

PHOTOCYCLOADDITION REACTIONS OF TRICYCLO[3.3.1.0^{2,8}]NONA-3,6-DIEN-9-ONE
(BARBARALONE) AND CARBONYL COMPOUNDS

Tsutomu Miyashi,* Akinori Konno, Yasutake Takahashi
Atsuko Kaneko, Takanori Suzuki, and Toshio Mukai†

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

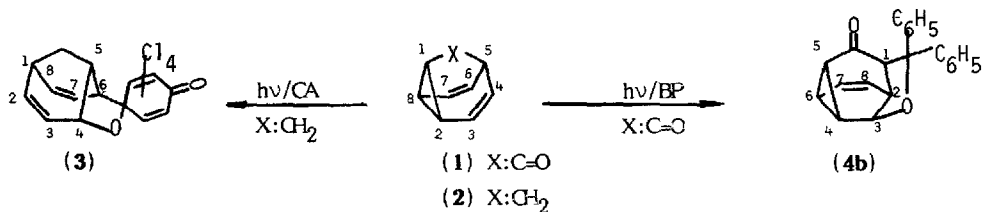
Noboru Koga†† and Hiizu Iwamura††

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Summary: Barbaralone undergoes two types of cycloadditions with photoexcited p-chloranil, p-bromanil, and p-fluoranil at the C₁-C₃ and C₄-C₆ positions possibly through a locally excited triplet exciplex and an ion radical pair, respectively.

Tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-one (barbaralone) (1) and tricyclo[3.3.1.0^{2,8}]nona-3,6-diene (barbaralane) (2), well known fluxional molecules,¹ are known to undergo cycloadditions either thermally with electron deficient dienophiles or photochemically with carbonyl compounds. The homo-Diels-Alder reaction with tetracyanoethylene is a typical ground state process.² In contrast, the photochemical cycloadditions of (1) and (2) with the carbonyl group are diverse depending upon carbonyl compounds. For example, the irradiation of benzophenone (BP) with (1) gave rise to (4b),³ whereas the p-chloranil (CA)-sensitized reaction of (2) was proposed to undergo the [6+2]cycloaddition leading to (3) though (3) eluded isolation.⁴

Scheme 1.



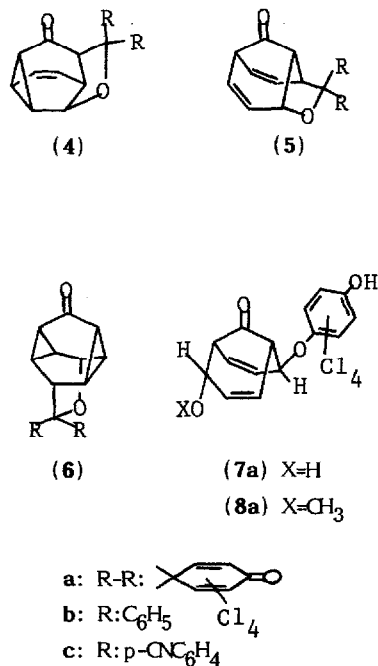
The former cycloaddition was formally accounted for by the addition of ³BP* to the C₁-C₃ (or C₃-C₅) carbons of (1).³ The latter, on the other hand, was explained by an electron-transfer mechanism on the basis of CIDNP effects observed during irradiation of CA with (2).⁴ In order to clarify a mechanistic connection between two different photoaddition types, we investigated the photoreactions of (1) and CA, BP and 4,4'-dicyanobenzophenone (DCNBP).

The irradiation ($\lambda > 330\text{-nm}$)⁵ of CA with (1) ($E_{1/2}^{\text{ox}} = +1.65\text{ V vs. s.c.e.}$)⁵ in benzene, 1,2,4-trichlorobenzene or dichloromethane afforded two adducts (4a) (m.p. 231-239°C)⁶ and (5a) (m.p. 240°C)⁶ in yields shown in Table 1. Similar results were obtained for the p-bromanil-(1) and p-fluoranil-(1) systems.⁷ In contrast, upon irradiation in the more polar anhydrous

acetonitrile or acetone did not give any photoadduct though both CA and (1) were consumed. Interestingly, the irradiation ($\lambda > 350$ -nm) in aqueous acetonitrile or acetone gave rise to the composite adduct (7a) (m.p. 202-205°C)⁶ instead of (4a) and (5a). Similarly, (8a) (m.p. 186-189°C)⁶ was isolated upon irradiation in dichloromethane, acetonitrile or acetone in the presence of methanol. Because neither (7a) nor (8a) was derived from (5a) upon irradiation under similar conditions, (7a) and (8a) are not the secondary product from (5a). The similarity in ¹H n.m.r. spectra between (7a) and (8a) and X-ray analysis of (8a) shown in Fig. 1 unequivocally determined their structures. The photoreaction ($\lambda > 330$ -nm) of (1) with BP gave the previously known adduct (4b)³ and two adducts (4c) (m.p. 205°C)⁶ and (6c) (m.p. 250°C)⁶ were isolated in 50% and 11% yields, respectively, upon irradiation of DCNBP with (1) in dichloromethane.

Table 1. Photoreactions of (1) and Carbonyl Compounds and Observed Triplet Quenching Rate Constants

| solvent | | yields | | | | | k_q $M^{-1}s^{-1}$ |
|--|--|--------|-----|-----|-----|-----|-------------------------|
| | | (4) | (5) | (6) | (7) | (8) | |
| | | % | | | | | |
| CA | C ₆ H ₆ | 19 | 6 | - | | | 1.3×10^9 |
| | 1,2,4-Cl ₃ C ₆ H ₃ | 29 | 10 | - | | | 1.5×10^9 |
| | CH ₂ Cl ₂ | 9 | 7 | - | | | 4.7×10^9 |
| | CH ₃ CN | - | - | - | | | 4.0×10^9 |
| | C ₆ H ₆ -CH ₃ CH(10%) | - | - | - | | 24 | |
| | CH ₂ Cl ₂ -CH ₃ CH(10%) | - | - | - | | 31 | |
| | CH ₃ CN-CH ₃ CH(10%) | - | - | - | | 35 | |
| | CH ₃ CN-H ₂ O(10%) | - | - | - | | 45 | |
| (CH ₃) ₂ CO-H ₂ O(10%) | - | - | - | | 25 | | |
| BP | C ₆ H ₆ | 51 | | | | | |
| | CH ₂ Cl ₂ | 31 | - | - | | | 1.1×10^8 |
| | CH ₃ CN | 67 | | | | | 1.9×10^8 |
| DCNBP | C ₆ H ₆ | 58 | - | 7 | | | |
| | CH ₂ Cl ₂ | 50 | - | 11 | | | 7.1×10^8 |
| | CH ₃ CN | 36 | - | 8 | | | 1.4×10^9 |



An intriguing facet is that two adduct types, (4) and (6) are different from the other three adduct types, (5), (7) and (8) with respect to the position of the carbon bearing the carbonyl oxygen. The carbonyl oxygen of CA with high reduction potential ($E_{1/2}^{red} = +0.01V$ vs. s.c.e.)⁸ attacks both the C₃ and C₄ of (1), while those of BP and DCNBP with low reduction potentials ($E_{1/2}^{red} = -1.77$ and -1.17 V vs. s.c.e, respectively)⁹ attack only the C₃.

Laser flash photolysis by using XeF excimer laser ($\lambda_{ex} = 351$ -nm) further gained insights into the initial quenching process for ³CA*, ³BP* and ³DCNBP* whose absorption maxima appeared at 510, 520 and 580-nm,¹⁰ respectively. As a transient anion radical species, CA⁻ ($\lambda = 450$ -nm)¹¹ was detected only in acetonitrile. As shown in Table 1, the k_q value for CA are nearly diffusion controlled limit, while the k_q value for BP are much larger than those expected for an electron-transfer. Similar trend has been observed in the case of ³BP* quenching by electron rich alkenes.¹² However, the k_q values for CA do not significantly depend on the solvent polarity. Those observations suggest that a full electron-transfer is not a

primary process for CA in solvent less polar than acetonitrile and that the exciplex formations are feasible for BP and DCNBP.

Combining those results, a plausible mechanism is shown in Scheme 2, in which two different processes stem from the initially formed locally excited triplet exciplexes.¹³ As a biradical process, the most electron rich C₃ carbon of (1) is attacked by ³CA*, ³BP* or ³DCNBP* to form biradicals (11) and (12). Those two biradicals further rearrange to the more stable (13) and (14), respectively, which, in turn, cyclize to form (4a)-(4c) and (6c). This process thus occur for CA, BP and DCNBP regardless of their reduction potentials. On the other hand, charge separation would occur to generate contact ion pair [1^{•+}/CA^{•-}] for CA, but not for BP and DCNBP. Evidence that (5a) was not formed in the polar acetonitrile where CA^{•-} was detected supports that (5a) is formed prior to dissociation of [1^{•+}/CA^{•-}]. In support of an electron transfer process through [1^{•+}/CA^{•-}] are the structure of the recently uncovered novel bis-homoaromatic cation radical (1^{•+})⁴ in which the charge and spin density localize at four corner carbons and the nucleophilic captures of [1^{•+}/CA^{•-}] by water and methanol. The additions of the carbonyl of CA and nucleophiles, thus, occur at corner carbons, affording (5a) and radical pairs (15). The successive recombinations¹⁴ of (15) can afford (7a) or (8a).

Scheme 2.

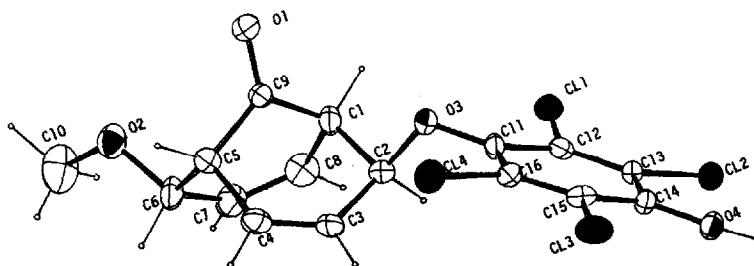
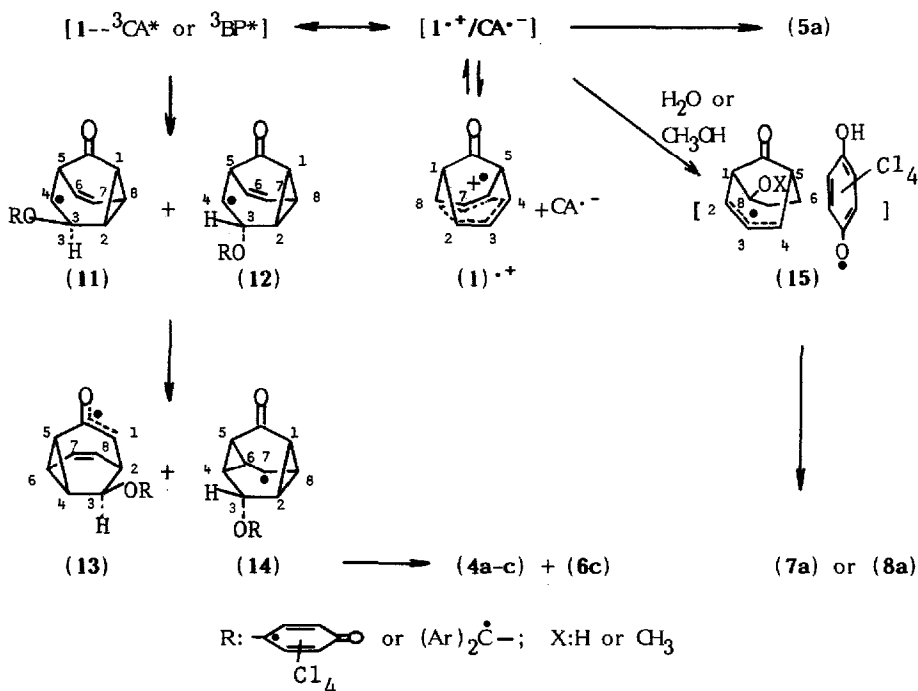


Fig. 1. Ortep Drawing of (8a)

Current Address: †, College of Engineering, Nihon University, Kohriyama 963, Japan; ‡, Department of Chemistry, Faculty of Science, University of Tokyo, Tokyo 113, Japan

References and Notes

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- 5) The solution was irradiated with light from a 2-kW xenon lamp through a Toshiba UV-35 cutoff filter. Half-wave oxidation potentials were measured by cyclic voltammetry at a platinum electrode in CH_3CN with 0.1M tetraethylammonium perchlorate as a supporting electrolyte.
- 6) Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds in this report. ^1H n.m.r of (**4a**), (**5a**), (**6c**), (**7a**) and (**8a**) are described here. (**4a**) (200 MHz, CDCl_3), δ 3.07 (d, $J=4.3$ Hz), 4.04 (dddd, $J=7.2, 5.9, 4.3, 1.9$ Hz), 4.98 (dd, $J=5.9, 3.9$ Hz), 2.35 (dd, $J=3.9, 1.9$ Hz), 2.44-2.47 (m), 6.26 (d, $J=9.0$ Hz), 5.72 (dd, $J=9.0, 7.2$ Hz). (**5a**) (200 MHz, CDCl_3), δ 3.38 (ddd, $J=6.8, 6.4, 2.2$ Hz), 6.31 (dd, $J=9.3, 6.4$ Hz), 6.11 (dd, $J=9.3, 3.8$ Hz), 5.41 (dd, $J=8.3, 3.8$ Hz), 4.06 (ddd, $J=8.5, 8.3, 2.2$ Hz), 3.72 (ddd, $J=8.5, 4.4, 1.8$ Hz), 5.47 (dd, $J=9.3, 4.4$ Hz), 6.23 (ddd, $J=9.3, 6.8, 1.8$ Hz). (**6c**) (90 MHz, CDCl_3), δ 1.59 (2H, m), 1.66-2.17 (4H, m), 3.74 (dd, $J=5.0$ Hz), 5.06 (dd, $J=6.0$ Hz), 7.63 (4H, m), 7.77 (4H, m). (**7a**) (200 MHz, $\text{DMSO}-d_6$), δ 2.98 (dd, $J=5.5, 1.6$ Hz), 3.26 (dd, $J=4.8, 1.9$ Hz), 4.46 (br. s), 4.49 (dd, $J=4.1, 1.6$ Hz), 5.03 (dd, $J=4.5, 1.9$ Hz), 5.75 (dd, $J=9.3, 4.1$ Hz), 5.79 (dd, $J=9.7, 4.5$ Hz), 5.94 (dd, $J=9.3, 4.8$ Hz), 6.20 (dd, $J=9.7, 5.5$ Hz), 9.46 (br. s). (**8a**) (400 MHz, CDCl_3), δ 3.32 (dddddd, $J=5.5, 2.0, 1.0, 1.0, 1.0$ Hz), 3.41 (s), 3.46 (dddddd, $J=5.5, 2.0, 1.0, 1.0, 1.0$ Hz), 4.17 (dd, $J=4.2, 2.0$ Hz), 5.02 (dd, $J=4.4, 2.0$ Hz), 5.84 (dddd, $J=9.5, 4.2, 1.0, 1.0$ Hz), 5.88 (dddd, $J=9.5, 4.4, 1.0, 1.0$ Hz), 5.98 (br.s), 6.01 (dd, $J=9.5, 5.5$ Hz), 6.11 (dd, $J=9.5, 5.5$ Hz).
- 7) Upon irradiation in dichloromethane, the (4)- and (5)-type adducts were isolated in 10% and 7% yields, respectively, for p-bromanil and 21% and 8% yields, respectively, for p-fluoranil.
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- 14) The close similarity in ^1H n.m.r. spectra between (**7a**) and (**3**)⁴ suggests an alternative (**7a**)-type composite adduct structure instead of (**3**) for the photoadduct of (**2**) and CA. The reported CIDNP polarization patterns⁴ observed during irradiation of CA with (**2**) in acetone- d_6 then seem to be accounted for by a mechanism through a radical pair similar to (**15**).

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