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FORMATION OF A 1,2 DIHYDRONAPHTHALENE VIA METHYLENE RADICAL ATTACK ON A NAPHTHALENE NUCLEUS

by

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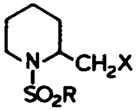
The unprecedented reactivity of α-methylene radicals generated from α-iodomethylpiperidine arylsulfonamides1) necessitated a further study on the effect of variations of the aryl substituent. In this communication the results from a number of aromatic and heteroaromatic derivatives are discussed.



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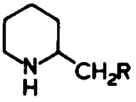

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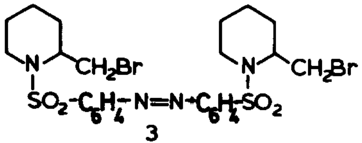

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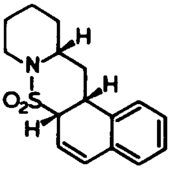
a)	R = 4-NO$_2$Ph	X = I	f)	R = 2-thienyl	X = H
b)	R = 4-NO$_2$Ph	X = Br	g)	R = 2-naphthyl	X = I
c)	R = 3-pyridyl	X = I	h)	R = 1-naphthyl	X = I
d)	R = 3-pyridyl	X = H	i)	R = 1-naphthyl	X = H
e)	R = 2-thienyl	X = I	j)	R = β-styryl	X = I



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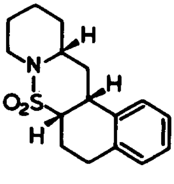

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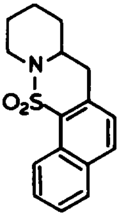

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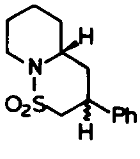

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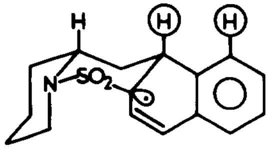
Reaction of the iodide 1a[2] (C_6H_6/80°C/7 h) with 2·7 equiv. of tributylstannane (SnH) gave a 56% yield of rearranged product 2a. Assuming an effective 1,5 addition process with mesomeric NO_2 stabilization of the intermediate radical, this behaviour could be expected. None of the eventually formed 1,6 addition or 2-methyl reduction products could be detected, the remaining 44% of material being composed of various NO_2 reduction products. Interestingly, a similar reaction with the bromide 1b gave the dimeric azo derivative 3 in 51% yield, in which reduction had taken place of the NO_2 group and the C-Br linkage was unaffected.

In contrast to the reported preference for α and γ alkylation in radical reactions with pyridine[3,4], none of the corresponding α or γ insertion product was found upon reaction (C_6H_6/80°C/9 h/2·7 equiv. of SnH) of 1c. Products obtained were the reduced compound 1d (23%) and rearranged material 2c (30%). The latter type of product 2e was also formed in 49% yield (C_6H_6/80°C/8 h/2·7 equiv. SnH) upon reaction with 1e, together with 35% of 1f, while none of the β insertion product was found[5]. Upon raising the temperature (anisole/152°C/3h/2·7 equiv. of SnH) 2e was formed in 72% yield in accordance with the trend described earlier[1].

A most remarkable result was noted upon reaction of the naphthyl sulfonamide 1g (C_6H_6/80°C/5 h/2·7 equiv. of SnH). In addition to 13% of rearranged material 2g the dihydronaphthalene 1,6 addition product 4 was formed in 81% yield; m.p. 128-132°C, 'H NMR δ($CDCl_3$) 1·1-2·1 m (8H), 2·8-3·2 m (1H), 3·35-3·80 m (3H), 3·90-4·18 m (1H), 6·09 d broadened J = 9·5 cps (1H), 6·6 double d J_1= 9·5 cps J_2= 3·0 cps (1H) and 6·95-7·4 (4H). Its structure was confirmed via mass spectral analysis, decoupling experiments and hydrogenation to the tetrahydroderivative 5, m.p. 195-198°C.

This to the best of our knowledge unprecedented course of intramolecular methylene radical addition is rationalized by assuming two intermediates for the addition process which can be visualized as extremes[6]. In the first one 8 the orbital interaction between the allylic radical centre and the π-system is favourable. The peri interaction, however, hampers the hydrogen abstraction from 8, which may lead to an alternative way of termination.



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The second possible intermediate in which the thiazine ring adopts a boat conformation is unfavourable because of the absence of allylic radical stabilisation.

Therefore hydrogen transfer of SnH is presumably the preferred process via intermediate 8 leading to formation of a dihydronaphthalene. Support for this assumption can be derived from the behaviour of the 1-naphthyl derivative 1h. In this molecule the intermediate radical cannot be stabilized via allylic interaction and the preferred process is abstraction of a hydrogen atom giving rise to the naphthothiazine 6 (28%) in addition to the reduced compound 1i (14%) and the rearranged product 2h (28%).

In order to determine the possibilities for attack on non aromatic π-systems the SnH reaction of the E-isomer of 1j was investigated. Reaction of 1j (C_6H_6/80°C/3 h/2·7 equiv. SnH) gave a vield of 18% of 2j together with 47% of a solid m.p. 42-45°C which according to ^{13}C-NMR analysis was composed of a 1:1 mixture of two epimers of 7. So far, attempts to separate the latter isomers have been unsuccessful.

Since the starting C=C geometry of 1j proved to be unaltered in the rearrangement product 2j a second experiment was also carried out with a 7:4 mixture of Z and E isomers[7,8] of 1j. After work-up an identical mixture of 2j and the two epimers of 7 were obtained as in the reaction of E - 1j, indicating that the starting C=C geometry is not maintained in the product. The most plausible explanation for this observation is that the initially formed radical has a sufficiently long enough life time to undergo isomerisation to the more stable E-isomer.

Although a fairly well consistent picture of the radical rearrangement of α-iodomethyl piperidine sulfonamides has now been established a number of questions still have to be answered, particularly with respect to the geometry of the transition state. Work on optically active derivatives is therefore currently in progress.

REFERENCES AND NOTES

1) Preceding communication, Tetrahedron Letters.

2a) Since NO_2-aryl derivatives show pronounced effects in radical behaviour[2b] **1a** was chosen as a first representative to detect a possible deviation from the generally observed pathway.

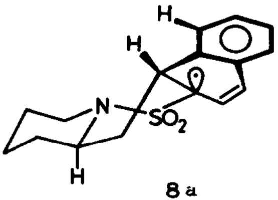
2b) G.H. Williams, Homolytic aromatic substitution. The Pergamon Press Ltd., London, 1960.

3) E. Hardegger and E. Nikles, *Helv.Chim.Acta*, **40**, 2421 (1957).

4) R.A. Abramovitch and K. Kenaschuk, *Can.J.Chem.*, **45**, 509 (1967).

5) C.M. Camaggi, R. Leardini, M. Tiecco and A. Tundo, *J.Chem.Soc.*(B), 1251 (1969).

6) Although not rigorously proven it is supposed that no conformational isomerisation is occurring of the iodomethyl substituent. Therefore, the intermediate **8a** in which the thiazine ring has a boat form and radical stabilisation is possible is rejected because of the equatorial methylene position.



8a

7) Obtained by irradiating with light of 300 nm a solution of the E-isomer of **1j** (1 mmol) in 10 ml methanol with 3 ml acetophenone as a photosensitizer.

8) A.P. Terentev, R.A. Gracheva and Z.F. Shcherbatova, *Dokl.Akad.Nauk.SSSR*, Ser.Khim, **84**, 975 (1952).