Communications TO THE EDITOR

Isotope Effects in the Free Radical Arylation of Aromatic Hydrocarbons

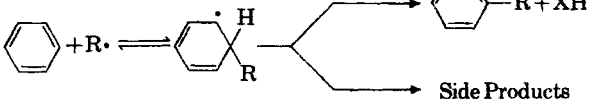
Sir:

There have been several recent reports[1-4] that the free radical arylation reaction of aromatic hydrocarbons by external reagents proceeds without an isotope effect. On the other hand, an isotope effect has recently been observed in certain intramolecular free radical aromatic substitution reactions.[5] It has already been pointed out[1c] that experiments[1b,2] involving low conversions and utilizing tritium at the tracer level are not conclusive.

We wish to report data indicating that there *is* an isotope effect in the free radical arylation and alkylation of benzene-*d*, at least with certain peroxides and under certain experimental conditions. The data are summarized below. The radicals indicated were, in all cases, generated by decomposing the appropriate diaroyl (or dialkyl) peroxide in benzene-*d* at 78°. The benzene-*d* was analyzed mass spectrometrically. The carefully purified biphenyls (purity checked by elementary analysis) were analyzed for deuterium by combustion and the falling drop method.[6] Product toluene was analyzed mass spectrometrically.

In all but two cases—*p*-nitrobenzoyl peroxide and benzoyl peroxide at the higher concentration—unequivocal isotope effects were observed.

The most likely mechanism of free radical aromatic substitution involves addition of the radical to the aromatic followed by hydrogen abstraction by some species *X*. In writing an adequate scheme for these steps one must consider that the addition step may be reversible and that the intermediate adduct radical may undergo side reactions (such as dimerization, tar formation, etc.[7,8]), as well as conversion to substitution product:



An isotope effect will be observed if *either* the reversal of the addition step *or* the step forming side products competes with the hydrogen abstraction step. In either case the intermediate formed by addition of R· at a hydrogen-bearing position of the aromatic ring will be converted to alkylation product in preference to intermediate formed by addition of R· at a deuterium-bearing position.

One can*not*, therefore, conclude from our results that the first step (addition of radical to aromatic) is appreciably reversible under the conditions of the substitution.[9] In fact, since substrate recovered from an arylation of a *m*-dinitrobenzene-2,4-dinitrobenzene-*t* mixture, driven to high conversion, showed no significant change in nuclide content,[1a] it appears that the isotope effect is *not* due to reversal of the first step, but due to the side reactions.[10] Experiments are presently under way in

Radical	Moles PhD / Moles $(RCOO)_2$	Isotopic Purity Benzene-*d*, %	Product M.P.	Product Atom % D	Product Isotope Effect
C_6H_5	42:1	93.7	71–72°	7.81	1.0
	420:1	98.2	71–72°	9.10	2.6
p-$CH_3C_6H_4$	50:1	97.9	47.5–48°	7.61	2.9
p-$CH_3OC_6H_4$	50:1	96.6	89°	6.98	1.3
p-ClC_6H_4	50:1	98.5	78.5–79°	9.80	1.7
	25:1	93.9	78.5–79°	9.30	1.7
p-$O_2NC_6H_4$	41:1	98.5	115.5–116°	9.13	1.0
CH_3	24:1	97.86	Liq.	11.05	1.7
	615:1	98.16	Liq.	11.00	1.7

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(1) (*a*) C. C. Price and R. J. Convery, *J. Am. Chem. Soc.*, **80**, 4101 (1958); (*b*) *J. Am. Chem. Soc.*, **79**, 2941 (1957); (*c*) *J. Am. Chem. Soc.*, **79**, 6579 (1957) (Correction).

(2) G. H. Williams, Abstracts, XIVth International Congress of Pure and Applied Chemistry, Paris, France, 1957, p. 27.

(3) Milyutinskaya, Bagdasaryan, and Izrailevich, *J. Phys. Chem.* (*U.S.S.R.*), **31**, 1019 (1957).

(4) See also D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 167 (1957).

(5) D. B. Denney and P. P. Klemchuk, *J. Am. Chem. Soc.*, **80**, 3289 (1958).

(6) By Mr. Josef Nemeth, University of Illinois.

(7) The importance of this point has been stressed previously by K. H. Pausacker, *Austral. J. Chem.*, **10**, 49 (1957).

(8) An important new side reaction, namely disproportionation, has very recently been uncovered by D. F. De Tar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

(9) This point appears not to have been considered in ref. 5.

(10) Still other possible causes of the isotope effect will be discussed at a later date.

our laboratories to elucidate the exact origin of the observed isotope effects and the reason for their variation with nature and concentration of the peroxide.

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Pyrolysis of Esters. I. Nonselectivity in the Direction of Elimination by Pyrolysis

Sir:

We wish to report that published[1] generalizations regarding the direction of elimination on pyrolysis of esters are in grave error. We now find that pyrolysis of secondary acetates gives in appreciable amounts both possible alkenes as well as *cis* and *trans* isomers when such isomerism is possible. Pyrolysis of 1-heptyl acetate (b.p. 186–187°, n_D^{25} 1.4120; lit.[2] b.p. 192.5°, $n_{\mathrm{He\,(yel.)}}^{15}$ 1.41653) at 540° and a flow rate of 0.6 g. per minute gave pure 1-heptene (b.p. 90–93°, n_D^{25} 1.3962; lit.[3] b.p. 93.5°, n_D^{20} 1.3998) in 56% yield. Homogeneity of this material was established by gas chromatographic analysis using the Wilkins Aerograph equipped with a 5-foot silicone column and with a 10-foot Ucon Polar column. Pyrolysis of 2-heptyl acetate (b.p. 171–173°, n_D^{25} 1.4050; lit.[4] b.p. 71° at 17 mm., n_D^{20} 1.4089) at 485° and a flow rate of 0.67 g. per minute gave a mixture of isomeric heptenes (b.p. 92–98°, n_D^{25} 1.3994; lit.,[5] *trans*-2-heptene, b.p. 97.5–99°, n_D^{24} 1.4056, *cis*-2-heptene, b.p. 98.5–99.5°, n_D^{25} 1.4052) in 84% yield. Gas chromatographic analysis over the 10-foot Ucon Polar column showed 53.9% 1-heptene, 29.3% *trans*-2-heptene (low boiling), and 16.8% *cis*-2-heptene (higher boiling). Above a critical lower temperature, the composition of the pyrolyzate appears to be independent of the temperature and extent of pyrolysis. Thus, pyrolysis of 2-heptyl acetate at 450° and a flow rate of 1 g. per minute gave only 35% of heptenes identical in composition with the product described above.

Pyrolysis of 4-heptyl acetate, which can lead to only one structural isomer without bond rearrangement, on pyrolysis at 485° and flow rate 0.8 g. per minute gave 86% of 3-heptene (b.p. 93–95.5°, n_D^{25} 1.4012; lit.[6] b.p. 95.8–96.1°, n_D^{20} 1.4090). This material was homogeneous to the Ucon chromatographic column except for a small shoulder on the high-retention side of the single peak; this shoulder is interpreted as being due to the presence of a small amount of *cis*-3-heptene, the major component being the *trans*-isomer. Pyrolysis of 3-heptyl acetate at 485° and flow rate 0.6 g. per minute gave a mixture of heptenes (b.p. 91–97°, n_D^{25} 1.4022) in 84% yield. Gas chromatographic analysis over the Ucon column showed 53.5% of 3-heptene, 34.7% of *trans*-2-heptene, and 11.8% of *cis*-2-heptene. The 3-heptene peak showed a shoulder on the high-retention side indicating the presence of a small amount of the *cis*-isomer.

We have also reinvestigated a specific example reported by Bailey and King.[1] Pyrolysis of methylisobutylcarbinyl acetate at 485° and flow rate 0.75 g. per minute gave in 72.2% yield an olefin mixture which on chromatographic analysis over the Ucon column showed two components in the amounts of 44.5% (low retention) and 55.4% (high retention). We assume that the low retention isomer is the lower boiling[7] 4-methyl-1-pentene, while the high retention isomer is the higher boiling[7] 4-methyl-2-pentene.

In view of these results, we must regretfully conclude that the generalizations and the experimental observations of Bailey and associates[1] are in error. We attribute this experimental error to failure of the earlier investigators to utilize precise fractional distillation, thus necessitating the assignment of structure and estimation of homogeneity on infrared analysis alone. Infrared analysis is not an infallible criterion when mixtures are being compared.

We do not wish to generalize our observations at this time. Extensive further investigations are planned.

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[1] W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955); W. J. Bailey, J. J. Hewlitt, and C. King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

[2] R. Bilterys and J. Gisseleire, *Bull. soc. chim. Belg.*, **44**, 576 (1935).

[3] M. L. Sherrill, K. E. Mayer, and G. F. Walter, *J. Am. Chem. Soc.*, **56**, 927 (1934).

[4] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 852 (1914).

[5] B. Gredy, *Bull. soc. chim. Belg.* (5) **2**, 1031 (1935).

[6] F. J. Soday and C. E. Boord, *J. Am. Chem. Soc.*, **55**, 3295, 3300 (1933).

[7] C. G. Schmitt and C. E. Boord, *J. Am. Chem. Soc.*, **54**, 754, 760 (1932).