Nucleophilic Displacement at Carbon bearing Nitrogen

By RICHARD S. GLASS
(*Department of Chemistry, The University of Arizona, Tucson, Arizona* 85721)

Summary Carbon–carbon bonds are formed at the expense of carbon–nitrogen bonds by nucleophilic displacement on trifluoromethanesulphonimides.

RECENTLY, nucleophilic substitution on the alkyl group of alkyl sulphonimides with the cleavage of the C–N bond has been reported.[1] Displacement was reported for nucleophiles in which the attacking atom was a halogen (I^-, Br^-) or nitrogen (aniline). However, no displacement was reported for the only carbon nucleophile studied (CN^-). I report results in which displacement by carbon nucleophiles on alkyl trifluoromethanesulphonimides to generate a carbon–carbon bond has been observed.

Alkylation with trifluoromethanesulphonimides

Trifluoromethanesulphonimide	Nucleophile	Product	Yield[a]
Benzyl	CN^-	$PhCH_2CN$[c]	80
	$CH(CO_2Et)_2^-$	$PhCH(CO_2Et)_2$[d]	57
n-Hexyl	CN^-[b]	$CH_3(CH_2)_5CN$[c]	75
	$CH(CO_2Et)_2^-$	$CH_3(CH_2)_5CH(CO_2Et)_2$[d]	57

[a] The yields were determined after distillation by g.l.c. and are based on the amount of trifluoromethanesulphonimide used.

[b] Appreciable amounts of n-hexyl cyanide were not formed by reaction of n-hexyltrifluoromethanesulphonimide with sodium cyanide in hexamethylphosphoramide, dimethyl sulphoxide, ethanol, or aqueous ethanol. n-Hexyl cyanide was obtained in the yield shown by treatment of n-hexyltrifluoromethanesulphonimide with potassium iodide in hexamethylphosphoramide followed by treatment with sodium cyanide.

[c] An authentic sample was prepared according to the method of L. Friedman and H. Shechter, *J. Org. Chem.*, 1960, **25**, 877.

[d] An authentic sample was prepared according to the method of C. S. Marvel, *Org. Syn. Coll. Vol. III*, 1955, 705.

Primary amines, as illustrated below, are converted into the corresponding trifluoromethanesulphonimides.[2] This conversion may be effected in one step as shown with sodium hydride as the base or in two steps in which the trifluoromethanesulphonamide is isolated in the first step and then transformed into the trifluoromethanesulphonimide. These derivatives undergo nucleophilic displacement reactions as shown.

$$RNH_2 \xrightarrow[\text{base}]{(CF_3SO_2)_2O} RN(SO_2CF_3)_2 \xrightarrow{X^-} R\text{–}X$$

$$R = CH_3(CH_2)_4CH_2,\ PhCH_2$$

Benzyltrifluoromethanesulphonimide slowly decomposes at room temperature but has been stored as a solid at −15° for short periods of time without decomposition. n-Hexyltrifluoromethanesulphonimide, on the other hand, is a stable, colourless liquid which may be distilled under reduced pressure without decomposition. The spectra (i.r., n.m.r., and m.s.) of these compounds support the assigned structures.

The Table lists the products and yields for the reactions of benzyl and n-hexyltrifluoromethanesulphonimides with nucleophiles in hexamethylphosphoramide {hexamethylphosphoric triamide, $[(CH_3)_2N]_3PO$} at room temperature which result in the formation of a carbon–carbon bond. The products listed were isolated in each case by preparative g.l.c. and shown to be identical (retention time on g.l.c., i.r., and n.m.r.) with authentic samples. The benzyl cyanide, prepared as above, in addition to being compared with authentic benzyl cyanide was hydrolysed to phenylacetamide. This material was the same (i.r., m.p., and mixed m.p.) as that prepared by the method of Wenner.[3]

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(*Received, October* 15*th*, 1971; *Com.* 1790.)

---

[1] (a) J. B. Hendrickson, S. Okano, and R. K. Bloom, *J. Org. Chem.*, 1969, **34**, 3434; (b) P. J. DeChristopher, J. P. Adamek, G. D. Lyon, J. J. Galante, H. E. Haffner, R. J. Boggio, and R. J. Baumgarten, *J. Amer. Chem. Soc.*, 1969, **91**, 2384; (c) P. J. DeChristopher, G. D. Lyon, J. P. Adamek, R. J. Swedo, S. A. Klein, and R. J. Baumgarten, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, California, March—April, 1971, No. 14.

[2] For the preparation of trifluoromethanesulphonic acid anhydride see: J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1957, 2574.

[3] W. Wenner, *Org. Syn. Coll. Vol. IV*, 1963, 760.