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Interception of 1,4-Radical Cations Derived from a Cage Ketone with Molecular Oxygen

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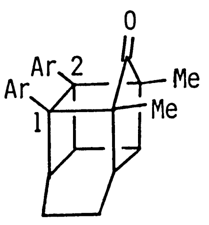
1,4-Radical cations, produced from a cage ketone containing a cyclobutane ring by a reaction with an aminium salt or photochemical reaction of an electron donor-acceptor complex with TCNE, were intercepted by molecular oxygen to give novel oxygenated products.

Electron-transfer oxygenations of three-membered compounds have been extensively studied.[1)] The similar oxygenations of cyclobutanes are also interesting since molecular oxygen might intercept 1,4-radical cations formed by their electron-transfer bond cleavage.[2)] However, there is only one report on such reactions[3)] probably because cyclobutanes easily undergo electron-transfer cycloreversion to olefins.[4)] We recently demonstrated that cage ketone **1** undergoes an unusual cycloaddition to give **2** upon irradiating the electron donor-acceptor (EDA) complex with tetracyanoethylene (TCNE) under Ar.[5)] The results indicate that a 1,4-radical cation derived from a cyclobutane contained in cage ketone **1** could be intercepted by TCNE. Therefore, we have examined the electron-transfer reactions of cage ketone **1** under O_2 to intercept intermediate 1,4-radical cations with molecular oxygen and found unusual oxygenation reactions.



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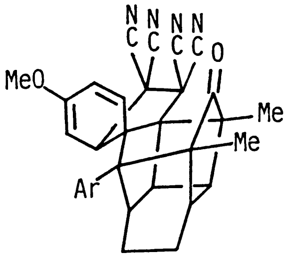
Ar=p-MeOC$_6$H$_4$



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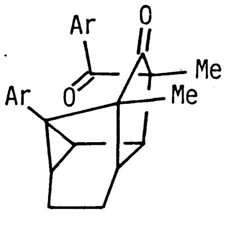

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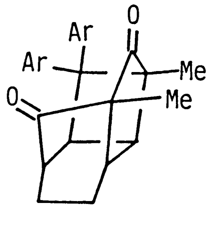

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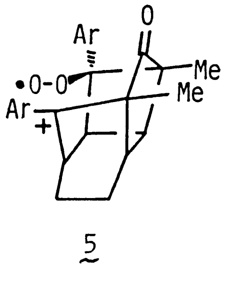

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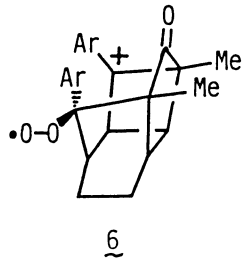

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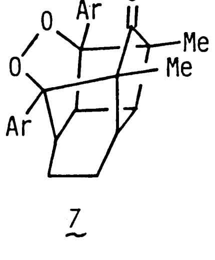

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When cage ketone **1** was reacted with 0.1 equiv. of tris-(p-bromophenyl)aminium hexachloroantimonate, which is a useful reagent to produce radical cations of donors,[6] in dichloromethane under Ar at room temperature, **1** was recovered unchanged. However, the reaction under O_2 gave oxygenated products **3** (oil, 25%) and **4** (mp 201-202 °C, 23%) together with recovery of **1** (43%). The structures of the products **3** and **4** were determined on the basis of the spectral data.[7,8] They are considered to be formed via oxygen adducts **5** and **6**, respectively, indicating that initially formed 1,4-radical cations were intercepted by molecular oxygen. Endoperoxide **7** was not obtained in this reaction.

Oxygenation reactions of the EDA complex of cage ketone **1** with TCNE were examined because the reactions of EDA complexes of three-membered compounds with TCNE under O_2 suggested that oxygenated products and cycloadducts with TCNE are formed from the diffused radical cations and the geminate radical ion pairs, respectively.[1] Although no reaction occurred upon heating **1** with TCNE under O_2 in boiling acetonitrile, irradiation of an EDA complex of **1** (λmax 398, 516 nm) in dichloromethane with a 2 kW xenon lamp under O_2 gave an oxygenated product **8** [mp 263-265 °C (dec)] together with recovery of **1** and TCNE adduct **2** (run 1 in Table 1). The structure of **8**, an unusual oxygenated TCNE-adduct, was deduced from the spectral data[9] and confirmed by the X-ray crystal analysis as shown in Fig. 1.[10] When the irradiation was carried out in acetonitrile, the yield of **2** decreased and **8** was mainly obtained together with **3** (run 2). Addition of 1,2,4,5-tetramethoxybenzene (TMB) (E_1^{ox}=0.81 V vs. SCE) suppressed the formation of **8** rather than that of **2** (run 3). These facts suggest that **2** and **8** are formed from a geminate radical ion pair and a diffused radical cation, respectively, since the latter is favorable in polar solvents and more easily quenched by TMB compared to the former.[1] Furthermore, the ratio of **2** to **8** increased when much amount of TCNE was used (run 4), indicating that in the formation of **8**, an oxygen-addition precedes a TCNE-addition.

On the basis of these findings, we propose a plausible mechanism shown in Scheme 1. Irradiation of an EDA complex **9** forms a geminate radical ion pair **10** and then a ring-opened geminate radical ion pair **11**. Radical coupling in **11** gives a dipolar intermediate **12** from which adduct **2** is formed. A diffused radical cation **13** reacts with oxygen to give **5** from which **3** and **8** are formed although the mechanism of the formation of **8** is still ambiguous. It should be noted that another oxygenated product **4** was not obtained in the irradiation of the EDA complex, indicating the preferential formation of radical cation **13** in the photoreaction. The reason for this may be explained by considering that the formation of **11** from **10** takes place faster than the diffusion to **14** due to a strong interaction between TCNE and the more electron donating aryl group attached to the C_2 carbon.

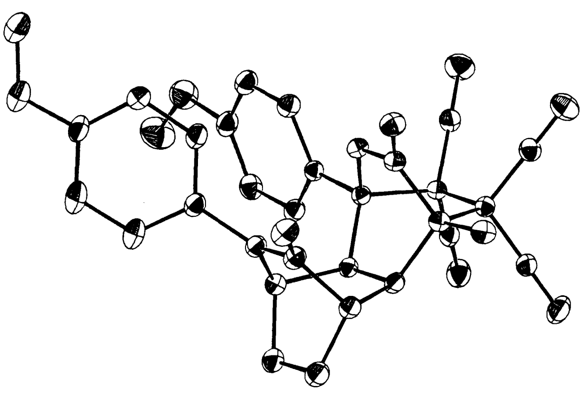
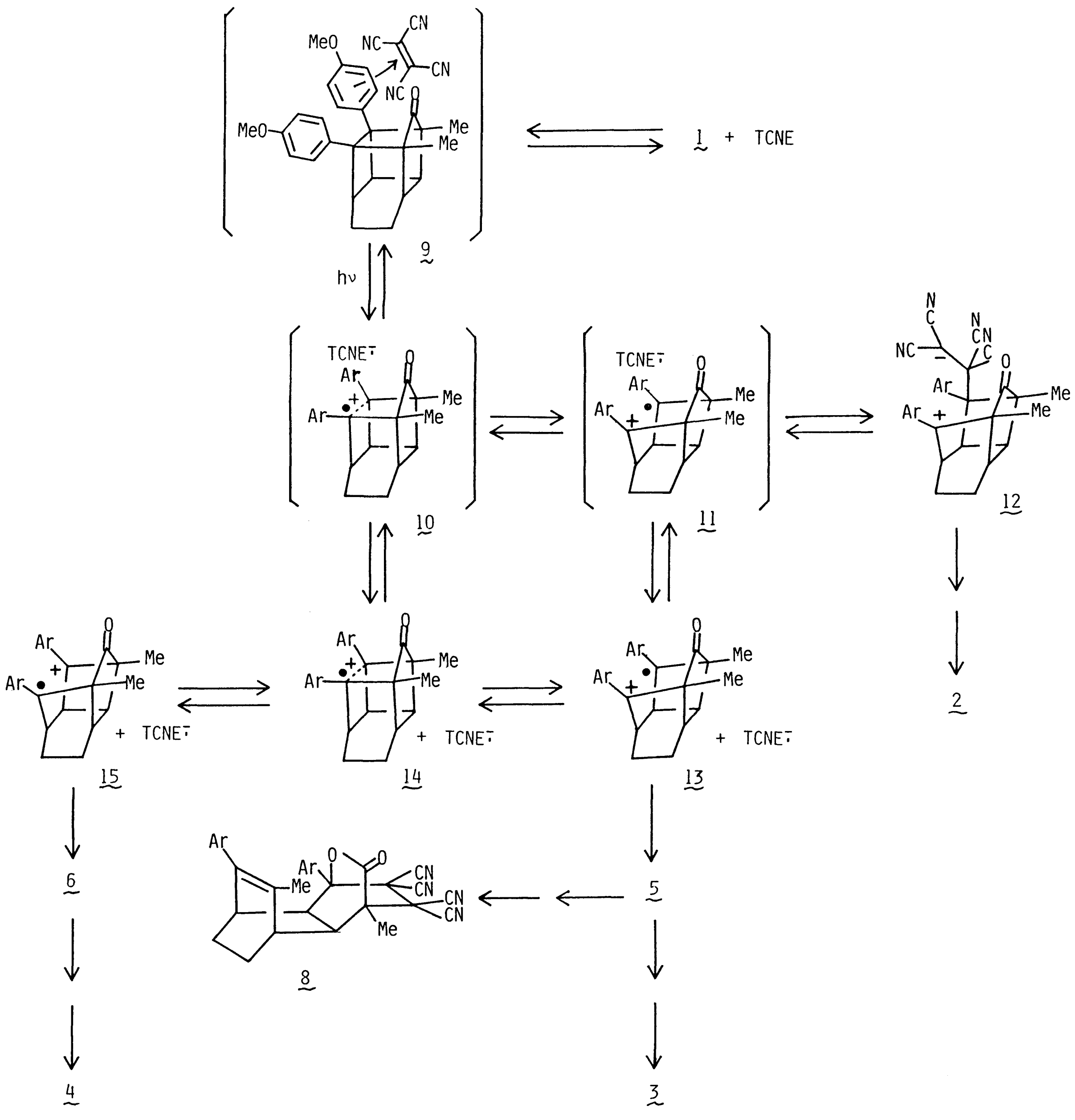


Fig. 1. The ORTEP diagram of 8.

Table 1. Photoreaction of an EDA complex of cage ketone **1** with TCNE under O_2 a)

Run	Solvent	TCNE/equiv.	TMB/equiv.	Irrad time/h	Yield/% b) **1**	**2**	**3**	**8**	Ratio of **2/8**
1	CH_2Cl_2	1	0	2	33	34	0	28	1.2
2	CH_3CN	1	0	1.5	27	trace	6	41	0
3	CH_2Cl_2	1	1	6	27	47	0	27	1.7
4	CH_2Cl_2	3	0	0.7	25	49	0	24	2.0

a) [**1**]=3.3×10^{-2} mol dm^{-3}. Irradiated with a 2 kW xenon lamp through a Toshiba L-42 filter (λ>390 nm). b) Determined by ^1H NMR using triphenylmethane as an internal standard.



Scheme 1.

The results found here demonstrate the utility of molecular oxygen to intercept reactive radical-cation intermediates. It is also interesting that two isomers of 1,4-radical cations derived from a cyclobutane could be distinguished by reactions with oxygen.

References

1) T. Miyashi, M. Kamata, and T. Mukai, J. Am. Chem. Soc., 109, 2780 (1987), and references cited therein.

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3) K. Mizuno, K. Murakami, N. Kamiyama, and Y. Otsuji, J. Chem. Soc., Chem. Commun., 1983, 462.

4) C. Pac, Pure Appl. Chem., 58, 1249 (1986).

5) H. Ikeda, Y. Yamashita, C. Kabuto, and T. Miyashi, J. Chem. Soc., Chem. Commun., submitted for publication. The structure of 2 was determined by the X-ray crystal analysis.

6) A. Ledwith, Acc. Chem. Res., 5, 133 (1972).

7) All new compounds obtained here showed satisfactory elemental analyses.

8) **3**; IR (neat) 1740, 1660 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (br d, 3H, J=0.5 Hz), 1.22 (ddd, 1H, J=7.3, 3.3, 2.5 Hz), 1.59 (s, 3H), 1.60 (ddd, 1H, J=7.3, 1.0, 1.0 Hz), 1.62 (dddd, 1H, J=13.5, 12.0, 6.0, 2.6 Hz), 1.67 (dddd, 1H, J=3.8, 2.6, 1.0, 1.0 Hz), 1.77 (dddd, 1H, J=13.5, 12.2, 4.5, 3.8 Hz), 2.00 (dddd, 1H, J=14.5, 12.0, 4.5, 2.0 Hz), 2.14 (dddd, 1H, J=14.5, 12.2, 6.0, 3.3 Hz), 2.98 (br ddd, 1H, J=1.0, 1.0, 0.5 Hz), 3.67 (s, 3H), 3.84 (s, 3H), 6.68 (dd, 2H, J=8.0, 2.0 Hz), 6.95 (dd, 2H, J=8.0, 2.0 Hz), 7.00 (dd, 2H, J=8.0, 2.0 Hz), 8.12 (dd, 2H, J=8.0, 2.0 Hz), **4**; IR (KBr) 1730, 1695 cm^{-1}, ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (s, 3H), 1.17 (s, 3H), 1.80 (ddd, 1H, J=10.0, 3.5, 2.5 Hz), 1.85 (br dd, 1H, J=10.0, 2.5 Hz), 1.98 (br dd, 1H, J=10.0, 3.6 Hz), 2.02 (ddd, 1H, J= 10.0, 3.6, 3.5 Hz), 2.19 (ddd, 1H, J=5.2, 2.5, 2.5 Hz), 2.82 (ddd, 1H, J=3.8, 3.6, 3.6 Hz), 3.20 (dd, 1H, J=9.0, 5.2 Hz), 3.59 (dd, 1H, J=9.0, 3.8 Hz), 3.78 (s, 3H), 3.80 (s, 3H), 6.50-7.30 (br m, 2H), 6.80 (dd, 2H, J=8.0, 1.5 Hz), 6.88 (dd, 2H, J=9.0, 2.0Hz), 7.11 (dd, 2H, J=9.0, 2.0Hz).

9) IR (KBr) 1775 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (ddd, 1H, J=10.5, 8.0, 2.0 Hz), 1.58 (ddd, 1H, J=10.5, 9.0, 3.0 Hz), 1.74 (dd, 1H, J=8.0, 2.0 Hz), 1.76 (dd, 1H, J=9.0, 3.0 Hz), 1.84 (s, 3H), 1.87 (s, 3H), 2.64 (dd, 1H, J=2.0, 2.0 Hz), 2.78 (dd, 1H, J=3.0, 3.0 Hz), 2.82 (dd, J=10.0, 3.0 Hz), 3.15 (dd, 1H, J=10.0, 2.0 Hz), 3.80 (s, 3H), 3.82 (s, 3H), 6.74 (dd, 1H, J=8.8, 2.6 Hz), 6.76 (ddd, 2H, J=9.0, 3.5, 2.0 Hz), 6.93 (ddd, 2H, J=9.0, 3.5, 2.0 Hz), 6.98 (dd, 1H, J=8.8, 2.6 Hz), 7.35 (dd, 1H, J=8.8, 2.6 Hz), 7.42 (dd, 1H, J=8.8, 2.6 Hz)

10) Crystal data for **8**: MF $C_{33}H_{28}O_4N_4$ CH_2Cl_2, MW 629.53, monoclinic, space group P2$_1$/n, a=20.388(2), b=15.833(1), c=9.638(2) Å, β=92.59(1)°, V=3107.89(10) Å^3, Z=4, D_{calcd}=1.35 g cm^{-3}. A total of 5027 reflections was collected by Rigaku automated four-circle diffractometer (AFC-5R) using graphite monochromated CuK radiation, and solved by direct methods. Refinement was carried out by the block-diagonal least-squares method to R=8.62% for 3241 reflections within $|F_o| > 3\sigma|F_o|$.

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