

NUCLEOPHILIC AROMATIC ALKYLATION BY MEANS OF SULPHONYLCARBANIONS

H. Nozaki, Y. Yamamoto and T. Nisimura

Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

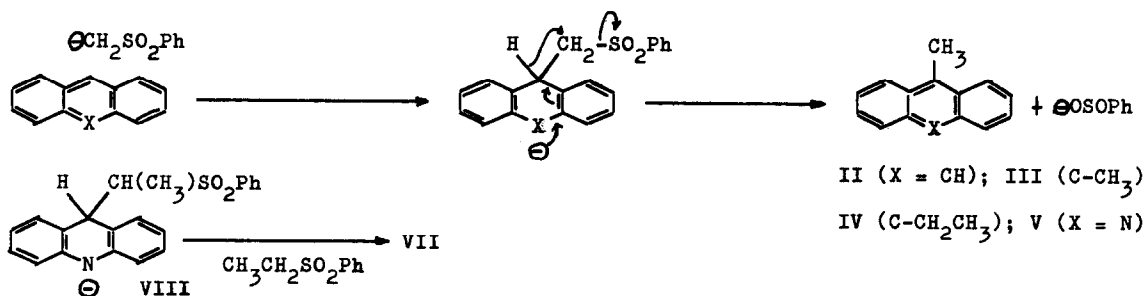
(Received in Japan 24 July 1968; received in UK for publication 6 August 1968)

Methylation of aromatic nuclei has been attained by the action of methylsulphinylcarbanion (1) or oxosulphonium methylide (2) upon condensed ring hydrocarbons, benzopyridines, or nitrobenzenes. We have now discovered that similar kind of nucleophilic alkyl-substitution can be effected by the action of sulphonylcarbanions (3) on anthracene and acridine in hexamethylphosphoric triamide (HMPA) as a solvent.

A mixture of sodium hydride (16.8 mmoles), methyl phenyl sulphone (I) (33.6 mmoles) and HMPA (40 ml) was heated at 65° for 3 hr to afford a reddish brown solution. To this was added a solution of anthracene (5.6 mmoles) in HMPA (20 ml) at room temperature. Heating at 60° for 15 hr gave a mixture of unchanged anthracene (4% recovery) and 9-methylanthracene (II)(1c)(53% yield, without considering the recovery), m.p. and mixed m.p. 81°. Gas chromatography (GC) of the mother liquor indicated the presence of 9,10-dimethylanthracene (III)(1c) (ca. 10%). In sharp contrast, however, heating of the same reaction mixture at 80° for 20 hr afforded mainly 9-ethyl-10-methylanthracene (IV)(43%), m.p. 145-146° (lit. (4) 144°), besides a polymeric tar. The structure of IV (5) was supported by NMR (CDCl<sub>3</sub>):  $\delta$  1.42 t 3H, 3.10 s 4.7H, 3.60 q 2H, 7.25-8.5 m (6). The NMR, GC and mass spectrum indicated the possible presence of III (ca. 13%) and a small amount of 9,10-diethylanthracene among the products at 80°.

To a solution of sodium hydride (16.8 mmoles), I (16.8 mmoles) and HMPA (40 ml) was added a solution of acridine (11.2 mmoles) in HMPA (20 ml) and the mixture was allowed to react at 25° for 4 hr. Work up gave 9-methylacridine (V)(1c)(60%), m.p. and mixed m.p. 118-119°. Heating of 2:2:1 mole ratio solution of the same components at 80° for 4 hr gave V (33%) and 9-methylacridane (VI)(7)(4%), m.p. and mixed m.p. 123-124°.

Attempted ethylation of acridine with ethyl phenyl sulphone in place of I yielded unexpectedly 9-( $\alpha$ -benzenesulphonyl ethyl)acridane (VII)(54%), m.p. 209-212°(dec) (5).



IR (Nujol): 3300 (NH), 1300, 1140  $\text{cm}^{-1}$  ( $\text{SO}_2$ ). NMR ( $\text{CD}_3\text{SOCD}_3$  at  $72^\circ$ ):  $\delta$  0.80 d 3H (J 8 Hz), 3.2 d of q 1H (J 2 and 8 Hz), 4.95 d 1H (J 2 Hz), 6.7-8.0 m 8H, 8.6 broad 1H.

The present methylation reaction can be formulated similarly as those previously recorded (1) as involving negatively charged  $\sigma$ -complex, which is decomposed under hydride-shift and elimination of benzenesulphinate anion. In view of our experiences with methylsulphinylcarbanion (1c), the origin of IV should be ascribed to the intermediacy of III, whose methyl group is deprotonated and the resulting carbanion attacks I in the  $\text{S}_{\text{N}}2$  fashion to remove benzenesulphinate anion. The anion VIII presumably prefers proton abstraction from the sulphone to afford VII rather than the hydride shift and the simultaneous elimination of sulphinate anion due to the methyl-substitution at  $\alpha$ -carbon. The formation of VI requires further work for explanation, which is now in progress in this laboratory.

#### R E F E R E N C E S

1. (a) P. A. Argabright, J. E. Hofmann and A. Schriesheim, *J. Org. Chem.* **30**, 3233 (1965).  
 (b) G. A. Russell and S. A. Weiner, *ibid.* **31**, 248 (1966).  
 (c) H. Nozaki, Y. Yamamoto and R. Noyori, *Tetrahedron Letters* 1123 (1966).
2. (a) H. König, H. Metzger and K. Seelert, *Chem. Ber.* **98**, 3712 (1965).  
 (b) V. J. Traynelis and Sr. J. V. McSweeney, O. P., *J. Org. Chem.* **31**, 243 (1966).  
 (c) B. M. Trost, *Tetrahedron Letters* 5761 (1966).
3. For other reactions of sulphonylcarbanions see, for example,  
 (a) J. W. McFarland and D. N. Buchanan, *J. Org. Chem.* **30**, 2003 (1965).  
 (b) D. F. Tavares and P. F. Vogt, *Can. J. Chem.* **45**, 1519 (1967).
4. A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.* 1108 (1956).
5. The C, H analyses gave correct values.
6. NMR spectra were taken on a JOEL C-60-H spectrometer and chemical shifts were given in p.p.m. from internal TMS reference.
7. E. Hayashi, S. Ohsumi and T. Maeda, *Yakugaku-Zasshi* **79**, 967 (1959).

Acknowledgement. The authors are grateful to Professor K. Sisido for generous help.