Preference of the Mesolytic Cleavage over the Nuclear Substitution Observed in the Ozone-mediated Nitration of Bicumene with Nitrogen Dioxide. Implication to the Electron Transfer Nature of the *Kyodai*-Nitration of Arenes

Hitomi Suzuki* and Tadashi Mori
Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-01

(Received April 18, 1996)

Ozone-mediated reaction of bicumene with nitrogen dioxide in dichloromethane at low temperature results in almost complete mesolytic cleavage of the hydrocarbon, accompanied by little or no nuclear nitration, in accordance with operation of the electron transfer process involving the nitrogen trioxide as initial electrophile.

Aromatic nitration has long been accepted to occur *via* the *single* mechanistic pathway involving the nitronium ion (NO_2^+) as the electrophile. Several years ago, however, we have observed that nitrogen dioxide is activated in the presence of ozone to react with a variety of arenes under *neutral* conditions, giving the corresponding nitro derivatives in high yields (the *kyodai*-nitration).[1] For this novel type of aromatic nitration, we have proposed a mechanism in which the reaction proceeds in a dual mode depending on the oxidation potential of aromatic substrate, *i.e.*, *ionic* or *electron transfer* (ET), where nitrogen trioxide (NO_3) has been postulated as the common active species.[2] In this paper, we wish to present a convincing evidence for the operation of the electron transfer mechanism in the *kyodai*-nitration of arenes.

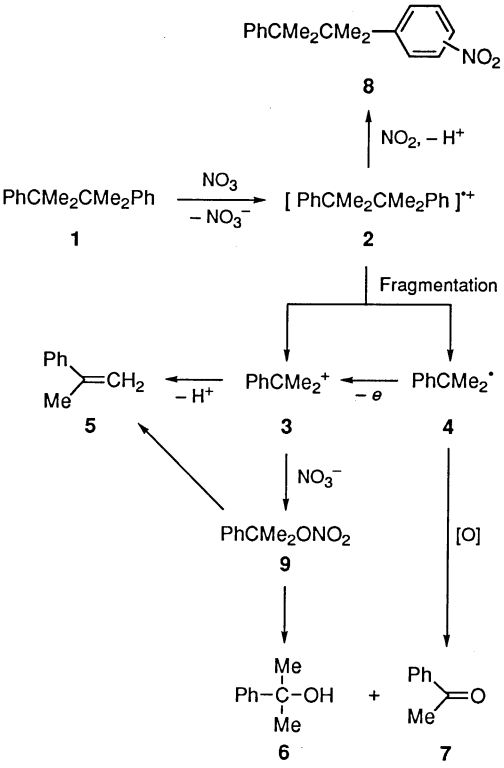
In recent years, bicumenes have been widely recognized as an excellent probe for the electron transfer process.[3] They readily form a cation radical[4] which undergoes facile cleavage of the central C-C bond,[5] giving one cumyl cation and one cumyl radical species. Bicumene **1** was stable toward nitrogen dioxide in a dilute dichloromethane solution at –20 °C. However, when ozone was introduced into this solution at the same temperature, hydrocarbon **1** was rapidly cleaved to produce 2-phenylpropene **5**, α-cumyl alcohol **6** and acetophenone **7** (Table 1). Little or no nuclear nitration products could be detected even at a stage of 50% conversion, although *tert*-butylbenzene readily gave the expected nitro derivatives under the same conditions. At a higher temperature (0 °C) or in a more concentrated solution, the formation of nitro derivatives **8** became considerable, but even under these conditions the proportion of the fragmentation products **5**–**7** was preponderant in the product distribution. In accordance with an observation by Kochi *et al.*,[6] treatment of compound **1** with nitronium tetrafluoroborate in sulfolane/dichloromethane at 0 °C furnished only nuclear nitration products.

Table 1. Reactions of bicumene (2,3-dimethyl-2,3-diphenylbutane) **1** with three different types of nitrating agents

ArH	NO_2			Conv.	Product distribution (%)			
c/mol L^{-1}		*t*/min	*T*/°C	(%)	**8** (*o* : *m* : *p*)	: **5**	: **6**	: **7**
NO_2–O_3 [a]								
2	4	1	0	45	5 (11:23:66)	: 73	: 14	: 8
2	4	1	–20	52	—[b] (—)	: 69	: 17	: 14
100	20	30	0	74	41 (20:15:67)	: 34	: 17	: 8
100	20	30	–20	74	27 (21:14:65)	: 50	: 16	: 7
$NO_2^+BF_4^-$ [c]								
20	—	5 h	0	61	100 (8:24:68)	: —[d]	: —[b]	: —[b]
$AcONO_2$ [e]								
10	—	1 h	–20	47	74 (11:20:69)	: 22	: 2	: 2

[a] All reactions were carried out in dichloromethane (50 mL). Ozone was introduced at a rate of 0.16 mmol min^{-1}. [b] Not detected. [c] Nitronium tetrafluoroborate (1.2 equiv) in sulfolane (10 mL) was added dropwise over 30 min to a dichloromethane solution of the substrate (40 mL) under argon atmosphere. [d] Trace. [e] Acetyl nitrate (*ca.* 10 equiv) was added dropwise over 30 min to a dichloromethane solution of the substrate (10 mL).

A plausible reaction pathway for the mesolytic fragmentation of bicumene is depicted in Scheme 1. Nitrogen trioxide generated *in situ* oxidizes compound **1** to the cation radical **2**, which dissociates into cumyl cation **3** and cumyl radical **4**; the former species loses proton to form olefin **5** and the latter is oxidized to alcohol **6** and ketone **7**. Part of the cation **3** combines with nitrate anion to form α-cumyl nitrate **9**, eventually leading to alcohol **6** after aqueous workup.



Scheme 1.

In connection with the present work, it would be pertinent to mention briefly about the classical aromatic nitration based on acetyl nitrate. This nitrating agent is known to exist in an equilibrium with dinitrogen pentaoxide (N_2O_5), which has long been accepted as the precursor to the actual nitrating species, NO_2^+.[7] In gaseous phase or in a non-polar solution, however, dinitrogen pentaoxide is known to dissociate homolytically to produce nitrogen dioxide and nitrogen trioxide,[8] which suggests us an alternative possibility about the mechanism of nitration with acyl nitrates that this type of classical nitration may occur, at least in part, *via* the *kyodai*-nitration. Accumulation of our experimental results appears to support this view.[2,9] In fact, the nitration of compound **1** with acetyl nitrate in dichloromethane was found to produce a significant amount of the fragmentation products, along with the expected nitro derivatives (Table 1).

In summary, we have confirmed the ET nature of the *kyodai*-nitration using bicumene as a probe and now suggest its possible mechanistic implication to the classical aromatic nitration based on acetyl nitrate.

Financial support of this work from a grant-in-aid for Scientific Research (No. 05554023) of the Ministry of Education, Science, Sports and Culture of Japan is gratefully acknowledged. T. M. thanks the Japan Society for the Promotion of Science for the Fellowship (No. 5026).

References and Notes

1 For a survey, see: T. Mori and H. Suzuki, *Synlett*, **1995**, 383.

2 a) H. Suzuki and T. Mori, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 677; **1994**, 479; b) H. Suzuki, T. Murashima, I. Kozai, and T. Mori, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1591.

3 a) L. Bardi, E. Fasani, and A. Albini, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 545; b) E. Bosch and J. K. Kochi, *J. Org. Chem.*, **59**, 3314 (1994); c) P. Maslak and W. H. Chapman, Jr., *J. Org. Chem.*, **55**, 6334 (1990); d) E. Baciocchi and R. Ruzziconi, *J. Chem. Soc. Chem. Commun.*, **1984**, 445; e) D. M. Camaioni, and J. A. Franz, *J. Org. Chem.*, **49**, 1607 (1984); f) L. W. Reichel, G. W. Griffin, A. J. Muller, P. K. Das, and S. N. Ege, *Can. J. Chem.*, **62**, 424 (1984).

4 Cyclic voltammogram of a dichloromethane solution of bicumene (1 mmol L^{-1}) exhibited an irreversible oxidation wave (E_{pc} = 2.32 V *vs* NHE) under the following conditions: working electrode, Pt; reference electrode, $Ag/AgNO_3$; scan rate, 100 mV sec^{-1}; supporting electrolyte, 0.1 mol L^{-1} $^{n}Bu_4NPF_6$.

5 PM3 calculations revealed that the ΔH value of the mesolytic cleavage of bicumene radical cation **2** was amazingly low (−82.6 kJ mol^{-1}) as compared to that of bibenzyl radical cation (+105.4 kJ mol^{-1}). In accordance with the theoretical prediction, the *kyodai*-nitration of bibenzyl gave three isomeric nitro derivatives in a ratio 2- : 3- : 4-nitro = 43 : 5 : 52 in 80% yield at a stage of 64% conversion.

6 E. K. Kim, K. Y. Lee, and J. K. Kochi, *J. Am. Chem. Soc.*, **114**, 1756 (1992).

7 For a general survey of aromatic nitration with acetyl nitrate, see: a) G. A. Olah, R. Malhotra, and S. C. Narang, "Nitration, Methods and Mechanisms," VCH Publishers Inc, New York (1989), p. 43; b) K. Schofield, "Aromatic Nitration," Cambridge University Press, London (1980), p. 54.

8 a) C. H. Wu, E. D. Morris, Jr., and H. Niki, *J. Phys. Chem.*, **77**, 2507 (1973); b) S. M. Japar and H. Niki, *J. Phys. Chem.*, **79**, 1629 (1975); c) R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.*, **88**, 1210 (1984); d) **88**, 4446 (1984).

9 a) H. Suzuki, S. Yonezawa, and T. Mori, *Bull. Chem. Soc. Jpn.*, **68**, 1535 (1995); b) H. Suzuki, A. Tatsumi, T. Ishibashi, and T. Mori, *J. Chem. Soc., Perkin Trans. 1*, **1995**, 339.