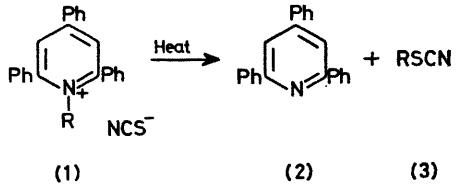
Steric Acceleration in the Decomposition of Pyridinium Cations: a Safe Alternative to the Diazonium Conversion of Aryl Amines into Aryl Thiocyanates[1]

By ALAN R. KATRITZKY* and SUKHPAL S. THIND
(*School of Chemical Sciences, University of East Anglia, Norwich* NR4 7TJ)

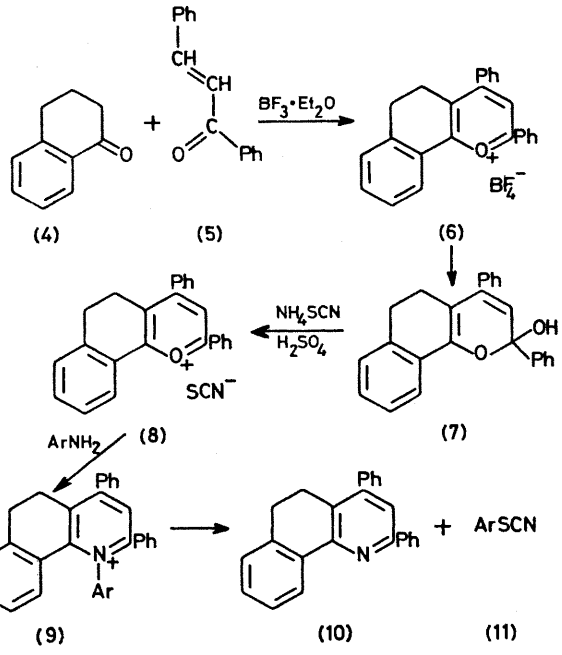
Summary The diphenyl-dihydronaphthopyrylium thiocyanate (**8**) reacts with aryl amines to give the corresponding *N*-aryl-dihydrobenzoquinolinium thiocyanates (**9**) (average yield 88%) which thermolyse smoothly at *ca.* 200 °C to the aryl thiocyanates (average yield 69%).

THE standard method for the preparation of aryl thiocyanates has been diazotisation followed by reaction with aqueous $K_3[Cu(SCN)_4]$ or CuSCN.[2] This procedure possesses obvious disadvantages, particularly for large scale operation in view of hazardous intermediates. Furthermore isothiocyanates[3] can be formed as by-products.



(1) (2) (3)

We therefore sought to extend our method[4] for the preparation of alkyl thiocyanates from alkyl amines (**1**) → (**2**) + (**3**) to the aromatic analogues. Pyrolysis of 1-aryl-2,4,6-triphenylpyridinium thiocyanates (**1**, R = aryl) does yield some of the aryl thiocyanate, but the yields are poor and high pyrolysis temperatures are required. Kinetic investigations[5] have demonstrated the sensitivity of the pyrolysis of 1-substituted pyridinium salts towards steric acceleration by the groups in the 2- and 6-positions. We reasoned that twisting of the 2- and 6-phenyl groups relieved steric strain in compounds of type (**1**) and, by preventing such twisting, increased steric acceleration could be achieved. Therefore α-tetralone (**4**), chalcone (**5**), and boron trifluoride–diethyl ether were treated together to give the novel diphenyl-dihydronaphthopyrylium tetrafluoroborate (**6**) which was converted *via* the pseudobase [(**7**) and other tautomeric forms] by sulphuric acid and ammonium thiocyanate into the corresponding pyrylium thiocyanate (**8**) (overall yield 77% from α-tetralone).†



The thiocyanate (**8**) reacts readily in refluxing ethanol with aryl amines to give the diphenyl-dihydrobenzoquinolinium thiocyanates (**9**) (average yield 88%). Pyrolysis of the quinolinium thiocyanates (**9**) with the eutectic mixture of KSCN and NaSCN (3:1 by weight) at 160—230 °C gives the aryl thiocyanates, in preparatively useful yields, of which the following were prepared in this way: phenyl (67%), *m*-methylphenyl (60%), *p*-methylphenyl (43%), *p*-chlorophenyl (75%), *m*-chlorophenyl (79%), and 3-chloro-4-methylphenyl (90%).

(*Received, 8th November* 1978; *Com.* 1202.)

† Satisfactory analytical figures were obtained for all new compounds reported.

[1] *Cf.* our series 'Heterocycles in Synthesis.' Part 27, A. R. Katritzky, Z. Zakaria, E. Lunt, P. G. Jones, and O. Kennard, in preparation.
[2] 'Preparative Organic Chemistry,' eds. G. Hilgetag and A. Martini, Wiley-Interscience, New York, 1972, p. 269; A. Hantzsch and B. Hirsch, *Ber.*, 1896, **29** (I), 947; L. Gattermann and W. Haussknecht, *ibid.*, 1890, **23**, 738; G. Thurnauer, *ibid.*, p. 769.
[3] J. W. Dienske, *Rec. Trav. chim.*, 1931, **50**, 407.
[4] A. R. Katritzky, U. Gruntz, N. Mongelli, and M. C. Rezende, *J.C.S. Chem. Comm.*, 1978, 133.
[5] Unpublished work with G. Musumarra and Ch. Sana-Ullah.