Tetrahedron Letters No. 17, pp 1429 - 1430, 1977. Pergamon Press. Printed in Great Britain.

TELE SUBSTITUTION[1] IN THE NAPHTHALENE SERIES. REACTION OF 1,4-DIMETHYL-2,3-DINITRONAPHTHALENE WITH SECONDARY ALIPHATIC AMINES

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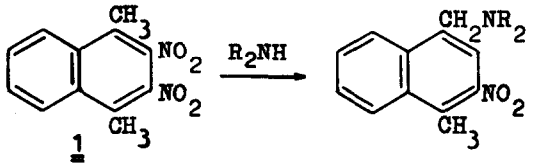
(Received in UK 22 February 1977; accepted for publication 14 March 1977)

In connection with our studies on the cine substitution reaction of 2,3-dinitronaphthalene with piperidine,[2] which yields 3-nitro-1-piperidino-naphthalene, it seemed to us of interest to investigate the behaviour of 1,4-dimethyl-2,3-dinitronaphthalene (1) toward amines. Our idea was that blocking the α positions of the substituted ring by substitution of two methyl groups for the two replaceable hydrogens of 2,3-dinitronaphthalene, the normal substitution of a nitro-group by the nucleophile would take place.

Reaction of 1 (100 mg, 0.4 mmol) in neat piperidine (5 ml, 50 mmol) at 110° in sealed ampoule for 16 hours followed by column cromatography gave a light yellow product (2) [80% yield, m.p. 105-107° from light petroleum (b.p. 30-50°)]. The elemental analysis indicated the formula $C_{17}H_{20}N_2O_2$. An analogous reaction with morpholine yielded a product (3), m.p. 117-118° from methanol. Compound 2 gave ^{1}H n.m.r. signals at τ ($CDCl_3$) 1.79 (m, 2H), 2.29 (broad s, 1H), 2.44 (m, 2H), 6.20 (broad s, 2H), 7.23 (broad s, 3H), 7.57 (m, 4H), and 8.50 p.p.m. (m, 6H). Compound 3 gave ^{1}H n.m.r. signals at τ ($CDCl_3$) 1.78 (m, 2H), 2.26 (broad s, 1H), 2.39 (m, 2H), 6.13 (broad s, 2H), 6.32 (m, 4H), 7.21 (broad s, 3H), and 7.49 p.p.m. (m, 4H). By leading the reaction of 1 with [1-^{2}H]piperidine (70% deuteriated) a compound analogous to 2 was obtained whose ^{1}H n.m.r. spectrum showed a strong decrease in intensity of the signals at τ 2.29, 6.20, and 7.23 p.p.m. Moreover, compound 2 exchanged its hydrogens at τ 7.23 for deuterium when dissolved in CH_3OD in the presence of a trace amount of sodium methoxide. An analogous isotope exchange with the labelled solvent was observed for the hydrogens at τ 7.21 of compound 3.

On the basis of these results,[3,4,5] and in analogy with the spectral data reported for 1,4-dimethyl-2-nitronaphthalene[6] the structures of 1-piperidino-methyl- and 1-morpholinomethyl-4-methyl-3-nitronaphthalene were assigned to



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2; $R_2N = C_5H_{10}N$ (piperidino)
3; $R_2N = C_4H_8ON$ (morpholino)

compounds 2 and 3 respectively. The isomeric structures of 1-piperidinomethyl- and 1-morpholinomethyl-4-methyl-2-nitronaphthalene with the methylene- instead of the methyl-group ortho to the nitro-group were ruled out also on the basis of the exchange data[4] of compound 2 in CH_3OD.

The formation of compounds 2 and 3 instead of the expected 2-piperidino- and 2-morpholino-1,4-dimethyl-3-nitronaphthalene represents, to our knowledge, an unprecedented example of nucleophilic substitution occurring on an aromatic carbocyclic[7] substrate, where the nucleophile attacks on a side-chain α-carbon atom and the leaving group departs from the ring.

REFERENCES AND FOOTNOTES

1. The term "tele substitution has been already proposed (J. Arens, Bull. Soc. Chim. France, 1968, 3037), although unsuccesfully, to designate a somewhat different class of substitution reactions. Now we repropose it with the aim to designate with such term all those substitution reactions in which the entering group occupies a position separated by one or more atoms from that vacated by the leaving group. In our opinion, the term "tele substitution" could be conveniently adopted to designate all those reactions of the aforementioned type for which different (but not always proper) terms are used [e.g. "Substitution with rearrangement" (F. Pietra, Quart. Rev., 1969, 23, 504), "Abnormal substitution" (e.g. F.G. Bordwell, R.W. Hemwell, and D.A. Schexnayder, J. Org. Chem., 1968, 33, 3226) etc.].
2. G. Guanti, S. Thea, and C. Dell'Erba, Tetrahedron Letters, 1976, 461.
3. L.M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969, 2nd Edn, Ch. 2.2 and 3.2.
4. E. Buncel, A.R. Norris, and K.E. Russell, Quart. Rev., 1968, 22, 123; J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, p. 381.
5. Any effort to resolve the broad singlets into signals of higher multiplicity was unsuccesful probably owing to weak coupling between the methylene- (and -a fortiori- the methyl-) group and the proton of the substituted ring [a J value of ca. 0.5 Hz has been reported for methyl substituted naphthalenes (P.R.Wells, Aust. J. Chem., 1964, 17, 967)].
6. A. Fischer and A.L. Wilkinson, Canad. J. Chem., 1972, 50, 3988.
7. A somewhat similar behaviour has been recently found by some of us (M. Novi, F. Sancassan, G. Guanti, and C. Dell'Erba, Chem. Comm., 1976, 303) for an aromatic heterocyclic substrate, namely 2,5-dimethyl-3,4-dinitrothiophen, which furnished for treatment with sodium arenethiolates the corresponding aryl 2-(5-methyl-4-nitro)thenyl sulphides.