

NUCLEOPHILIC AROMATIC METHYLATION WITH METHYLSULPHINYLCARBANION

H. Nozaki, Y. Yamamoto and R. Noyori

Department of Industrial Chemistry

Kyoto University, Kyoto, Japan

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A recent note (1) on the methylation of unsaturated hydrocarbons by dimethyl sulphoxide (DMSO) has prompted the publication of independent findings on the highly selective methylation reaction of certain condensed aromatic compounds in DMSO. As summarized in Table I, this reaction furnishes good yields of ring-methylated products which are otherwise difficultly available.

While the American authors (1) have used potassium *t*-butoxide as a basic catalyst, the present modification involves treatment with methylsulphinylcarbanion obtained from DMSO and sodium hydride (2). Addition of the aromatics dissolved in DMSO to the carbanion solution at room temperature gave an intensively coloured mixture and stirring was further continued at 60-70° for several hrs. Treatment of the dark coloured mixture with water discharged the colour and the following work-up yielded the methylated products. Naphthalene did not react under the present condition, although a 15% yield of methyl-naphthalenes has been recorded in the presence of potassium *t*-butoxide (1). Benzene and pyridine were also inert to this

Table I. Methylation of Condensed Ring Aromatics with DMSO[Ⓢ]

Aromatics	DMSO [Ⓢ]	Reaction	Position of Attack ^a
	Mole Ratio	Time (hr)	(Yield, %) ^b
anthracene	5	5	9- (77) ^{c,d} and 9,10- (13) ^{c,e}
phenanthrene	10	21	9- (86) ^{c,f}
acridine	5	4	9- (74) ^{c,g}
quinoline	5	5.5	4- (29) ^{c,h,i}
isoquinoline	3	3	1- (51) ^{h,j}

a. Numbered in accord with "The Ring Index", 2nd Edition, American Chemical Society.

b. Isolation yield. All products gave correct C,H-analyses.

c. UV spectra were found to be identical with those recorded.

d. M.p. 79-80° (lit. (3) 81°); picrate, m.p. 136-137° (lit. (3) 137°).

e. M.p. 178-179° (lit. (4) 181°).

f. M.p. 89-90° (lit. (5) 91°); picrate, m.p. 153-153.5° (lit. (5) 151°).

g. M.p. 115-116° (lit. (6) 117-118°); picrate, m.p. 213-214° (lit. (7) 214°).

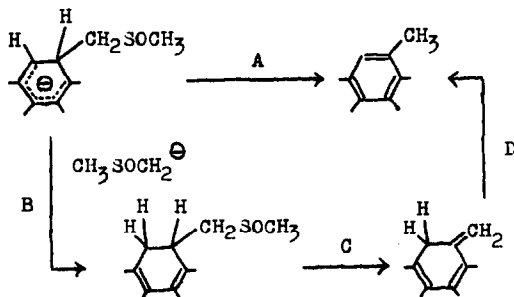
h. An oil giving a single peak on g.l.c. (high vacuum silicone grease, helium).

i. The structure was established by comparison of IR spectrum with that of an authentic sample. Picrate, m.p. 206-208° (lit. (8) 210-211°); sulphate, m.p. 222-223° (lit. (8) 227-227.5°).

j. Picrate, m.p. 228-229° (lit. (9) 226-227°); sulphate, m.p. 251-252° (lit. (10) 248-250°).

methylation. In these unfavourable cases the characteristic colouring was not observed. Phenanthrene, which reacted more slowly than anthracene (1), afforded the monomethylated product only. To the authors' best knowledge the simple and direct introduction of methyl group into the pyridine ring of acridine, quinoline and isoquinoline at the indicated position is unrivaled (11).

Based on these results, the aromatic substitution must proceed via nucleophilic attack of methylsulphinylcarbanion. The orientation is in accord with the one predicted theoretically (12). The fate of negatively charged σ -complex initially formed may be explained as involving concerted hydride shift and liberation of methylsulphenate anion (A) or alternatively protonation of the σ -complex by DMSO (B) followed by elimination of elements of methylsulphenic acid (C) and by subsequent fast aromatization (D). In view of our observation that the reaction of 9-deuterio-phenanthrene resulted in roughly 50% reduction of the deuterium content in the monomethylation product which was isolated in 87% yield, we have been tempted to support the latter route.



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11. Similar treatment of acenaphthylene yielded a mixture of mono-, di- and trimethylation products. Comparison of IR and UV spectra of the monomethylated one with those of authentic 1-methylacenaphthylene showed remarkable differences and clearly indicated that methylation had occurred at aromatic carbons, the orientation being still obscure.
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