NOTES Bull. Chem. Soc. Jpn., 65, 2875—2877 (1992)

Photochemistry of 1,2 : 4,5-Benzenebis(dicarboximide). Insertion of Alkenes into the C–N Bond of *N,N′*-Dihexyl-1,2 : 4,5-benzenebis(dicarboximide)

Yasuo Kubo* and Seiichi Tanabe
Department of Chemistry, Faculty of Science, Shimane University,
Matsue, Shimane 690

(Received June 4, 1992)

Synopsis. In the photolyses of acetonitrile solutions of *N,N′*-dihexyl-1,2 : 4,5-benzenebis(dicarboximide) (**1**) and alkenes, insertion of the double bond in the alkenes into the C–N bond of the imide function of **1** was observed. The insertion reaction proceeded along with a retention of the stereochemistry of the alkenes in reactions with *trans*- and *cis*-2-butene.

The photochemistry of arenedicarboximides has received much attention during the last two decades,[1)] especially regarding their photoreactions with alkenes, leading to arene-fused azepinedione-type molecules following insertion of the alkenes into the C–N bond of the imide function.[2)] However, few systematic investigations concerning the basic photochemistry of arenebis(dicarboximide)s have been carried out so far, although these diimides have attracted considerable interest in recent years as potent electron donors in artificial photosynthetic systems.[3)]

This paper describes the photoreactions of *N,N′*-dihexyl-1,2 : 4,5-benzenebis(dicarboximide) (**1**) with alkenes. The predominant reaction of **1** with alkenes has been found to involve an insertion of the double bond in the alkenes into the C–N bond of the imide function of **1**, proceeding along with a retention of the stereochemistry of the alkenes.

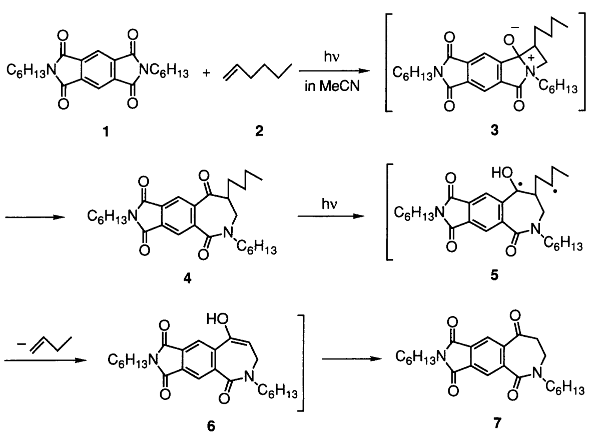
Results and Discussion

Irradiation of an acetonitrile solution of **1** (1.3 mM, 1 M=1 mol dm^{-3}) and 1-hexene (**2**) (800 mM) by light that was >320 nm (uranium filter) resulted in the formation of two products, **4** and **7**. It was found that compound **4** was an insertion product of **2** into the C–N bond of the imide function of **1**, and that compound **7** was produced by an elimination of 1-butene from **4** (Eq. 1). The structures of **4** and **7** were supported by their spectral resemblance to the analogous benzazepinediones obtained by photoreactions of *N*-methylphthalimide with alkenes.[2b,h)] The yields of **4** and **7** largely depend on the irradiation time (Table 1). Table 1 indicates that the yield of **4** is higher than that of **7** during the early stage of the reaction, but decreases markedly with the passage of the irradiation time. On the other hand, the yield of **7** first increases and then gradually decreases with passing irradiation time. These results clearly show that **7** is a secondary photoproduct of **4**, as shown in Eq. 1. The photoconversion of **4** to **7** was confirmed by the photoreaction of isolated **4** in acetonitrile under the same conditions. The formation of **4** and **7** is rationalized by the mechanism shown in Eq. 1, which involves an initial 2π+2π cycloaddition between **1** and **2** to give **3**, followed by a C–N bond cleavage in **3** to **4**, and the type-II photoelimination of **4** to afford **7** through a 1,4-biradical **5** and an enol **6**. Although the corresponding two-step mechanism had already been proposed for the photoreaction of *N*-methylphthalimide and 1-pentene, no primary product corresponding to **4** could be isolated in that case.[2h)] These results may indicate a lower efficiency of the type-II photoreaction of **4**, compared with that of the corresponding primary product from *N*-methylphthalimide.

Table 1. Yields of Photoproducts **4** and **7** in the Photoreaction of *N,N′*-Dihexyl-1,2 : 4,5-benzenebis(dicarboximide) (**1**) with 1-Hexene (**2**) in Acetonitrile[a)]

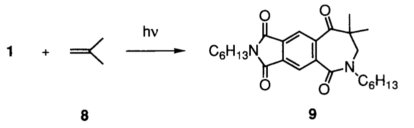
Irradiation Time	Conversion of **1**	Yield[b)]/%	
min	%	**4**	**7**
15	42	48	12
60	81	18	19
120	95	5	17
270	99	—	15

a) Reaction conditions: [**1**]=1.3 mM, [**2**]=800 mM, *hν* (λ>340 nm), under N$_2$. b) Yields were based on consumed **1**.



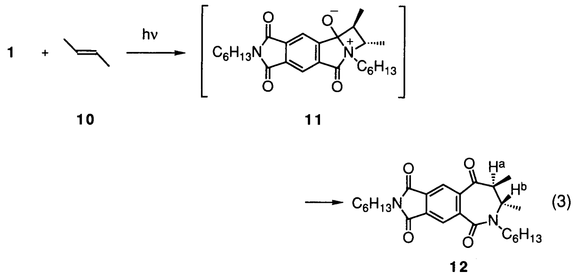
(1)

Irradiation of an acetonitrile solution of **1** (1.3 mM) and isobutene (**8**) (1 M) gave the corresponding insertion product **9** in a yield of 48% (Eq. 2).

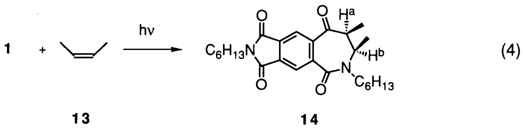


(2)

An important characteristic of this photoreaction is the stereochemical course. Irradiation of **1** in the presence of 1 M of *trans*-2-butene (**10**) and *cis*-2-butene (**13**) gave the corresponding insertion products, **12** and **14**, in yields of 19 and 9%, respectively (Eqs. 3 and 4).



(3)



(4)

The stereochemistry of **12** and **14** can be assigned by comparing the coupling constants between two methine hydrogens, H^a–H^b, of the azepine ring with those of the corresponding arene-fused azepinediones, which are reported to be J=10.1,[2e)] 11.0,[2i)] and 11.6 Hz[2i)] for the trans-isomer and J=2.3,[2e)] and 3.2 Hz[2i)] for the cis-isomer. Products **12** and **14** have coupling constants of J= 8.8 and 2.4 Hz, respectively, suggesting a trans-stereochemistry for **12** and a cis-stereochemistry for **14**, as shown in Eqs. 3 and 4. The fact that no detectable amounts of cis–trans-isomerized products were observed in the reaction of **1** with **10** and **13** in the course of the photoreaction obviously indicate the stereospecificity of the reaction, thus suggesting that the reactions occur directly from the singlet excited state of **1**.

In the photoreactions of *N*-methylphthalimide with alkenes, the insertion of alkenes is reported to proceed along with a retention of the stereochemistry of the alkenes only during the extremely early stage of the reaction. A concomitant cis–trans isomerization of the alkenes, however, always occurs to give nonstereospecific mixtures of the products.[2b)] Although the mechanism of the cis–trans isomerization in the reactions of phthalimides has not been fully clarified,[2e)] the contribution of the reaction from the triplet state of *N*-methylphthalimide may account for the isomerization.[4)] The fact that no such cis–trans isomerization is observed in the reaction of **1** seems to indicate a small contribution of the reaction from the triplet excited state of **1** in the reaction of **1** with the alkenes.

The results obtained here clearly indicate that the insertion of a double bond in the alkene into the C–N bond of the imide function of **1**, proceeding with retention of the stereochemistry of the alkenes, is a characteristic photoreaction of **1** with alkenes, as in the cases of the photoreactions of phthalimides with alkenes. There are, however, some discrepancies between the photoreactions of **1** with alkenes and those of phthalimides: i.e., the primary photoproduct **4** can be isolated in the case of the photoreaction of **1** with **2**, and no detectable amounts of cis–trans-isomerized products are observed in the reaction of **1** with **10** and **13** in contrast with the corresponding photoreactions of phthalimides.

Experimental

^{1}H NMR spectra were determined on a JEOL JNM-GX-270 (270 MHz) instrument in $CDCl_3$. IR spectra were obtained with a Hitachi 260-50 spectrophotometer. Low-resolution (EI, 70 eV) and high-resolution (EI) Mass spectra were measured on a Hitachi M-80B mass spectrometer. The mp was measured using a Yanagimoto micromelting point apparatus, and is uncorrected. A microanalysis was performed on a Yanagimoto CHN corder MT-5.

Materials. *N,N'*-Dihexyl-1,2:4,5-benzenebis(dicarboximide) (**1**) was prepared by heating pyromellitic dianhydride with hexylamine according to the general procedure for the synthesis of *N,N'*-dialkyl-1,2:4,5-benzenebis(dicarboximide)s,[5)] and was purified by recrystallization from dichloromethane-hexane: Mp 200.0—202.0 °C; ^{1}H NMR δ=0.88 (t, J= 6.8 Hz, 6H, 2×Me), 1.2—1.3 (m, 12H, 6×CH_2), 1.6—1.8 (m, 4H, $NCH_2C\underline{H}_2$), 3.73 (t, J=7.3 Hz, 2H, NCH_2), and 8.25 (s, 2H, Arom H); IR ($CHCl_3$) 1765, 1710 (imide), 1448, and 1385 cm^{-1}. Found: C, 68.81; H, 7.31; N, 7.26%. Calcd for $C_{22}H_{28}N_2O_4$: C, 68.72; H, 7.34; N, 7.29%.

Alkenes **2**,**8**,**10**,**13** were commercially available and **2** was purified by distillation. Acetonitrile was purified by distillation after dehydration.

General Procedure for Irradiation and Product Isolation. UV irradiation of 10 cm^3 of N_2 purged acetonitrile solutions containing 5 mg (1.3 mM) of **1** and alkenes **2**,**8**,**10**,**13** was carried out with an Eikosha EHB-WI-300 high-pressure Hg-lamp through a uranium filter (λ>320 nm) at ambient temperature. The reaction was monitored by ^{1}H NMR measurements. After evaporation of the solvent, the residue was subjected to column chromatography (Wakogel C-200). Dichloromethane or benzene–ether (10%) was used as the eluant for separating the products.

Irradiation of 1 and 1-Hexene (2). 8-Butyl-2,6-dihexyl-7,8-dihydroazepino[3,4-*f*]isoindole-1,3,5,9(2*H*,6*H*)-tetrone (4): Oil; ^{1}H NMR (35 °C) δ=0.8—1.0 (m, 9H, 3×CH_3), 1.2—1.8 (m, 22H, 11×CH_2), 3.01 (m, 1H, COCH), 3.40 (dd, J=4.2, 15.4 Hz, 1H, 1H of $NC\underline{H}_2CH$), 3.51 (dt, 1H, 1H of $NC\underline{H}_2CH_2$), 3.61 (dd, J=10.5, 15.4 Hz, 1H, 1H of $NC\underline{H}_2CH$), 3.63 (dt, 1H, 1H of $NC\underline{H}_2CH_2$), 3.71 (t, 2H, $NC\underline{H}_2CH_2$), 7.89 (s, 1H, Arom H), and 8.32 (s, 1H, Arom H); IR ($CHCl_3$) 2960, 2940, 1778, 1724, 1716, 1645, 1396, and 1368 cm^{-1}; MS (70 eV) m/z (rel intensity) 468 (M$^+$, 2), 413, (7), 342 (7), 301 (8), 230 (10), 158 (15), 114 (25), 59 (90), and 42 (100). Found: m/z 468.2994. Calcd for $C_{28}H_{40}N_2O_4$: M, 468.2986.

2,6-Dihexyl-7,8-dihydroazepino[3,4-*f*]isoindole-1,3,5,9-(2*H*,6*H*)-tetrone (7): Oil; ^{1}H NMR (35 °C) δ=0.88 (t, 3H, CH_3), 0.91 (t, 3H, CH_3), 1.1—1.8 (m, 16H, 8×CH_2), 3.01 m, 1H, 1H of $COCH_2$), 3.5—3.8 (m, 7H, 1H of $COCH_2$+3× $NC\underline{H}_2CH$), 8.05 (s, 1H, Arom H), and 8.35 (s, 1H, Arom H); IR ($CHCl_3$) 2955, 2930, 1776, 1722 (sh), 1718, 1645, 1398, and 1368 cm^{-1}; MS (70 eV) m/z (rel intensity) 412 (M$^+$, 12), 342 (8), 328 (7), 149 (7), 114 (7), 57 (50), and 42 (100). Found: m/z 412.2360. Calcd for $C_{24}H_{32}N_2O_4$: M, 412.2360.

Irradiation of 1 and Isobutene (8). 2,6-Dihexyl-8,8-dimethyl-7,8-dihydroazepino[3,4-*f*]isoindole-1,3,5,9(2*H*,6*H*)-tetrone (9): Oil; ^{1}H NMR (35 °C) δ=0.88 (t, 3H, CH_3), 0.91 (t, 3H, CH_3), 1.28 [s, 6H, $COC(CH_3)_2$], 1.2—1.4 (m, 12H, 6×CH_2), 1.5—1.8 (m, 4H, 2×CH_2), 3.41 [s, 2H, $NC\underline{H}_2C(CH_3)_2$], 3.58 (br t, 2H, $NC\underline{H}_2CH_2$), 3.71 (t, 2H, $NC\underline{H}_2CH_2$), 7.89 (s, 1H, Arom H), and 8.32 (s, 1H, Arom H); IR ($CHCl_3$) 2960, 2930, 1776, 1722 (br), 1648, 1398, and 1368 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 440 (M$^+$, 3), 327 (23), 257 (11), 149 (12), 114 (100), 57 (32), and 42 (92). Found: *m*/*z* 440.2642. Calcd for $C_{26}H_{36}N_2O_4$: M, 440.2672.

Irradiation of 1 and *trans*-2-Butene (10). 2,6-Dihexyl-*trans*-7,8-dimethyl-7,8-dihydroazepino[3,4-*f*]isoindole-1,3,5,9(2*H*,6*H*)-tetrone (12): Oil; ^{1}H NMR (35 °C) δ=0.8—1.0 (m, 6H, 2×CH_3), 0.89 (d, *J*=8.3 Hz, 3H, $\mathrm{COCHC\underline{H}_3}$), 1.16 (d, *J*=8.3 Hz, 3H, $\mathrm{NCHC\underline{H}_3}$), 1.2—1.8 (m, 16H, 8×$\underline{\mathrm{CH}}_2$), 2.94 (dq, *J*=8.3, 8.8 Hz, 1H, $\mathrm{COC\underline{H}CH_3}$), 3.23 (m, 1H, 1H of $\mathrm{NC\underline{H}_2CH_2}$), 3.70 (t, *J*=7.1 Hz, 2H, $\mathrm{NC\underline{H}_2CH_2}$), 3.85 (dq, *J*=8.3, 8.8 Hz, 1H, $\mathrm{NC\underline{H}CH_3}$), 3.93 (m, 1H, 1H of $\mathrm{NC\underline{H}_2CH_2}$), 7.93 (s, 1H, Arom H), and 8.32 (s, 1H, Arom H); IR ($CHCl_3$) 2955, 2930, 1772, 1722 (br), 1640, 1396, and 1368 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 440 (M$^+$, 3), 384 (14), 313 (12), 149 (22), 112 (8), 59 (100), and 41 (80). Found: *m*/*z* 440.2669. Calcd for $C_{26}H_{36}N_2O_4$: M, 440.2672.

Irradiation of 1 and *cis*--2-Butene (13). 2,6-Dihexyl-*cis*-7,8-dimethyl-7,8-dihydroazepino[3,4-*f*]isoindole-1,3,5,9-(2*H*,6*H*)-tetrone (14): Oil; ^{1}H NMR (35 °C) δ=0.8—1.0 (m, 6H, 2×CH_3), 0.89 (d, *J*=8.3 Hz, 3H, $\mathrm{NCHC\underline{H}_3}$), 1.25 (d, *J*=8.3 Hz, 3H, $\mathrm{COCHC\underline{H}_3}$), 1.2—1.8 (m, 16H, 8×$CH_2$), 3.00 (dq *J*=2.4, 8.3 Hz, 1H, $\mathrm{COC\underline{H}CH_3}$), 3.3—3.7 (m, 2H, $\mathrm{NC\underline{H}_2CH_2}$), 3.71 (t, *J*=7.3 Hz, 2H, $\mathrm{NC\underline{H}_2CH_2}$), 4.05 (dq, *J*=2.4, 8.3 Hz, 1H, $\mathrm{NC\underline{H}CH_3}$), 8.13 (s, 1H, Arom H), and 8.39 (s, 1H, Arom H); IR ($CHCl_3$) 2960, 2930, 1770, 1722 (sh), 1718, 1640, 1396, and 1366 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 440 (M$^+$, 3), 385 (8), 313 (10), 242 (1), 149 (15), 128 (18), 112 (68), 56 (100), and 42 (88). Found: *m*/*z* 440.2690. Calcd for $C_{26}H_{36}N_2O_4$: M, 440.2672.

References

1) For reviews see: Y. Kanaoka, *Acc. Chem. Res.*, **11**, 407 (1978); P. H. Mazzocchi, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker, New York (1981), Vol. 5, p. 421; J. D. Coyle, *Pure Appl. Chem.*, **60**, 941 (1988).

2) a) P. H. Mazzocchi, M. Bowen, and N. Narian, *J. Am. Chem. Soc.*, **99**, 7063 (1977); b) P. H. Mazzocchi, S. Minamikawa, and M. Bowen, *J. Org. Chem.*, **43**, 3079 (1978); c) K. Maruyama and Y. Kubo, *Chem. Lett.*, **1978**, 769; d) Y. Kanaoka, K. Yoshida, and Y. Hatanaka, *J. Org. Chem.*, **44**, 664 (1979); e) P. H. Mazzocchi, S. Minamikawa, and P. Wilson, *ibid.*, **44**, 1186 (1979); f) P. H. Mazzocchi, P. Wilson, F. Khachik, L. Klingler, and S. Minamikawa, *ibid.*, **48**, 2981 (1983); g) Y. Kubo, S. Tojo, M. Suto, R. Toda, and T. Araki, *Chem. Lett.*, **1984**, 2075; h) K. Maruyama and Y. Kubo, *J. Org. Chem.*, **50**, 1426 (1985); i) Y. Kubo, R. Toda, K. Yamane, and T. Araki, *Bull. Chem. Soc. Jpn.*, **59**, 191 (1986); j) Y. Kubo, M. Suto, T. Araki, P. H. Mazzocchi, L. Klingler, D. Shook, M. Edwards, and C. Somich, *J. Org. Chem.*, **51**, 4404 (1986); k) Y. Kubo, S. Togawa, K. Yamane, A. Takuwa, and T. Araki, *ibid.*, **54**, 4929 (1989).

3) C. A. Hunter, J. K. M. Sanders, G. S. Beddard, and S. Evans, *J. Chem. Soc., Chem. Commun.*, **1989**, 1765.

4) P. H. Mazzocchi, L. Klingler, M. Edwards, P. Wilson, and D. Shook, *Tetrahedron Lett.*, **1983**, 143; P. H. Mazzocchi and L. Klingler, *J. Am. Chem. Soc.*, **106**, 7567 (1984).

5) H. Meyer and K. Steiner, *Monatsh. Chem.*, **35**, 391, (1914).