and 500 mL of trifluoroacetic acid. The solution was saturated with chlorine and irradiated for 21 h at which time NMR analysis showed a 98/2 ratio of **5b** to **4b**. Evaporation of the solvent at reduced pressure provided 1.950 g of beige solid, which failed to show a sharp melting point. No convenient method was found that would allow purification for analysis, and the entire sample was therefore converted to the diester **5d** by reaction with oxalyl chloride followed by methanol. The yield of **5d** was 67%, based on unreacted starting material at 71% conversion: mp 42.0–42.5 °C; ^{1}H NMR δ 2.48 (s, 2 H), 3.01 (s, 2 H), 3.81 (s, 6 H); ^{13}C NMR δ 49.60, 52.35, 52.80, 91.40, 164.86; IR (CS_2) 864, 1063, 1204, 1302, 1744 (C=O) cm^{-1}; EIMS m/z 224 (0.8, M − MeOH), 222 (4.6, M − MeOH), 220 (7.1, M − MeOH), 196 (2.7, M − COOMe), 194 (14.6, M − COOMe), 192 (23.3, M − COOMe), 99 (34), 73 (33), 59 (100). Anal. Calcd for $C_9H_{10}Cl_2O_4$: C, 42.70; H, 3.95; Cl, 28.04. Found: C, 42.76; H, 3.95; Cl, 27.99.

Chlorination of 1,3-Bis(chlorocarbonyl)bicyclo[1.1.1]pentane (4c). The chlorination of **4c** was conducted in the same manner as that of **4b**. The crude yield was nearly quantitative. Due to instability at VPC conditions no analytical sample could be obtained, although ^{1}H NMR analysis of crude material showed complete conversion to an 80/20 mixture of **5c** and an unidentified impurity with vinylic-type resonances. The crude mixture was therefore converted directly to the diester **5d** by the addition of absolute methanol and provided material identical with that described above.

Chlorination of Dimethyl Bicyclo[1.1.1]pentane-1,3-dicarboxylate (4d). Upon chlorination in the manner described above for **4a**, complete loss of the methyl groups was noted by ^{1}H NMR analysis. The crude mixture was hydrolyzed immediately, and the acidic product was isolated by removal of the solvent at reduced pressure. The diacid **5b** was isolated in 55% yield. The structure was established by esterification using oxalyl chloride followed by methanol, which gave material identical with **5d**.

Chlorination of Bicyclo[1.1.1]pentane-1-carboxylic Acid (4e). The acid **4e** (0.357 g) was chlorinated as above in carbon tetrachloride solvent saturated with chlorine. A white solid (0.488 g) was isolated and immediately converted to the methyl ester **5f** with oxalyl chloride followed by methanol. This produced 0.298 g of crude material, 44% of which was shown to be **5f**. The overall yield of **5f** isolated by VPC was 22%. No impurities were detected by VPC on SE-30. A second experiment on a 0.524-g scale led to a 35% yield of VPC-purified material: ^{1}H NMR δ 2.23 (br s, 2 H), 2.81 (br s, 2 H), 3.12 (s, 1 H), 3.81 (s, 3 H); ^{13}C NMR δ 46.07, 47.57, 52.04, 56.98, 92.00, 165.18; IR (neat film) 859, 1155, 1209, 1343, 1725, 1743 cm^{-1}; EIMS m/z 161 (7, M − Cl), 159 (20.5, M − Cl), 127 (10), 101 (30), 99 (81), 73 (35), 59 (100). Anal. Calcd for $C_7H_8Cl_2O_2$: C, 43.09; H, 4.10; Cl, 36.37. Found: C, 43.15; H, 4.08; Cl, 36.25.

Reduction of 5d with Tri-*n*-butyltin Hydride. Into a 25-mL round-bottom flask were placed 500 mg of **5d**, 690 mg of tri-*n*-butyltin hydride, and 15 mL of benzene, which was freshly distilled from sodium. A small amount of AIBN was added, and the mixture was refluxed under an argon atmosphere for 2 h. The solvent was evaporated, and the residue was dissolved in diethyl ether and an equal volume of excess aqueous potassium fluoride. Over a period of 2 days further portions of KF were added to the stirred solution. The layers were separated, and the resulting white powder was carefully sublimed (60 °C, 26 Torr) and recrystallized from hexanes at −78 °C to give 101 mg (23%) of an analytically pure sample: mp 40–40.5 °C; ^{1}H NMR δ 2.16 (dd, J_1 = 10 Hz, J_2 = 3 Hz, 1 H), 2.39 (dd, J_1 = 7 Hz, J_2 = 3 Hz, 1 H), 2.58 (d, J = 3 Hz, 1 H), 3.11 (dd, J_1 = 10 Hz, J_2 = 3 Hz, 1 H), 3.72 (s, 6 H), 4.51 (d, J = 7 Hz, 1 H); ^{13}C NMR δ 43.99, 48.16, 48.70, 52.08, 70.46, 166.77; IR (CS_2) 787, 813, 1207, 1299, 1742 cm^{-1}; EIMS m/z 183 (10, M − Cl), 160 (7.6, M − COOMe), 158 (23.4, M − COOMe), 100 (16), 95 (33), 65 (75), 59 (100). Anal. Calcd for $C_7H_8ClO_2$: C, 49.44; H, 5.07; Cl, 16.22. Found: C, 49.52; H, 5.09; Cl, 16.31.

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Registry No. **4a**, 82783-71-9; **4b**, 56842-95-6; **4c**, 115913-31-0; **4d**, 115913-32-1; **4e**, 22287-28-1; **5a**, 119327-49-0; **5b**, 119327-50-3; **5c**, 119327-51-4; **5d**, 115913-32-1; **5f**, 106813-54-1; **6**, 119327-52-5.

Electron-Transfer-Induced Rearrangements of Phenylated Tricyclo[4.2.0.0^{2,5}]octane and 1,5-Cyclooctadiene

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The hitherto unknown examples of cation radical isomerizations of tricyclo[4.2.0.0^{2,5}]octane and 1,5-cyclooctadiene derivatives are reported. Photoreaction of 1,2,5,6-tetraphenyltricyclo[4.2.0.0^{2,5}]octane (**1**) with 9,10-dicyanoanthracene (DCA) afforded 1,2,5,6-tetraphenyl-1,5-cyclooctadiene (**2**) and 1,2,5,6-tetraphenyltricyclo[3.3.0.0^{2,6}]octane (**3**). Upon a similar irradiation, **2** was converted to **3**. Likewise, other electron acceptors, such as tetracyanoethylene (TCNE), 1,2,4,5-tetracyanobenzene (TCNB), and tris(*p*-bromophenyl)aminium hexachloroantimonate, catalyzed these reactions. Quenching experiments using 1,2,4,5-tetramethoxybenzene (TMB) and naphthalene (NAP) supported the occurrence of cation radical isomerizations among **1**, **2**, and **3**.

Recently organic photoinduced electron-transfer chemistry has provided many interesting examples of ion radical reactions in solution that are comparable to redox reactions induced by electrochemical methods or chemical reagents.[4] Cyanoaromatics, quinones, and some cationic salts, such as pyrylium and iminium salts, are known to serve as electron-accepting sensitizers.[4] Single electron transfer

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(3) Author to whom correspondence should be addressed regarding X-ray data.

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(SET) from ground-state electron donor to excited-state sensitizer affords a pair of cation radical of donor and anion radical of sensitizer. Cation radicals formed undergo chemical processes as described by eq 1–4.[4] One of the

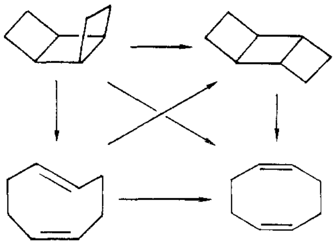
$$D^{\bullet+}\text{—}E \rightarrow D^{\bullet} + E^{+} \text{ fragmentation} \quad (1)$$

$$D^{\bullet+} + N{:} \rightarrow D^{\bullet}\text{—}N \text{ nucleophile addition} \quad (2)$$

$$D^{\bullet+} + O_2 \rightarrow D^{+}\text{—}O\text{—}O^{\bullet} \text{ oxygen addition} \quad (3)$$

$$D^{\bullet+} \rightarrow P^{\bullet+} \text{ rearrangement} \quad (4)$$

recent topics in cation radical chemistry is a pericyclic reaction of organic cation radicals that have been studied by Bauld[5] and others.[6,7] The photoinduced electron-transfer process is an effective means to investigate such chemical reaction. Thus, we have studied the photoinduced electron-transfer reactions of tricyclo[4.2.0.0^{2,5}]octane and 1,5-cyclooctadiene derivatives. Thermally induced isomerizations of tricyclo[4.2.0.0^{2,5}]octane and 1,5-cyclooctadiene investigated by Martin and co-workers demonstrated that tricyclo[4.2.0.0^{2,5}]octane rearranges to 1,5-cyclooctadiene through a process involving sequential conformational change and bond fission of the bicyclo[4.2.0]octane 1,4-diradical.[8] In contrast, the chemical behavior of the corresponding cation radical species has not been investigated in detail.[9] We report herein the first example of the cation radical valence isomerizations among phenylated tricyclo[4.2.0.0^{2,5}]octane 1, 1,5-cyclooctadiene 2, and tricyclo[3.3.0.0^{2,6}]octane 3.



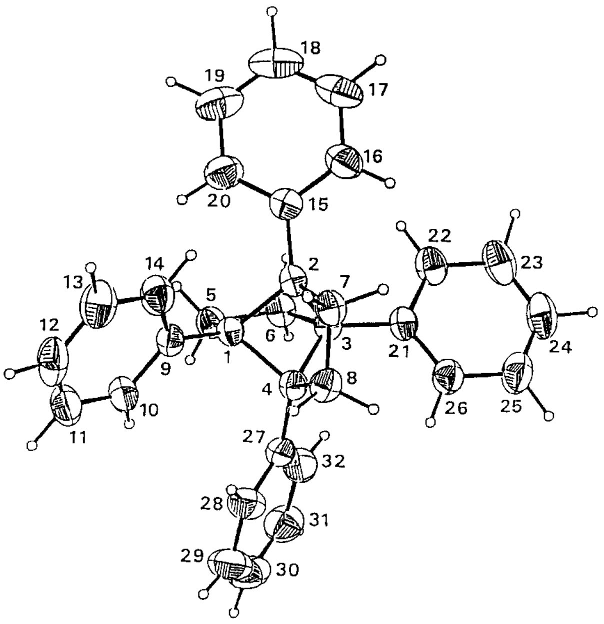
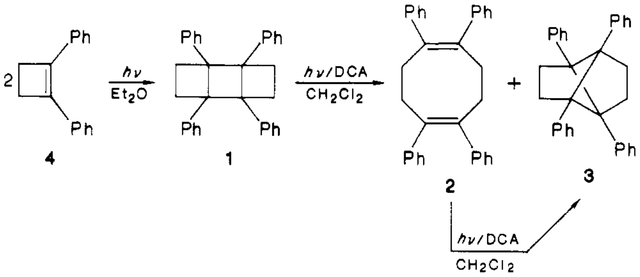


Figure 1. Molecular structure of 3. Selected bond distances (Å): C(1)–C(2), 1.577 (2); C(1)–C(4), 1.606 (2); C(1)–C(9), 1.505 (2); C(2)–C(7), 1.540 (2); C(4)–C(8), 1.530 (2); C(7)–C(8), 1.525 (3). Selected bond angles (deg): C(2)–C(1)–C(7), 82.5 (1); C(1)–C(2)–C(7), 104.8 (1); C(1)–C(4)–C(8), 102.1 (1); C(2)–C(7)–C(8), 100.7 (1); C(4)–C(8)–C(7), 100.6 (1).

Results and Discussion

Phenylated tricyclo[4.2.0.0^{2,5}]octane 1 was prepared by the photoreaction of 1,2-diphenylcyclobutene (4).[10] Irradiation of 4 in ether afforded 1 in moderate yields (50–60%). Upon irradiation of a methylene chloride solution of 1 in the presence of 9,10-dicyanoanthracene (DCA), 1,5-cyclooctadiene 2 and tricyclo[3.3.0.0^{2,6}]octane 3 were obtained along with recovered 1. DCA-sensitized photoreaction of 2 resulted in formation of 3. The structure of 2 was confirmed by comparing its spectroscopic data with those of the product obtained by pyrolysis of 1.[10a]



The structure of 3 could not be resolved by spectroscopic data but was finally elucidated by X-ray crystalographic

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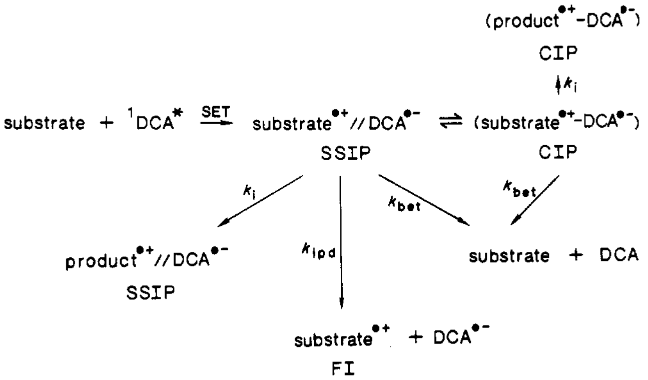
Scheme I



analysis (Figure 1).[11] It is interesting to note that the C–C bond distances of the central four-membered ring are significantly longer than those in normal C–C single bonds.[12] This may be due to the strained structure, which requires the least steric repulsion of the four bulky phenyl groupings. This is supported by a comparison of the bond distances and bond angles of **3** with those of unsubstituted tricyclo[3.3.0.0^{2,6}]octane.[13] Preparations of tricyclo[3.3.0.0^{2,6}]octane derivatives have been reported in a few cases[14] since Srinivasan first synthesized a parent compound by irradiation of 1,5-cyclooctadiene.[15] However, in most of the cases, the yields were relatively low.[14] In this sense, it would be noteworthy that **3** was obtained from **2** in reasonably high yield via a cation radical species.

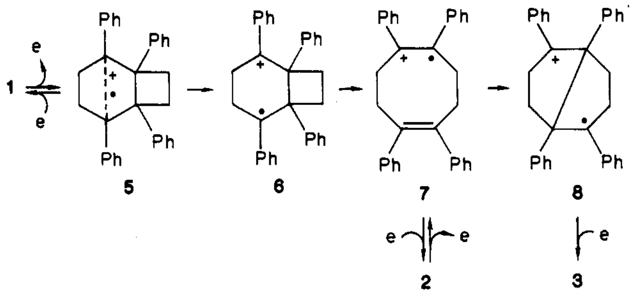
One can anticipate that the primary process which occurs between **1** and singlet excited state of DCA (^{1}DCA*) is SET to generate the cation radical of **1** ($\mathbf{1}^{\bullet+}$) and the anion radical of DCA ($\mathrm{DCA}^{\bullet-}$). In support of this concept, the free energy change (ΔG) for the SET process was calculated by employing the Rehm–Weller equation.[16] In the case of **1** and DCA, the calculated ΔG in methylene chloride was −3.1 kcal/mol. Similar calculation gave −12.3 kcal/mol for ΔG of the SET process between **2** and ^{1}DCA*. These results suggest that SET processes from **1** or **2** to ^{1}DCA* are exothermic ones. Indeed, both **1** and **2** quenched the fluorescence of DCA efficiently ($k_q = 5.03 \times 10^9$ M^{-1} s^{-1} for **1** and $k_q = 1.65 \times 10^{10}$ M^{-1} s^{-1} for **2**).[20]

Table I. DCA-Sensitized Photoreactions of 1 and 2[a]

			yield,[b] %		
expt no.	startg matl	10^2[addtve], M	**1**	**2**	**3**
1	**1**		54	9	15
2	**1**	TMB, 2.54	86	7	0
3	**1**	NAP, 4.80	10	0	70
4	**2**			70	24
5	**2**[c]	TMB, 2.47		100	0
6	**2**	NAP, 12.2		68	30
7	**2**[d]			83	14
8	**2**[d]	NAP, 7.59		51	35

[a] A methylene chloride solution was irradiated for 3 h for **1** and for 5 min for **2** ([**1**] = [**2**] = 2.48×10^{-2} M, [DCA] = 7.45×10^{-4} M). [b] Determined by ^{1}H NMR. [c] Irradiation time was 3 h. [d] [**2**] = 3.67×10^{-3} M.

Scheme II



Since the reactions (**1** → **2**, **2** → **3**) did not occur without DCA and in the dark, neither direct excitations of the substrates nor interactions with DCA in their ground states would be important in the formation of the observed products. The SET mechanism between **1** or **2** and ^{1}DCA* is consistent with above results.

An SET process from **1** or **2** to ^{1}DCA* first gives a solvent–separated ion pair (SSIP) in which the cation radical of those substrates undergoes rearrangement to the cation radical of the other isomers, in competition with back electron transfer (BET) and with ion pair dissociation to give free ions (FI) (Scheme I). Also, SSIP rapidly attains equilibrium with a contact ion pair (CIP). Rates of BET (k_{bet}) and ion pair dissociation (k_{ipd}) are dependent on the energy of the ion pair formed and the surrounding medium.[21] On the other hand, the efficiency of isomerization (k_i) depends on the nature of the cation radical itself rather than the ion pair stage. This means that more reactive cation radical ($k_i > k_{\mathrm{ipd}}$) isomerizes to a product cation radical in SSIP and/or CIP rather than in FI, while a less reactive cation radical ($k_i < k_{\mathrm{ipd}}$) results in product cation radical formation mostly in FI. Thus, addition of other donors to these systems would change product distributions depending on the ion pair stage. Highly electron donating substances are known to quench cation radical species at the FI stage better than at the SSIP and CIP stages.[21b,22] To gain insights into this point, quenching experiments were carried out with 1,2,4,5-tetramethoxybenzene (TMB) and naphthalene (NAP). The results are summarized in Table I. Addition of TMB clearly depressed the conversions of **1** and **2** (expt 2 and 5). Since TMB ($E_{1/2}^{\mathrm{ox}}$ = +0.81 V vs SCE)[23] is a stronger electron

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(11) Crystal data: space group *Pbca*, a = 21.299 (2) Å, b = 17.449 (2) Å, c = 12.488 (1) Å, Z = 8, d_{calcd} = 1.18 g cm^{-3}, 2402 unique reflections with $I > 3\sigma(I)$ were collected on an Enraf-Nonius CAD 4 diffractometer with use of Cu Kα (1.5418 Å) radiation. The structure was solved by direct methods (MULTAN 11/82: Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN 11/82, A System of Computer Program for the Automatic Solutions of Crystal Structures from X-ray Diffraction Data*, Univs. of York and Louvain, 1982) and refined by full-matrix least squares to final R = 0.035 and R_w = 0.046. Tables of positional and thermal parameters are available as supplementary material.

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(17) Halfwave oxidation potentials ($E_{1/2}^{\mathrm{ox}}$(V) vs SCE) were obtained by cyclic voltummetry (Pt electrode, scan rate 100 mV/s) in acetonitrile containing 0.1 M tetraethylammonium perchlorate, which showed irreversible oxidation processes: $E_{1/2}^{\mathrm{ox}}$ = +1.75 V for **1**; $E_{1/2}^{\mathrm{ox}}$ = +1.35 V for **2**; $E_{1/2}^{\mathrm{ox}}$ = +1.77 V for **3**.

(18) Chandros, E. A.; Ferguson, J. *J. Phys. Chem.* **1967**, *47*, 2557: $E_{1/2}^{\mathrm{red}}$ = −0.82 V vs SCE for 9,10-dicyanoanthracene.

(19) Singlet energy was estimated to be 66 kcal/mol from the absorption and the fluorescence spectra of 9,10-dicyanoanthracene.

(20) The quenching rate constant (k_q) was calculated from $k_q\tau$ and the singlet lifetime (τ = 11.7 ns) of 9,10-dicyanoanthracene in methylene chloride (Barber, R. A.; de Mayo, P.; Okada, K.; Wong, S. L. *J. Am. Chem. Soc.* **1982**, *104*, 4995).

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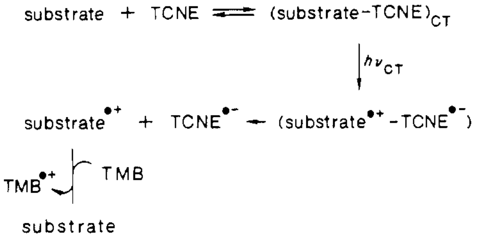
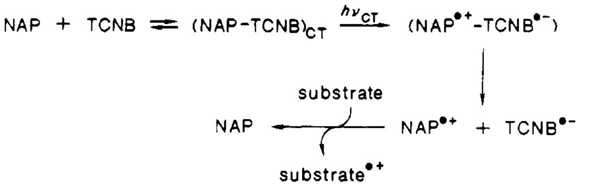
Scheme III



donor than both 1 and 2, TMB could quench not only ^{1}DCA* ($k_q = 2.12 \times 10^{10}$ M^{-1} s^{-1})[20] but also cation radicals of 1 and 2 by exothermic SET. By contrast, NAP, which has an oxidation potential ($E_{1/2}{}^{ox} = +1.65$ V vs SCE)[17] close to that of 1, accelerated the isomerization of 1 (expt 3). At low concentration of 2 where about 42% of ^{1}DCA* could be quenched by 2, the acceleration of the reaction by NAP is more obvious than at high concentration of 2 (compare expt 4 with expt 6 and compare expt 7 with expt 8).[24] NAP$^{\bullet+}$ formed by SET from NAP to ^{1}DCA* ($k_q = 8.80 \times 10^9$ M^{-1} s^{-1})[20] could oxidize 1 and 2 by SET resulting in formation of their cation radicals.[25] All these observations are consistent with the cation radical isomerizations illustrated in Scheme II.[26]

After SET from 1 to ^{1}DCA*, the initially formed cation radical 5 undergoes a facile bond fission to give the bicyclo[4.2.0]octane 1,4-cation radical 6. Recent investigations of the cation radical olefin-cyclobutane conversions suggest that the reactions proceed more favorably via 1,4-cation radical intermediates than by a concerted mechanism.[6a–c] The cation radical 6 then isomerizes to the 1,5-cyclooctadiene cation radical 7 which can be also obtained from 2 by SET to ^{1}DCA*. Subsequently, 7 would rearrange to the bicyclo[3.3.0]octane 1,5-cation radical 8 by transannular interaction. The cation radical isomerization of 1 to 2 must be faster than that of 2 to 3 since strain release is a driving force for the former process,[27] while the latter one requires some conformational change and bond-forming steps. In other words, the lifetime of 5 would be shorter than that of 7. Thus, 7 may have a chance to escape from a solvent cage competing with BET from DCA$^{\bullet-}$. If these assumptions are correct, the formation of 3 could be influenced more than that of 2 by addition of TMB since the formation of 7 would be expected more than that of 5 in FI. Indeed, isomerization of 2 to 3 was completely quenched by TMB. Similarly, TMB quenched the formation of 3 but not that of 2 in the DCA-sensitized photoreaction of 1. These results suggest that rapid bond cleavage in 5 could compete with dissociation of the ion pair and BET from DCA$^{\bullet-}$ to 5.[28]

Scheme IV



Further information about the cation radical isomerization was obtained by irradiation of 1 or 2 with tetracyanoethylene (TCNE) or 1,2,4,5-tetracyanobenzene (TCNB). Solution of 1 or 2 with TCNE in methylene chloride showed charge-transfer (CT) absorption bands ($\lambda_{max} = 405$ nm, $\lambda_{sh} \simeq 500$ nm for 1; $\lambda_{max} = 400$ nm, $\lambda_{max} = 580$ nm for 2). Upon CT band irradiation of a methylene chloride solution of 1 and TCNE for 7 h, 2 (32%) was obtained along with 3 (4%) and recovered 1 (60%). Similar irradiation of 2 afforded 3 (9%) and recovered 2 (89%). These reactions did not take place in the dark. Addition of TMB completely quenched conversion of 2 to 3, whereas CT band irradiation of 1 and TCNE in the presence of TMB produced 2 (18%). Excitation of CT complexes that consist of TCNE and electron-donating compounds results in formation of CIP whose lifetimes are usually much shorter than those of CIP derived from cyanoaromatics and electron donors.[29] Thus, the yields of FI are thought to be lower in the former systems than those in the latter systems, which means that TMB quenching might be less efficient in the TCNE and donor systems (Scheme III). The above observations suggest that a small amount of 7 produced in FI is quenched by TMB in photoreaction of 2 and that isomerization of 5 occurs in short-lived CIP, which is relatively insensitive to TMB quenching in the photoreaction of 1. On the other hand, a methylene chloride solution of TCNB and 1 or 2 only showed a weak CT absorption. In fact, irradiation of TCNB and 1 for 2 h gave no products. However, addition of NAP, which showed a CT absorption band ($\lambda_{max} = 405$ nm), with TCNB to the solution of 1 and TCNB resulted in formation of 3 (53%). Similarly, a higher yield of 3 (89%) was obtained on irradiation of 2 and TCNB with NAP, while a smaller amount of 3 (31%) was formed without NAP. These results suggest that interaction of NAP$^{\bullet+}$ with 1 or 2 gives their cation radicals (Scheme IV). The predominant formation of 3 on addition of NAP to 1 and acceptor might be due to the endothermic SET from NAP to 7 ($\Delta G = +6.9$ kcal/mol).

The fact that NAP$^{\bullet+}$ catalyzed the reactions led us to treat 1 or 2 with other cationic catalysts. Tris(*p*-bromophenyl)aminium hexachloroantimonate[30] was effective for

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(23) Mann, C. K.; Barns, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1973; p 252.

(24) Similar catalytic effects for product formations were observed when other aromatic hydrocarbons such as phenanthrene and 1,2,4,5-tetramethylbenzene were added into the mixture of 1 and 9,10-dicyanoanthracene.

(25) (a) Farid, S.; Hartman, S. E.; Evans, T. R. *The Exciplex*; Academic Press: New York, 1975; p 327. (b) Steichen, D. S.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1885. (c) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *Ibid.* **1983**, *105*, 633. (d) Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *Ibid.* **1983**, *105*, 5149.

(26) Trapping experiments of proposed cation radical intermediates by addition of molecular oxygen or methanol were not successful. This might be due to their short lifetimes and/or their bulky tetra substitutents. Therefore, the cation radicals 5–8 represented in Scheme II are hypothetical ones. Anodic oxidation of 1,5-cyclooctadiene in nucleophilic medium affords several products, which suggest the involvements of 1,5-cyclooctadiene 1,2-cation radical and bicyclo[3.3.0]octane 1,5-cation radical.[9b] Thus, the cation radical 7 and 8 could be plausible as intermediates. The structures of 5 and 6 are pure speculations. Cation radical 5 is a cyclobutane cation radical possessing long bond structure (Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145) which returns to 1 via back electron transfer from DCA$^{\bullet-}$. Direct conversion of 1$^{\bullet+}$ to 7, which a reviewer indicated, may be an alternative mechanism.

(27) The strain energy of tricyclo[4.2.0.0^{2,5}]octane calculated by molecular mechanics is at least about 30 kcal/mol greater than those of other policyclic isomers (Engler, E. M.; Andose, J. D.; Schleyer, P. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005).

(28) Another issue to be considered is the involvement of chain mechanism, which a reviewer indicated. Considering the oxidation potentials of 1, 2, and 3,[17] an efficient propagation step may be possible for the conversion of 2 to 3 rather than that of 1 to 2 if a chain process is involved in the reaction courses. The results of TMB quenching experiments seem to be inconsistent with this interpretation. To solve this problem, it should be concluded that the rate of the conversion of 1$^{\bullet+}$ to 2$^{\bullet+}$ is faster than that of 2$^{\bullet+}$ to 3$^{\bullet+}$.

(29) (a) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167. (b) Itoh, M.; Kumano, Y.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 42. (c) Itoh, M.; Furuya, S.; Okamoto, T. *Ibid.* **1977**, *50*, 2509.

(30) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719.

the isomerizations of 1 and 2.[31] When a methylene chloride solution of 1 was stirred with the aminium salt for 2 h, 2 (4%) and 3 (33%) were produced with recovered 1 (44%). Treatment of 2 with the aminium salt for 1 h resulted in formation of 3 (93%). The difference in the reaction efficiencies between 1 and 2 can be rationalized in terms of their electron-donating abilities. Interestingly enough, the conversion of 1 as well as that of 2 was completely supressed by addition of TMB. This means that TMB$^{\bullet+}$ formed by exothermic SET with the aminium salt (ΔG = −5.5 kcal/mol)[32] did not produce $1^{\bullet+}$ and $2^{\bullet+}$. Therefore, an appreciable formation of 2 in the photoreaction of 1 in the presence of TMB would be attributed to incomplete interception of SSIP and/or CIP of an acceptor anion radical and $1^{\bullet+}$ by TMB, but not to interaction of 1 with initially formed TMB$^{\bullet+}$.

The observations described above show that the phenylated tricyclo[4.2.0.0^{2,5}]octane 1 isomerizes to 1,5-cyclooctadiene 2 with even lower activation energy in the cation radical species than in the neutral one. This reaction would be driven by cleavage of the strained central bond of 1, which is further weakened by possessing cation radical nature.[33] The cation radical of 2 undergoes cross-cycloaddition to give tricyclo[3.3.0.0^{2,6}]octane 3. Although this type of reaction of 1,5-cyclooctadiene has been seen under several photochemical conditions,[14,34] so far no example that proceeds via SET mechanism has been reported. Therefore, it should be stressed that 2 isomerizes to 3 in a high yield by the cation radical mechanism.[35,36]

Experimental Section

General. ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer. ^{13}C NMR spectra were obtained at 22.49 MHz on a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million downfield from Me_4Si as an internal standard. IR spectra were measured on a Shimadzu IR-27G spectrometer. UV spectra were obtained on a Hitachi 340 spectrometer. Mass spectra were recorded on a Hitachi M-52 mass spectrometer. Fluorescence spectra were measured on a Hitachi MPF-4 spectrophotometer. Redox potentials were determined by a Yanako P-1000 voltammetric analyzer. Preparative TLC was carried out on 20 cm × 20 cm plates coated with Merck 60PF$_{254}$ silica gel. Melting points were recorded on a Griffin Mel-Temp apparatus and reported uncorrected. Methylene chloride for photochemical studies was distilled over calcium hydride.

Preparation of 1,2-Diphenylcyclobutene (4).[37] To 20.5 mL (0.184 mol) of titanium tetrachloride was slowly added 500 mL of dry THF under an N_2 atmosphere. Then, 20.2 g (0.310 mol) of zinc powder and 20.5 mL (0.253 mol) of dry pyridine were added. The mixture was stirred at room temperature for 1 h followed by addition of 400 mL of dry THF containing 19.2 g (0.081 mol) of dibenzoylethane. After heating at 60 °C for 30 h, aqueous potassium carbonate (40 g in 200 mL) was added. After filtration, the solution obtained was extracted with ether. Extracted solution was washed with 1 M HCl, aqueous $NaHCO_3$, and aqueous NaCl and then dried over anhydrous Na_2SO_4. Concentration of the solution afforded 11.9 g (72%) of a colorless solid, which was recrystallized from MeOH: mp 51–52 °C (lit.[38] mp 51.5–52.5 °C).

Preparation of 1,2,5,6-Tetraphenyltricyclo[4.2.0.0^{2,5}]octane (1). An etheral solution (80 mL) containing 1.05 g (5.10 mmol) of 4 was irradiated with Pyrex-filtered light of Rayonet RUL 3000 Å on a RPR 204 photochemical reactor for 35 h. The solution was purged with N_2 before and during irradiation. Concentration of the photolysate gave the residue, which crystallized on addition of ether and ethanol. The colorless solid (652 mg, 63%) obtained was recrystallized from benzene–ethanol: mp 216–218 °C (lit.[10a] mp 222.5–223 °C). Spectroscopic data for 1: ^{1}H NMR ($CDCl_3$) 2.55 (s, 8 H), 7.20 (m, 20 H); ^{13}C NMR ($CDCl_3$) 30.94 (t), 57.18 (s), 125.72 (d), 127.75 (d), 143.22 (s); IR (KBr) 3030, 2970, 1599, 1493, 1445, 1172, 1020, 753, 695, 548 cm^{-1}; UV (C_6H_{12}) λ_{max} 231 nm (ϵ = 27 900), 257 (sh, 1320), 264 (1230), 270 (sh, 840), 274 (sh, 620); MS *m/e* (relative intensity) 412 (M$^+$, 100), 384 (32), 308 (76), 295 (52), 206 (44), 91 (30).

Anal. Calcd for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 93.14; H, 7.13.

Preparation of 1,2,5,6-Tetraphenyl-1,5-cyclooctadiene (2). A xylene (5 mL) solution of 217 mg (0.527 mmol) of 1 was heated at 150 °C for 24 h. Concentration of the resulted solution gave a crude solid of 2. This was recrystallized from benzene–ethanol: mp 219–221 °C (lit.[10a] mp 223–224 °C). Spectroscopic data for 2: ^{1}H NMR ($CDCl_3$) 2.97 (s, 8 H), 7.00 (s, 20 H); ^{13}C NMR ($CDCl_3$) 34.79 (t), 125.66 (d), 127.48 (d), 130.10 (d), 137.93 (s), 144.59 (s); IR (KBr) 3120, 2890, 1599, 1490, 1440, 749, 693, 510 cm^{-1}; UV (C_6H_{12}) λ_{max} 263 nm (ϵ = 15 850); MS *m/e* (relative intensity) 412 (M$^+$, 100), 384 (26), 308 (72), 295 (61), 206 (42), 91 (42), 18 (37).

Anal. Calcd for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 93.41; H, 7.04.

Preparation of 1,2,5,6-Tetraphenyltricyclo[3.3.0.0^{2,6}]octane (3). A mixture of 312 mg (0.514 mmol) of 2 and 8.5 mg (0.104 mmol) of tris(*p*-bromophenyl)aminium hexachloroantimonate in dry CH_2Cl_2 (25 mL) was stirred at room temperature for 3 h. The reaction was quenched by addition of 1,4-diazabicyclooctane. TLC separation (silica gel, *n*-hexane) gave 252 mg (81%) of 3. This was recrystallized from methylene chloride–ethanol: mp 253–253.5 °C. Spectroscopic data for 3: ^{1}H NMR ($CDCl_3$) 2.13 (s, 8 H), 7.25 (s, 20 H); ^{13}C NMR ($CDCl_3$) 28.98 (t), 64.17 (s), 126.44 (d), 127.75 (d), 128.40 (d), 139.17 (s); IR (KBr) 3060, 2970, 1603, 1499, 1451, 1303, 1027, 766, 700, 570, 510; UV (C_6H_{12}) λ_{max} 257 nm (ϵ = 1000), 263 (1080), 269 (740); MS *m/e* (relative intensity) 412 (M$^+$, 100), 384 (22), 308 (61), 295 (50), 206 (16), 91 (20), 18 (39).

Anal. Calcd for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 93.14; H, 7.02.

Fluorescence Quenching Experiments. Fluorescence quenching of 9,10-dicyanoanthracene was carried out by using methylene chloride solutions (6.1×10^{-5} M) at room temperature with excitation at 401 ± 1 nm. Fluorescence intensities were measured at five or more quencher concentrations. Slopes of Stern–Volmer plots were determined by least-square techniques and quenching rates were calculated from the known singlet lifetime of 9,10-dicyanoanthracene.[20]

9,10-Dicyanoanthracene-Sensitized Photoreactions. The general procedure was as follows. A methylene chloride solution of a substrate (2.48×10^{-2} M) containing 9,10-dicyanoanthracene (7.45×10^{-4} M) with or without additives was irradiated with a 300-W Xe lamp through a Corning 0-51 (λ > 360 nm) glass filter. The photolysate was concentrated in vacuo to give the residue, which was dissolved in $CDCl_3$ containing 1,1,2,2-tetrabromoethane as an internal standard for product yield calculation. Subsequently, this was analyzed by ^{1}H NMR spectroscopy to obtain yields of products.

Photoreactions of Charge-Transfer Complexes. A mixture of a substrate [$(2.5–2.6) \times 10^{-2}$ M] and an electron acceptor ([TCNE] = 5.10×10^{-2} M, [TCNB] = 1.42×10^{-2} M) with or without additives ([TMB] = 2.52×10^{-2} M, [NAP] = 7.81×10^{-2}

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(31) Interestingly, the corresponding perchlorate salt was ineffective. At the present time, such counter anion effects on the reaction pathways of cation radicals have not been mechanistically understood well. (a) Mlcoh, J.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 412. (b) Okada, K.; Hasegawa, E.; Mukai, T. *Chem. Lett.* **1983**, *305*.

(32) The oxidation potential ($E_{1/2}^{ox}$) of tris(*p*-bromophenyl)amine is reported to be +1.05 V vs SCE (Nelson, R. F.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 3925).

(33) A reviewer indicated the possibility of the acid-catalyzed rearrangements. However, this was easily ruled out by the observation that stirring of 1 with *p*-TsOH (>0.1 equiv) in CH_2Cl_2 at room temperature for 3 h resulted in nearly quantitative recovery of 1.

(34) (a) Salmon, R. G. *Tetrahedron* **1983**, *39*, 485. (b) Grobbelaur, E.; Kutal, C.; Orchard, S. W. *Inorg. Chem.* **1982**, *21*, 414. (c) Goto, S.; Takamuku, S.; Sakurai, H.; Inoue, Y.; Hakushi, T. *J. Chem. Soc., Perkin Trans. II* **1980**, 1678.

(35) Direct irradiation of 2 is known to produce phenanthrene derivatives instead of 3, probably because 2 has stilbene moiety.[10a]

(36) Triplet-sensitized reaction of 2 using benzophenone was slow and afforded complex mixtures that did not contain 3.

(37) We thank Professor F. Toda (Ehime University) for informing us of the experimental procedure for 1,2-diphenylcyclobutene preparation.

(38) Dodson, R. M.; Zielske, A. G. *J. Org. Chem.* **1967**, *32*, 28.

M) in methylene chloride was irradiated with a 300-W Xe lamp through a Corning 3-74 ($\lambda > 400$ nm) glass filter for tetracyanoethylene and a Corning 0-51 ($\lambda > 360$ nm) glass filter for 1,2,4,5-tetracyanobenzene. The photolysate was concentrated in vacuo followed by ^{1}H NMR analysis to determine product yields. When the solutions of substrates and acceptors at the same concentrations as photoreactions were stirred in the dark, no conversions of starting materials were observed.

Aminium Salt Catalyzed Reactions. To a methylene chloride solution (1 mL) of a substrate (0.049 mmol) with or without an additive (TMB, 0.052–0.056 mmol) was added tris(*p*-bromophenyl)aminium hexachloroantimonate (0.013 mmol for 1, and 0.0024 mmol for 2) in methylene chloride (1 mL). The solution was stirred at room temperature. The reaction was quenched on addition of 1,4-diazabicyclooctane. The reaction mixture was concentrated in vacuo to give the residue, which was subjected to ^{1}H NMR analysis.

Registry No. 1, 4759-04-0; $1^{\bullet+}$, 119391-88-7; 2, 96581-96-3; $2^{\bullet+}$, 119477-45-1; 3, 119391-87-6; 4, 3306-02-3; TMB, 2441-46-5; NAP, 91-20-3; NAP$^{\bullet+}$, 34512-27-1; NAP$^{\bullet+}$–TCNB$^{\bullet+}$, 740-98-7; DCA, 1217-45-4; TCNE, 670-54-2; TCNB, 712-74-3; dibenzoylethane, 495-71-6; tris(*p*-bromophenyl)aminium herachloroantimonate, 78065-12-0.

Supplementary Material Available: Listings of positional parameters, thermal parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

Computer-Assisted Evaluation of Oxidation Reactions[†]

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The scope and predictive capability of the CAMEO program have been enhanced to encompass the chemistry of 21 oxidative reagents including transition-metal acetates, metal and nonmetal oxides, hydrogen peroxide, peracids, and chromium(VI) oxidants. The implementation of the oxidation module required a strategy that deviates from the highly mechanistic approach employed by the other modules in CAMEO because of the dearth of mechanistic information on many oxidative transformations. The approach keys reactivity on the nature of the oxidant and utilizes the reaction conditions to narrow down the competing processes. This necessitated the formulation of "reactivity tables" for the featured reagents to help assess competitions among viable reactive sites. Algorithms for evaluating multipathway transformations for a specific site have also been devised based on reaction schemes that can presently account for all the observed transformations.

I. Introduction

CAMEO, an interactive computer program designed to predict the products of organic reactions, given the starting materials and conditions, is under continuous expansion. The incorporation of a reaction module that treats the chemistry of organic and inorganic oxidants into the program is addressed in this paper. Overall, the program now consists of modules that correspond to broad classes of reactions, namely, nucleophilic,[1] electrophilic,[2a,b] carbenoid,[2c] radical,[2d] thermal pericyclic,[3] heterocycle-forming,[4] and oxidative/reductive processes. The varying levels of sophistication found in these modules normally reflect the different states of knowledge in the corresponding areas. Thus, the nucleophilic module utilizes a mechanistic approach since a vast number of nucleophilic processes can be decomposed into a sequence of a few recurring fundamental mechanistic steps, whereas the pericyclic module goes beyond the usual mechanistic analysis and makes use of frontier molecular orbital (FMO) theory in predicting both the feasibility and regiochemistry of reactions.

A hierarchical approach, employing mechanistic reasoning for identifying and selecting the most reactive sites, and empirical rules, derived from literature precedents for evaluating competitions among several viable pathways, is a common key feature in most reaction modules in CAMEO. This approach, which relies on a mechanistic classification of reactions, is not generally viable when applied to oxidation reactions, for the following reasons: (a) knowledge of the mechanisms of oxidation reactions is oftentimes lacking or limited to specific reagent–substrate combinations; (b) oxidation chemistry encompasses diverse classes of reactions that involve many types of intermediates including radical ions, carbenes, and nitrenes; hence, reaction pathways are difficult to classify; and (c) the reaction pathways, and consequently the oxidation products, are highly dependent on the nature of the oxidizing agent and on the reaction conditions, such as temperature, pH of the medium, and stoichiometry. In view of these constraints, an alternative approach, which keys reactivity on the nature of the reagent, and which utilizes the reaction conditions to narrow down the potential oxidizable sites, has been adopted for the oxidation module. Importantly, this strategy permits sound predictions even for mechanistically obscure reactions. The oxidation module currently treats 21 reagents, which have been selected on the basis of their high synthetic utility. These reagents as well as the reaction conditions available to the user are listed on the menu shown in Figure 1. The major classes of oxidants that have been implemented are Cr(VI) com-

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[†] Based on the Ph.D. Thesis of G. D. Paderes, Purdue University, 1988.

(1) (a) Salatin, T. D.; Jorgensen, W. L. *J. Org. Chem.* **1980**, *45*, 2043. (b) Salatin, T. D.; McLaughlin, D.; Jorgensen, W. L. *Ibid.* **1981**, *46*, 5284. (c) Peishoff, C. E.; Jorgensen, W. L. *Ibid.* **1983**, *48*, 1970. (d) Peishoff, C. E.; Jorgensen, W. L. *Ibid.* **1985**, *50*, 1056. (e) Peishoff, C. E.; Jorgensen, W. L. *Ibid.* **1985**, *50*, 3714. (f) Gushurst, A. J.; Jorgensen, W. L. *Ibid.* **1986**, *51*, 3513. (g) Metivier, P.; Gushurst, A. J.; Jorgensen, W. L. *Ibid.* **1987**, *52*, 3724.

(2) (a) McLaughlin, D. Ph.D. Thesis, Purdue, University, 1983. (b) Bures, M. G.; Roos-Kozel, B. L.; Jorgensen, W. L. *J. Org. Chem.* **1985**, *50*, 4490. (c) Helson, H. E. *J. Org. Chem.*, in press. (d) Laird, E. R. *J. Org. Chem.*, in press.

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(4) Bures, M. G.; Jorgensen, W. L. *J. Org. Chem.* **1988**, *53*, 2504.

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