.

NITRATION OF BRIDGED HYDRONAPHTHALENES. FUSED ortho-EFFECT

Hiroshi Tanida and Ryonosuke Muneyuki

Shionogi Research Laboratory, Shionogi & Co., Ltd.

Fukushima-ku, Osaka, Japan

We wish to report the striking orientation effect observed on the nitration of some

bridged hydronaphthalenes, in comparison with analogous non-bridged compounds. The

nitration of benzonorbornene (I) and benzobicyclo[2,2,2]octene (II) (1) was carried out

at $0-2°$ by nitric acid in a mixed solvent of sulfuric acid and nitromethane.[1] The

identities and isomer ratios of mononitro compounds formed were determined by gas

chromatography using the isolated pure products as internal references. Some model

compounds, such as indane (III), tetralin (IV), 1,3-dimethylindane (V),[2] 1,4-dimethyl-

tetralin (VI) (2), and two reference compounds cumene and t-butylbenzene were nitrated

under the same condition. The structures of the new compounds[3] were established by

n.m.r. studies (in $CDCl_3$). The a-nitro derivatives showed an aromatic proton at

$2.0-2.2\tau$ as a second order quartet of an ABK system and two aromatic protons at

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[1] The nitration of I with different kinds of reagents, such as nitric acid in acetic
     anhydride or benzoyl nitrate in carbon tetrachloride, gave almost the same isomer
     distribution.

[2] Prepared by the catalytic reduction of 1,3-dimethylindene. The cis-configura-
     tion was determined by n.m.r. studies to be reported elsewhere.

[3] Satisfactory analyses were obtained for all compounds described.

2.7 - 2.8τ as an AB part (multiplet) of an ABK system. The β-nitro derivatives[*4] showed two aromatic protons at 2.0 - 2.1τ as an AB part (multiplet) of an ABK system and an aromatic proton at 2.7 - 2.8τ as a second order quartet of an ABK system.

In order to investigate the relative reactivities of the above compounds, competitive nitration under a condition similar to the above was carried out with hexamethylbenzene as an internal reference for gas chromatographic analysis (4). The relative reactivity was calculated from the expression of Ingold and Shaw (5). Our experimental data are summarized in Table I.

TABLE I

Nitration of 1,2-Cycloalkenobenzenes

Compound	Isomer ratio, %		Relative reactivity
	α	β	
I[a]	6.9	93.1	285
II[b]	3.3	96.7	110
III	50.0	50.0	187
IV	51.6	48.4	147
V[c]	26.5	73.5	100
VI[d]	23.2	76.8	66

	Isomer ratio, %		
	ortho	meta	para
Cumene	23.2	6.3	70.5
t-Butyl-benzene	10.3	8.6	81.1

[a] α-Nitro-I, b.p. 140 - 141° (6 mm.), $n^{26}D$ 1.5789; β-Nitro-I, b.p. 140 - 142° (6 mm.), $n^{26}D$ 1.5855. [b] β-Nitro-II, m.p. 69 - 70°. [c] α-Nitro-V, b.p. 118 - 120° (7 mm.), $n^{24}D$ 1.5482; β-Nitro-V, m.p. 81 - 82°. [d] α-Nitro-VI, b.p. 136 - 137° (6 mm.), $n^{25}D$ 1.5417; β-Nitro-VI, m.p. 44 - 45°.

[*4] The catalytic reduction of β-nitro-I followed by the Sandmeyer reaction afforded β-chloro-I, b.p. 86.5° (5 mm.), $n^{25}D$ 1.5655, whose structure was confirmed by comparison with an authentic sample independently prepared from β-chloro-benzonorbornadiene (3).

The most remarkable fact is that, in spite of no depression of reactivity, the formation of α-nitro derivatives of I and II is much lower than those of any other model compounds. Moreover, the yields of α-products of I and II are lower than the yields of ortho-products of the parent compound, cumene, and of t-butylbenzene.*[5]

The ortho-product of monoalkylbenzenes decreases in the order of toluene, ethylbenzene, cumene, and t-butylbenzene, along with the increasing steric require- ment of the substituent. The lower yields of α-nitro derivatives of V and VI than those of III and IV are easily understandable by consideration of the steric requirements of their cycloalkeno rings. The compounds, I, II, V, and VI are considered as the variants of ortho-diisopropylbenzene and, in the first approximation, there seems to be no reason to estimate that the bridged rings of I and II are more bulky than the other non-bridged rings. The polar and conjugation effects of these ring systems would not be significantly different. Consequently, the most important contribution for the difference between the bridged form and the non-bridged form seems to be due to the conformation and flexibility of the rings. The mechanism of aromatic substitution is believed to involve the formation of a π-complex, followed by its transformation into a σ-complex. The conformation of the rigid bridged ring might give a unusually serious steric hindrance*[6] to the above transformation of nitronium ion towards an

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*[5]   The α-position of 1,2-cycloalkenobenzene is regarded as ortho and meta rela- tive to an alkeno ring, and the β-position is regarded as meta and para. There- fore, for comparison of the isomer ratio of 1,2-cycloalkenobenzene with that of monoalkylbenzene, it may be argued that α/β ratio of 1,2-cycloalkenobenzene and 1/2 ortho/para ratio of monoalkylbenzene should be used. If so, α/β ratio of I (0.074) is lower than 1/2 ortho/para ratio of cumene (0.17) and higher than that of t-butylbenzene (0.063), but α/β ratio of II (0.034) is much lower than 1/2 ortho/para ratio of t-butylbenzene.

*[6]   The authors acknowledge to Prof. H. C. Brown for giving the name of "fused ortho-effect" to this finding.

α-position. The σ-complex formed at an α-position might receive a large interference from the interaction between the nitro group at C_α and the C_2-methylene.
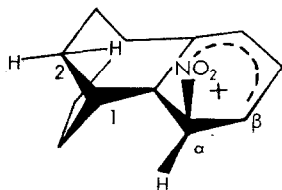
On the other hand, the substituent of monoalkylbenzene can rotate to minimize the above factors. A flexible non-bridged ring compound would possibly decrease the above hindrance by ring deformation.

The increased partial nitration rates at the β-positions of I and II are also interesting. Further study of this point is in progress.

REFERENCES

1.   (a) B. A. Kazanskii and P. I. Suirskaza, Zhur. Obshchei Khim., 29, 2588 (1959). (b) K. Kitahonoki and Y. Takano, Tetrahedron Letters, No. 24, 1597 (1963).

2.   M. C. Kloetzel, J. Am. Chem. Soc., 62, 1708 (1940).

3.   H. Tanida, J. Am. Chem. Soc., 85, 1703 (1963); H. Tanida, R. Muneyuki, and T. Tsuji, Bull. Chem. Soc. Japan, 37, 40 (1964).

4.   As an example of a standard procedure, refer to H. C. Brown and A. W. Moerikofer, J. Am. Chem. Soc., 85, 2065 (1963).

5.   C. K. Ingold and F. R. Shaw, J. Chem. Soc., 2918 (1927).