbon tested was cinnamalfluorene (VI), in which an extra double-bond is present in conjugation with the semi-cyclic bond. In this case, both double bonds were reduced. This is hardly surprising, as it may be assumed that whatever the direction of initial reduction, any of the dihydro compounds VII and VIII which might be formed would isomerize,[14] under the strongly basic conditions prevailing, to the (reducible) third possible isomer (IX).



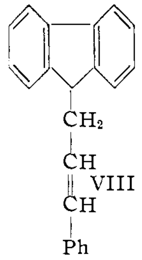
IV V



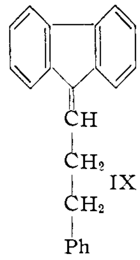
VI X



VII

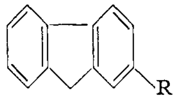


VIII

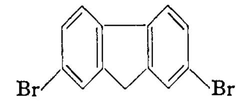


IX

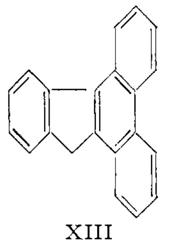
The benzylation reaction has been applied successfully to some of the more available fluorene derivatives, including 2-methyl (XI, R = CH_3), 2-bromo (XI, R = Br), 2,7-dibromo (XII), 1,2,3,4-dibenzo (XIII), 2-amino (XI, R = NH_2), 2-hydroxy (XI, R = OH) and 4-carboxyfluorene (XIV). In the case of the two last-mentioned compounds, potassium hydroxide had to be used in excess of the amount necessary for the neutralization of the hydroxyl and carboxyl groups. In the case of the amino compound, refluxing was used in preference to the water distillation technique, to avoid benzylation of the amino group,[15] and the reaction was conducted under nitrogen, as the amino compound



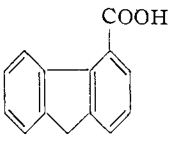
XI



XII



XIII



XIV

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(10) D. Lavie and E. D. Bergmann, *Bull. soc. chim. France*, [5] **18**, 250 (1951).

(11) K. Ziegler and W. Schäfer, *Ann.*, **511**, 101 (1934).

(12) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 2014 (1946).

(13) For references see E. D. Bergmann and E. Fischer, *Bull. soc. chim. France*, [5] **17**, 1084 (1950).

(14) *Cf.* R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 125 (1928).

(15) See Y. Sprinzak, French Patent 1082636, Jan. 8, 1953.

was somewhat sensitive to air under the conditions used. In the case of the bromo compounds, care was taken to use as little potassium hydroxide as possible and short reaction times, as even with this precaution bromine was displaced by solvolysis to the extent of a few per cent. In all but the cases of the amino and bromo compounds, the yields were close to quantitative.

In addition, the reaction has been tried with two substituted benzyl alcohols, *viz.*, *p*-tolylcarbinol and *p*-anisyl alcohol. Both reacted with fluorene readily to yield the expected products.

Experimental

Benzalfluorene.—A mixture of 4.15 g. (0.025 mole) of fluorene, 4 ml. of benzaldehyde, 20 ml. of benzyl alcohol and 2 g. of potassium hydroxide was heated at 110° for 75 minutes. After cooling, the mixture was treated with 200 ml. of water. The product, which crystallized slowly in the lower layer, was filtered and washed with water; yield 4.1 g. (64%), m.p. 73–74°; after one recrystallization from heptane, m.p. and mixed m.p. 75–76°.[6]

Reduction Experiments. 9-Benzylfluorene.—A mixture of 2.00 g. of benzalfluorene, 6 ml. of benzyl alcohol and 0.5 g. of KOH was heated at 180° for 10 minutes. There appeared a voluminous precipitate of potassium benzoate. After cooling, 20 ml. of water was added, and the product was filtered and washed with water; yield 1.97 g. (97%), m.p. and mixed m.p. 134–134.5°.[6]

The aqueous filtrate was washed with ether, and benzoic acid was isolated by acidifying and extracting with ether; yield 0.60 g., m.p. 110–117°; after recrystallization from water, m.p. and mixed m.p. 121–122.5°.

Dibiphenylene-ethane.—A mixture of 1.00 g. of dibiphenylene-ethylene,[16] 3 ml. of benzyl alcohol and 0.25 g. of KOH was refluxed for 6 minutes. The orange-red color of the solution disappeared and potassium benzoate precipitated. The mixture was worked up as above. The yield was 1.00 g. (100%) of dibiphenylene-ethane, m.p. and mixed m.p. 247–250° cor.[17]

9-(γ-Phenylpropyl)-fluorene.—Fifty ml. of benzyl alcohol, accompanied by a little water, was distilled off from a mixture of 125 ml. of benzyl alcohol and 4 g. of KOH. After cooling to about 100°, 8 g. (0.0285 mole) of cinnamalfluorene[18] was added, and the mixture was refluxed for 30 minutes. The yellow color disappeared, and potassium benzoate precipitated. After cooling, 50 ml. of water was added, the organic layer was extracted with ether, washed with water and dried over Na_2SO_4. After distilling the ether at ordinary pressure, the benzyl alcohol was removed under 30 mm. vacuum and at a temperature of up to 155°. The oily residue was shaken with enough alcohol to dissolve it completely. On standing, colorless crystals collected gradually. They were filtered and washed with alcohol; yield 6.6 g. (81%), m.p. 71–71.5°; after one recrystallization from methyl alcohol or heptane, m.p. and mixed m.p. 71–72°.[19]

Anal. Calcd. for $C_{22}H_{20}$: C, 92.96; H, 7.04. Found: C, 92.8; H, 7.15.

Benzylation Experiments. 9-Benzylfluorene. (a) By Reflux.—4.15 g. (0.025 mole) of fluorene, 10 ml. of benzyl alcohol and 2 g. of KOH were refluxed for 2 hours. The cooled mixture was treated with 10 ml. of water, and the crystals were filtered and washed with water; yield 6.30 g. (99%), m.p. 131.5–133.5°; after one recrystallization from heptane, m.p. and mixed m.p. 134–135°.

(b) By Distillation.—A mixture of 4.15 g. of fluorene, 10 ml. of benzyl alcohol, 0.05 ml. of benzaldehyde and 0.4 g. of KOH was placed in a metal-bath at 150°. The temperature was raised to 170° during 2 minutes, and water began to distil. The temperature was then raised gradually to 208° in 12 minutes, during which 0.6 ml. of water and 1.4 ml. of benzyl alcohol were collected as distillate. The product was isolated as above; yield 6.35 g. (100%), m.p. 133–134°.

When the experiment was carried out under nitrogen and with benzyl alcohol which was purified by washing with sodium bisulfite and sodium carbonate and redistilled twice *in vacuo*, working up of the mixture as above yielded unchanged fluorene, m.p. and mixed m.p. 112–114°.

2-Methyl-9-benzylfluorene.—1.80 g. (0.01 mole) of 2-methylfluorene,[20] 2 ml. of benzyl alcohol and 0.1 g. of KOH were heated rapidly to 182°, and the temperature was raised to 228° during 17 minutes. The total distillate amounted to 0.7 ml. On working up as above, 2.68 g. (99%) of 2-methyl-9-benzylfluorene of m.p. 100.5–102° was obtained; after one recrystallization from heptane, m.p. 102–103°.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.34; H, 6.66. Found: C, 93.1; H, 6.8.

9-Benzyl-1,2,3,4-dibenzofluorene.—1.00 g. (0.00375 mole) of 1,2,3,4-dibenzofluorene,[21] 2 ml. of benzyl alcohol, 0.04 g. of KOH and a small drop of benzaldehyde were rapidly heated to 220° and then to 240° during 13 minutes; 0.5 ml. of distillate was collected. On working up, there was obtained 1.32 g. (99%) of the 9-benzyl derivative, m.p. 188–189° cor.; after one recrystallization from benzene, m.p. 190–191° cor.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.38; H, 5.62. Found: C, 94.6; H, 5.65.

2-Hydroxy-9-benzylfluorene.—0.91 g. (0.005 mole) of 2-hydroxyfluorene,[22] 2.5 ml. of benzyl alcohol, 0.025 ml. of benzaldehyde and 0.5 g. of KOH were heated during 17 minutes to 182°, at which temperature boiling began, and then during 68 minutes to 206°. After cooling, 3 ml. of water was added, and the mixture was acidified with dilute hydrochloric acid, whereupon the product precipitated in colorless crystals. It was filtered and washed with water; yield 1.32 g. (97%), m.p. 178–180° cor., after one recrystallization from toluene, m.p. 180.5–181.5° cor.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.23; H, 5.88. Found: C, 88.2; H, 6.05.

9-Benzylfluorene-4-carboxylic Acid.—1.05 g. (0.005 mole) of fluorene-4-carboxylic acid,[23] 2.5 ml. of benzyl alcohol and 0.5 g. of KOH were rapidly heated to 187°, and then during 11 minutes to 220°. The distillate amounted to 0.7 ml. After cooling, the thick, clear, slightly yellow mass was dissolved in 15 ml. of water, and the clear solution was washed twice with ether and acidified with dilute hydrochloric acid. The product precipitated as an oil that soon solidified to colorless crystals; yield 1.49 g. (99%), m.p. 170–175° cor.; after one recrystallization from toluene, m.p. 174.5–175.3° cor.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.00; H, 5.33. Found: C, 84.2; H, 5.38.

9-Benzyl-2-bromofluorene.—2.45 (0.01 mole) of 2-bromofluorene,[24] 2 ml. of benzyl alcohol, 0.04 g. of KOH and a small drop of benzaldehyde were heated to 178°, and then during 41 minutes to 220°. There was obtained 3.41 g. of crude product, m.p. 112–117°. One recrystallization from 18 ml. of glacial acetic acid afforded 2.76 g., m.p. 118.5–121°. Recrystallization from isopropyl alcohol did not change the melting point.

Anal. Calcd. for $C_{20}H_{15}Br$: C, 71.6; H, 4.48; Br, 23.88. Found: C, 71.1; H, 4.80; Br, 23.7.

The product apparently contained some impurity, as its melting point could be raised to 121–123° by three successive recrystallizations from benzene–heptane 1:1.

The aqueous filtrate from the working up of the reaction mixture was washed with ether and titrated for bromine by Volhard's method. It contained 4.3% of the total bromine present in the starting material.

9-Benzyl-2,7-dibromofluorene.—6.48 g. (0.02 mole) of dibromofluorene,[25] 10 ml. of benzyl alcohol, 0.05 ml. of benzaldehyde and 0.4 g. of KOH, were heated to 180°, and then during 15 minutes to 193°. The distillate amounted

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(16) J. Thiele and A. Wanscheidt, *Ann.*, **376**, 269 (1910).

(17) R. J. S. Jennings and A. Fowler-Williams, *J. Appl. Chem.*, **3**, 426 (1953).

(18) Reference 14, p. 121.

(19) Reference 14, p. 139.

(20) L. Mascarelli and B. Longo, *C. A.*, **32**, 4564 (1938).

(21) E. D. Bergmann and F. Bergmann, THIS JOURNAL, **60**, 1805 (1938).

(22) C. Ruiz, *Chem. Zentr.*, **101**, II, 1074 (1930).

(23) W. E. Bachmann and C. Sheehan, THIS JOURNAL, **62**, 2689 (1940).

(24) J. T. Thurston and R. L. Shriner, *ibid.*, **51**, 2163 (1935).

(25) Ch. Courtot, *Ann. chim.*, [10] **14**, 5 (1930).

to 1.5 ml., of which about 0.35 ml. was water. There was obtained 8.00 g. of crude product, m.p. 121–123°. One recrystallization from butyl alcohol yielded 6.85 g. (83%), m.p. 124–125°; reported melting point 126–127°.[26] The melting point was not further changed by recrystallization from butyl alcohol, glacial acetic acid or benzene–heptane.

Anal. Calcd. for $C_{20}H_{14}Br$: Br, 38.64. Found: Br, 38.40.

Displaced bromine, determined as above, amounted to 2.9% of the total bromine.

9-Benzyl-2-aminofluorene.—A mixture of 6 g. (0.033 mole) of 2-aminofluorene,[27] 10 ml. of benzyl alcohol, 0.1 ml. of benzaldehyde and 0.1 g. of KOH was refluxed for 4 hours in an atmosphere of nitrogen. After cooling, it was treated with 20 ml. of water and filtered. As filtration became increasingly slow owing to the presence of some oil, the mass was taken off the filter, treated with petroleum ether, filtered, washed with petroleum ether and water and dried in a vacuum oven at 60°; yield 9.1 g., m.p. 110–120°. The crude amine was converted to the hydrochloride by heating with 55 ml. of alcohol and 5.5 ml. of concentrated hydrochloric acid on a steam-bath for 40 minutes. After cooling, the hydrochloride was filtered and washed with alcohol and benzene; yield 8.5 g., m.p. 240°. It was reconverted to the amine by refluxing with 50 ml. of alcohol and 5 ml. of a 30% sodium hydroxide solution. After cooling, the amine was filtered, washed with 80% alcohol and with water, and dried in a vacuum desiccator; yield 7.1 g. (80%), m.p. 126–127°; after one recrystallization from benzene–heptane 1:3, m.p. and mixed m.p. 126.5–127°.[28]

9-(*p*-Methylbenzyl)-fluorene.—4.15 g. (0.025 mole) of fluorene, 7 g. of *p*-tolylcarbinol,[29] 0.05 ml. of *p*-tolualdehyde[30] and 0.12 g. of KOH were heated to 186°, and then during 40 minutes to 232°. The distillate amounted to 0.5 ml. After treating with 10 ml. of water, the product was filtered and washed with water and with 15 ml. of 80% alcohol; yield 6.55 g., 97%, m.p. 136–138°; after one recrystallization from heptane, m.p. 137–138°; reported m.p. 136–137°.[31]

9-(*p*-Methoxybenzyl)-fluorene.—4.15 g. of fluorene, 8 g. of *p*-anisyl alcohol, 0.1 ml. of anisaldehyde and 0.4 g. of KOH were heated to 185°, and then, during 15 minutes, to 223°. The distillate consisted of 0.6 ml. of water. After cooling, the mixture was treated with 10 ml. of water; the crystals were filtered and washed with water and with 20 ml. of 80% alcohol; yield 6.86 g. (96%), m.p. 107–109°; after one recrystallization from heptane and a little charcoal, m.p. 109–110°; reported m.p. 112°.[15]

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.11; H, 6.29. Found: C, 88.0; H, 6.44.

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[26] A. Sieglitz, *Ber.*, **53**, 2241 (1920).

[27] W. E. Kuhn, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 448.

[28] E. D. Bergmann, B. Pullman and Y. Sprinzak, *Bull. soc. chim. biol.*, **34**, 586 (1952).

[29] Reference 27, p. 590.

[30] Reference 27, p. 583.

[31] A. Sieglitz and H. Jassoy, *Ber.*, **54**, 2133 (1921).

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Pyrolysis of Labeled Copolymers in Relation to Structure[1]

BY F. W. MORTHLAND AND WELDON G. BROWN

RECEIVED SEPTEMBER 12, 1955

Copolymers of styrene-β-C^{14} with *m*-methylstyrene and with *p*-methylstyrene, when degraded thermally, give rise to monomer mixtures in which the distribution of the radioactive tracer between the two monomers closely approximates the theoretical (3:1) ratio for randomly constructed copolymers. This proves that the degradation process is not one of spallation from the original chain ends, that the initial chain breaks produce odd and even fragments with equal probability, and that no reversal (re-polymerization of monomers) occurs during degradation. The potential utility of the carbon isotope exchange as a means of studying alternation tendencies in copolymerization is indicated.

If the thermal depolymerization of vinyl-type polymers is initiated by the random fission of C–C bonds, the net result of a polymerization–depolymerization sequence must be an exchange of carbon atoms between monomers. This will be observable in the case of a copolymer derived from two monomers, $R_1CH{=}\overset{*}{C}H_2$ (isotopically labeled) and $R_2CH{=}CH_2$, the structure of which will contain segments such as

$$----\mid-R_1CH-\vdots-\overset{*}{C}H_2-\mid-R_2CH-\vdots-CH_2-\mid----$$

Of the two equally probable modes of cleavage, one, indicated by the vertical dashed lines, re-forms monomers of the original isotopic constitution. The other, indicated by the dotted lines, is accompanied by a transposition of the terminal carbon atoms of the resulting monomer molecules. There will thus have been effected a carbon exchange between monomers, the extent of which will depend upon the number of points in the polymer chain at which two unlike monomer units are contiguous. It will be greatest for copolymers showing regular alternation in structure and least where there is no true cross-polymerization. The predicted distribution ratios for a number of special cases are given in Table I.

TABLE I

PREDICTED DISTRIBUTION OF ISOTOPE IN MONOMERS GENERATED FROM EQUIMOLAR COPOLYMERS OF $R_1CH{=}\overset{*}{C}H_2$ AND $R_2CH{=}CH_2$

	Copolymer type	$R_1CH{=}\overset{*}{C}H_2$/$R_2CH{=}\overset{*}{C}H_2$
I	Regular alternation of monomer units	1:1
II	Random sequence of monomer units	3:1
III	Predominantly sequences of like units	>3:1
IV	No cross-polymerization	No exch.

The occurrence of carbon exchange will exclude from further consideration any mechanism of depolymerization involving the shedding of monomer units from the chain ends (reversal of the chain-growth process) but it will not be inconsistent with a mechanism of irregular primary fragmentation followed by spallation of monomer from the newly formed ends. According to Jellinek[2] the experimental observations relating to thermal degrada-

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[1] Paper presented at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 8–12, 1951.

[2] H. H. G. Jellinek, *J. Polymer. Sci.*, **4**, 13 (1949).