rule is applicable in situations where only second-order effects are operative.

(6) Support by the Alfred P. Sloan Foundation is gratefully acknowledged.

(7) Trubek Fellow, 1958–1959; N.S.F. Cooperative Fellow, 1959–1960.

(8) Trubek Fellow, 1959–1960.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK 53, N. Y.

KURT MISLOW[6]
ROBERT E. O'BRIEN[7]
HANS SCHAEFER[8]

RECEIVED AUGUST 15, 1960

PERFLUOROALKYLATION OF AROMATIC COMPOUNDS

Sir:

While trifluoromethyl-substituted aromatic compounds are well known,[1,2,3,4,5] and certain perfluoroethyl- and perfluoropropyl-substituted benzenes have been obtained by much more lengthy syntheses,[3,4,5] no procedure has been available for the direct introduction of perfluoroalkyl groups into aromatic nuclei. It is thus of particular importance to report a very general new reaction for the perfluoroalkylation of aromatic compounds, based upon free-radical substitution of aromatic hydrogen, which appears to be limited in scope only by the stability of the aromatic compound under the rather strenuous reaction conditions.

The course of the reaction is indicated by the equation

$$\mathrm{ArH} + 2\mathrm{R_fI} \xrightarrow{250°} \mathrm{R_f\text{-}Ar} + \mathrm{R_fH} + \mathrm{I_2}$$

with yields of 60 to 65% commonly being attained; disubstitution also occurs, the corresponding yield rising as high as 25% when no excess of aromatic compound is present. A wide variety of aromatic hydrocarbons and their derivatives have been perfluoroalkylated successfully, examples being benzene, toluene, naphthalene, halobenzenes, perfluoroalkylbenzenes, benzonitrile, phthalic anhydride, even fully formed dyes.

The perfluoroheptylation of benzene provides an illustration of the general procedure. Perfluoroheptyl iodide was prepared by the method of Brice and Simons[6]; it had b.p. 138.5° and $n^{25}\mathrm{D}$ 1.3274.

Anal. Calcd. for $C_7F_{15}I$; C, 16.95; F, 57.46. Found: C, 17.1; F, 58.1.

Into a 43 ml. Aminco stainless steel autoclave was placed 26.0 g. (0.052 mole) of n-$C_7F_{15}I$ and 2.1 g. (0.027 mole) of benzene. The autoclave was sealed, a 3000 p.s.i.-nickel rupture disk being employed, and the contents were heated for 15 hours at 250°, then chilled to 0°. The autoclave was opened cautiously and rinsed out with 50 ml. of cyclo-$C_6F_{12}O$[7] (b.p. 55°), the free iodine remaining undissolved. The solution was fractionally distilled through a 10-cm. Podbielniak "Heli-pak" column. There was obtained 7.2 g. (62%) of n-$C_7F_{15}C_6H_5$, b.p. 200°, $n^{25}\mathrm{D}$ 1.3576, and 2.8 g. (26%) of (n-$C_7F_{15})_2C_6H_4$, b.p. 270°, m.p. 88° (after recryst. from cyclo-$C_6F_{12}O$).

Anal. Calcd. for $C_{13}H_5F_{15}$: C, 34.99; F, 63.88. Found: C, 35.0; F, 64.0. Calcd. for $C_{20}H_4F_{30}$: C, 29.50; F, 70.00. Found: C, 29.5; F, 69.9.

When twice as much benzene was used, disubstitution was reduced to 8% but the yield of monosubstituted product was not improved substantially.

The infrared spectra of such compounds are unusually difficult to interpret, owing to the exceedingly strong bands contributed by the perfluoroalkyl groups in the "fingerprint region" which ordinarily is highly characteristic for aromatic derivatives. Retention of the benzenoid structure is confirmed by ultraviolet spectroscopy, electrophilic bromination and nitration, and especially by proton and fluorine nuclear spin resonance spectroscopy.

I am particularly indebted to B. W. Nippoldt and P. B. Olson for elementary analyses, and to Dr. W. E. Keiser and Dr. John McBrady for infrared spectroscopy.

CONTRIBUTION NO. 182 FROM THE
CENTRAL RESEARCH DEPARTMENT OF THE
MINNESOTA MINING & MFG. CO.
ST. PAUL 19, MINN.

GEORGE V. D. TIERS

RECEIVED SEPTEMBER 12, 1960

---

(1) J. H. Simons, ed., "Fluorine Chemistry," Academic Press, New York, N. Y., Vol. I, 1950, pp. 494–498 and 506–513; Vol. II, 1954, pp. 220–223.

(2) R. N. Haszeldine and A. G. Sharpe, "Fluorine and its Compounds," Methuen and Co., Ltd., London, 1951, pp. 116–126.

(3) E. T. McBee and O. R. Pierce, *Ind. Eng. Chem.*, **39**, 397, 399 (1947).

(4) E. T. McBee, C. W. Roberts and A. F. Meiners, THIS JOURNAL, **79**, 335 (1957).

(5) W. R. Hasek W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(6) T. J. Brice and J. H. Simons, U. S. Patent 2,614,131 (1952).

(7) T. J. Brice and R. I. Coon, THIS JOURNAL, **75**, 2921 (1953).