BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 301(1972)

# The Nucleophilic Cyclopropylation of the Condensed Aromatic Ring with Sulfonylcarbanion

Hitosi NOZAKI, Tetuya NISIMURA, and Yasusi YAMAMOTO

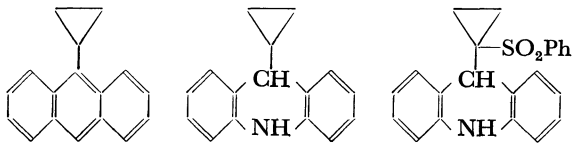
*Department of Industrial Chemistry, Kyoto University, Yoshida, Sakyo-ku, Kyoto*

(Received August 17, 1971)

The nucleophilic methylation of aromatic nuclei has been attained by the action of methylsulfinylcarbanion[1] or dimethyloxosulfonium methylide[2] upon condensed ring hydrocarbons, benzopyridines, or nitrobenzenes. We previously reported that the nucleophilic alkyl-substitution can be effected by the action of sulfonyl-carbanions[3] on anthracene and acridine in hexamethyl-phosphoric triamide (HMPA) as a solvent. We now wish to report a one-step introduction of the cyclopropyl group in anthracene and acridine by means of a sulfonylcarbanion which had been prepared from cyclopropyl phenyl sulfone[4] and sodium hydride in HMPA.

The reaction with anthracene gave 9-cyclopropyl-anthracene (I) (79%). In contrast to the methylation by means of methylsulfinylcarbanion and phenylsulfonylcarbanion, 9,10-dicyclopropylated product was not obtained. The structure of I was supported by its NMR, IR, and mass spectra as well as by the results of elemental analysis.

The treatment of acridine with this carbanion gave 9-cyclopropylacridane (II) (25%) besides a considerable amount of a crystalline, insoluble solid.[5] Phenanthrene, quinoline, or isoquinoline did not react with this carbanion.




I II III

The cyclopropylated product may be ascribed to the nucleophilic attack of the carbanion on the aromatic ring, followed by a concerted hydride shift and the elimination of the sulfinate anion. This route has previously been proposed in the cases of the methylation by means of methylsulfinylcarbanion[1a] and phenylsulfonyl-carbanion.[3b] On the other hand, 9-cyclopropylacridane seems to be attributable to the decomposition of transient 9-(1-phenylsulfonylcyclopropyl)acridane (III), as 9-(1-phenylsulfonylethyl)acridane is the sole isolable product of the reaction of acridine with the carbanion derived from ethyl phenyl sulfone.[3b]

## Experimental

All the mps are uncorrected. The microanalyses were performed by Mrs. Kiyoko Fujimoto of this department. The NMR spectra were taken on a 60 MHz instrument (JEOL C-60 H spectrometer) in deuteriochloroform with tetramethylsilane as the internal standard. The mass spectra were obtained on a Hitachi RMU-6L spectrometer.

*Reaction of Anthracene with a Carbanion.* A carbanion solution was prepared under $N_2$ from sodium hydride (0.48 g, 20 mmol) and cyclopropyl phenyl sulfone (3.64 g, 20 mmol) in HMPA (30 m*l*) at 60—70°C for 2 hr. To this, a solution of anthracene (1.78 g, 10 mmol) dissolved in HMPA (20 m*l*) was added, and the reaction mixture was stirred at 90°C for 23 hr. Work-up followed by recrystallization (EtOH) then gave 9-cyclopropylanthracene (I) (1.71 g, 79%); mp 133—134°C. IR (Nujol): 1030 $cm^{-1}$ (cyclopropane ring). MS: 218 ($M^+$). NMR ($CDCl_3$): $\delta$ 0.60—0.95 and 1.25—1.60 (m, 4H, methylenes of cyclopropane), 2.15—2.65 (m, 1H, methine of cyclopropane), and 7.25—8.95 (m, 9H, aromatic protons).

Found: C, 93.3; H, 6.5%. Calcd for $C_{17}H_{14}$: C, 93.5; H, 6.5%.

*Reaction of Acridine with a Carbanion.* A carbanion solution prepared from sodium hydride (0.48 g, 20 mmol) and cyclopropyl phenyl sulfone (3.64 g, 20 mmol) was allowed to react with acridine (1.79 g, 10 mmol) at 70°C for 15 hr. The reaction mixture was treated with water and extracted with benzene. The evaporation of benzene *in vacuo* and subsequent treatment with ether gave a crystalline solid. The structure of this solid could not be confirmed, as the attempted purification of this solid failed. Meanwhile, the chromatography of the dissolved part in ether on a silica-gel column gave 9-cyclopropylacridane (II) (0.56 g, 25%). The product, II, showed a mp of 122—124°C. IR (Nujol): 3350 $cm^{-1}$ (NH). MS: 221 ($M^+$). NMR ($CDCl_3$): $\delta$ 0.25—0.75 (m, 4H, methylenes of cyclopropane), 0.75—1.00 (m, 1H, methine of cyclopropane), 3.38 (d ($J$=8 Hz), 1H, benzylic proton), and 6.65—7.75 (m, 9H, aromatic protons and NH).

Found: C, 86.6; H, 6.8%. Calcd for $C_{16}H_{15}N$: C, 86.8; H, 6.8%.

The authors are grateful to Professor Keiiti Sisido for his generous help. The financial support of the Ministry of Education, the Japanese Government, and of the Toray Science Foundation is acknowledged with pleasure.

1) a) H. Nozaki, Y. Yamamoto, and R. Noyori, *Tetrahedron Lett.*, **1966**, 1123. b) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965), c) G. A. Russell and S. A. Weiner, *ibid.*, **31**, 248 (1966).

2) a) H. König, H. Metzger, and K. Seelert, *Chem. Ber.*, **98**, 3712 (1965). b) V. J. Traynelis and S. J. V. McSweeney O. P., *J. Org. Chem.*, **31**, 243 (1966).

3) a) H. Nozaki, Y. Yamamoto, and T. Nisimura, *Tetrahedron Lett.*, **1968**, 4625, b) Y. Yamamoto, T. Nisimura, and H. Nozaki, This Bulletin, **44**, 541 (1971).

4) H. E. Zimmerman and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, **82**, 2505 (1960).

5) The structure of this product could not be confirmed, as an attempted purification of this solid failed.