(relative intensity) 200 (M^+, 3), 202 (2), 121 (77), 119 (87), 105 (98), 91 (83), 81 (90), 41 (100); high-resolution mass spectroscopy (m/z) calcd for $C_{15}H_{24}O$ 220.1827, found 220.1824; 1.4 ppm error.

Method B. To a solution of ketone 14 (34.2 mg, 0.15 mmol) in reagent MeOH (2.0 mL) stirred at -15 °C (ice-MeOH bath) under N_2 was added powdered $NaBH_4$ (0.288 g, 7.61 mmol). The resulting mixture was allowed to stir for 30 min at -15 °C and then warmed to room temperature over a period of 1 h. The reaction mixture was diluted with H_2O (15 mL) and extracted with Et_2O (5 × 10 mL). The combined ethereal extracts were washed with H_2O (2 × 10 mL) and saturated NaCl solution (10 mL), dried Na_2SO_4), filtered ($MgSO_4$), and concentrated in vacuo to give 34.5 mg (100%) of tricyclic alcohols **13**, the GLC, TLC, and spectra of which were nearly identical with the above data.

(1α,4α,4aβ,6α,8aβ)-Octahydro-1,4,8a-trimethyl-9-methylene-1,6-methanonaphthalen-7(1*H*)-one (14). Chromic acid reagent[9] (2.67 M, 2 drops) was added to a solution of alcohols **13** (14.7 mg, 0.067 mmol) in reagent acetone (0.5 mL) at 23 °C. After being stirred for 5 min, the orange mixture was quenched with *i*-PrOH (3 drops) and H_2O (10 mL). The aqueous solution was extracted with Et_2O (5 × 10 mL). The combined ethereal extracts were washed with saturated $NaHCO_3$ solution (5 mL) and saturated NaCl solution (5 mL), dried Na_2SO_4), filtered $MgSO_4$), and concentrated in vacuo to give 14.6 mg (100%) of white crystalline tricyclic ketone **14**: mp 35.5-36.5 °C; IR ($CHCl_3$) 3080, 1640, 900 ($C{=}CH_2$), 1380, 1370 (CH_3), 1715 ($C{=}O$) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.820 (d, 3, J = 6.78 Hz, CH_3CH), 0.952 (s, 3, CH_3), 0.992 (s, 3, CH_3), 1.92, 1.99, 2.35, 2.42 (AB, 2, J_{AB} = 19.6 Hz, CH_2CO), 2.91 (t, 1, J = 2.9 Hz, $CH_2{=}CCHCO$); 4.84 and 5.02 (2 s, 2, $C{=}CH_2$); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 18.90, 19.54, 24.24, 24.51, 25.92, 29.41, 36.74, 38.83 (4°), 39.97 (4°), 43.21, 48.13, 55.95, 110.16 ($C{=}CH_2$), 153.38 ($C{=}CH_2$), 212.50 (CO); mass spectrum, m/z (relative intensity) 218 (M^+, 39), 111 (56), 120 (80), 105 (78), 91 (81), 81 (58), 41 (100); high-resolution mass spectroscopy (m/z) calcd for $C_{15}H_{22}O$ 218.1671, found 218.1675; 1.8 ppm error.

(±)-Seychellene (1). A mixture of ketone 14 (67 mg, 0.306 mmol), KOH (535 mg, 8.1 mmol), and $N_2H_4{\cdot}H_2SO_4$ (340 mg, 2.61 mmol) was heated slowly under N_2 from 23 °C to 200 °C over a period of 2 h and then held at 200 °C for an additional 2 h. The reaction was cooled to 23 °C, diluted with H_2O (40 mL), and extracted with Et_2O (5 × 10 mL). The combined ethereal extracts were washed with H_2O (5 × 10 mL) and saturated NaCl solution (10 mL), dried Na_2SO_4), filtered ($MgSO_4$), and concentrated in vacuo to give 55 mg (87%) of a pale yellow oil. Chromatography on silica gel (1 g) using hexane as the eluant produced 46 mg (73%) of pure (±)-seychellene (1): IR ($CHCl_3$) 3070, 1640, 885 ($C{=}CH_2$), 1370, 1380 (CH_3); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.752 (d, 3, J = 6.77 Hz, CH_3CH), 0.830 (s, 3, CH_3), 0.961 (s, 3, CH_3), 2.20 (m, 1, $CH_2{=}CCH$), 4.59 and 4.79 (2 d, 2, J = 1.4 Hz, $C{=}CH_2$); ^{13}C NMR ($CDCl_3$, 20.2 MHz) 18.75, 20.71, 24.94, 26.44, 26.56, 27.81, 29.90, 31.65, 35.16, (4°), 37.26, 37.66, 39.81 (4°), 44.77, 103.49 ($C{=}CH_2$), 162.41 ($C{=}CH_2$); mass spectrum, m/z (relative intensity) 204 (M^+, 12), 189 (5), 122 (100), 93 (33), 41 (27); high-resolution mass spectroscopy (m/z) calcd for $C_{15}H_{24}$ 204.1878, found 204.1879; 0.5 ppm error.

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Competitive Photochemical $\sigma^2 + \pi^2$ Addition and Electron Transfer in the *N*-Methylphthalimide-Alkene System

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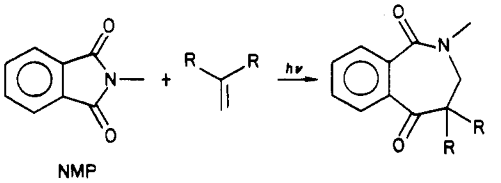
N-Methylphthalimide (NMP) undergoes a pair of competing photochemical reactions in the presence of alkenes. In one of these reactions the alkene adds to the C(O)-N bond of NMP in a concerted $\pi^2 + \sigma^2$ process that ultimately leads to 2-benzazepine-1,5-diones (**5**). A competing electron-transfer process results in the formation of a radical cation-radical anion pair which can be efficiently trapped in alcohol solvents such as **4**. The regiochemistry of these products is consistent with expectations for addition of an alcohol to a radical cation. Calculations using the Weller equation accurately predict when electron transfer should dominate the $\pi^2 + \sigma^2$ process, when the $\pi^2 + \sigma^2$ process should dominate the electron-transfer process, and when the two should be directly competitive. Product studies on the formation of **4** and **5** for various alkenes in methanol solution are entirely consistent with this hypothesis.

The photochemistry of phthalimides in the presence of alkenes is characterized by three major processes:[1] (1) The addition of the alkene to the C(O)-N bond resulting in the formation of a ring expanded benzazepinedione[2] (eq 1).



(1)

This reaction is regiospecific and stereospecific, and studies indicate that it is a concerted process that probably occurs through the zwitterionic "enolate" of the imide.[3] The reaction has some generality in that it occurs with alkenes, dienes, vinyl ethers, vinyl esters, and an allene.[2d]

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[1] For reviews see: Mazzocchi, P. H. "Organic Photochemistry"; Padwa, A.; Ed.; Marcel Dekker: New York, 1981; Vol. 5. Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407.

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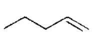
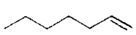
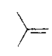
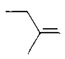
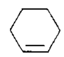
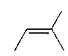
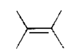
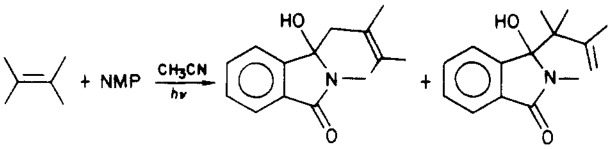
Table I. ΔG_{ET} Values for NMP–Alkene Pairs

alkene									
E^{ox}, V		2.78[a]	2.64[b]	2.39[b]	2.37[b]	2.26[a]	2.05[a]	1.79[b]	1.63[b]
ΔG_{ET}, kcal		14.4	11.2	5.4	2.4	2.4	−2.4	−8.4	−12.7
yield,[c] %	5	60	46	44	43	32	0	0	0
yield,[d] %	4	NA	0	15	NA	12	28	51	42
	5	NA	45	60	NA	22	0	0	0

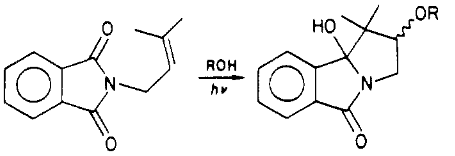
[a] Experimentally determined value.[10] [b] Calculated value. [c] Reaction in acetonitrile. [d] Reaction in methanol.

(2) A photoreduction reaction[4] originally discovered by Kanaoka and Hatanaka for NMP and cyclohexene.[4a] We have recently shown that, at least in the case of 2,3-dimethyl-2-butene, this photoreduction reaction is an electron-transfer-mediated process from the singlet state of NMP[4b] (eq 2).



(2)

(3) Solvent trapping of the radical ion pair[5] resulting from electron transfer from the alkene (donor) to the NMP (acceptor) as first described by Maruyama et al.[5a] for the intramolecular case (eq 3).



(3)

In this paper we wish to present the full details of our work[6a] on the competition between the electron-transfer and addition processes.[5]

Results and Discussion

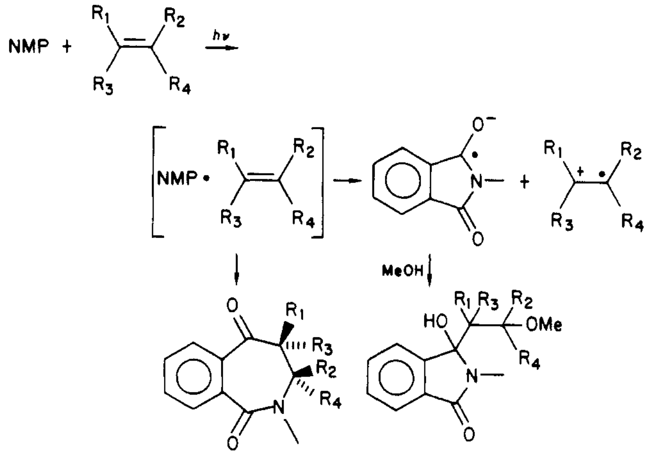
In our initial reports[2a,c] on the addition reaction (eq 1) we noted that those alkenes and dienes with low ionization potentials did not undergo this reaction and suggested that electron transfer might be a competing process. This suggestion was substantiated[6a] by examination of ΔG_{ET} values for a variety of alkenes with NMP calculated using a form of the Weller equation[7]

$$\Delta G_{ET} = 23.06(E_D{}^{ox} - E_A{}^{red}) - \Delta E_\infty - C$$

where ΔG_{ET} is the free energy for electron transfer, $E_D{}^{ox}$ and $E_A{}^{red}$ are the oxidation and reduction potentials of the donor and acceptor, respectively, E_∞ is the transition energy of the excited species, and C is the coulombic interaction term.

The value of 80 kcal/mol for the singlet energy of NMP (E_∞) was used[8] along with the measured reduction potential of NMP (−1.37 V).[9] Oxidation potentials for a number of alkenes were obtained by linear correlation of ionization potentials with measured oxidation potentials.[10] The value of C has been estimated at 1.3 kcal/mol.[7]

Scheme I



	R_1	R_2	R_3	R_4
a	n-Bu	H	H	H
b	Me	H	Me	H
c	Me	Me	H	H
d	H	H	$-(CH_2)_4-$	
e	Me	Me	Me	H
f	Me	Me	Me	Me
g	H	H	H	H

As shown in Table I the $\pi^2 + \sigma^2$ addition reaction (eq 1) occurs in acetonitrile solution only in cases in which ΔG_{ET} is positive. The fact that *cis*- and *trans*-2-butene undergo the $\pi^2 + \sigma^2$ reaction whereas cyclohexene does not make it clear that steric effects cannot be important and indicates that electron-transfer processes must effectively complete with the $\pi^2 + \sigma^2$ reaction. In order to test this proposition we studied the photochemistry of NMP and alkenes in methanol as solvent. It had been shown that photochemically generated radical cations can be trapped by alcohols[11] and Maruyama et al.[5a] have shown that the intramolecular radical anion–radical cation pair of *N*-alkenylphthalimides are very effectively trapped by alcohol solvents (eq 3). Thus it was expected that this experiment would show which of the alkenes underwent efficient electron transfer to NMP (ΔG_{ET} negative) since they should afford only solvent-trapped products. On the other hand, those alkenes whose interaction with NMP resulted in positive ΔG_{ET} values should afford only the $\pi^2 + \sigma^2$ product. The results we obtained, vide infra, are consistent

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(4) (a) Kanaoka, Y.; Hatanaka, Y. *Chem. Pharm. Bull.* **1974**, *22*, 2205. (b) Mazzocchi, P. H.; Klinlger, L. *J. Am. Chem. Soc.* **1984**, *106*, 7567. (c) Mazzocchi, P. H., Khachik, F. *Tetrahedron Lett.* **1983**, 1879.

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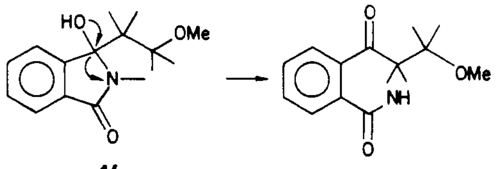
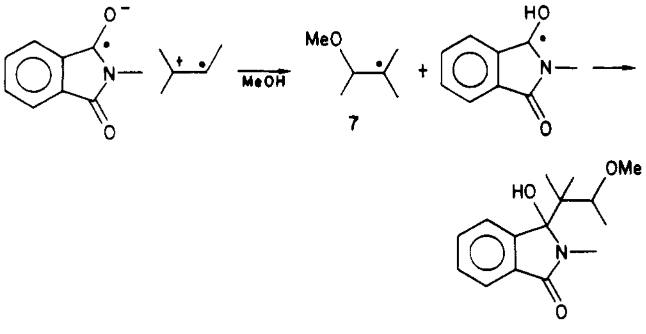
with this proposition (Scheme I).

Irradiation of a solution of NMP and 1-hexene (**1a**) in methanol gave only the addition product **5g** as predicted from the large calculated positive ΔG_{ET} (Table I). In a comparative study, samples of NMP and 1-heptene in methanol and acetonitrile were irradiated in parallel. Workup gave **5g** as the only product in yields of 25% and 26%, respectively. Under similar conditions 2,3-dimethyl-2-butene (**1f**) afforded **6**, which must arise from opening of the carbinolamide **4f**, along with photoreduction products (eq 2) which we have reported on elsewhere.[4b,c] It is perhaps noteworthy that alcohol-trapped products from **1f** are the only ones that show ring-opened **6** as their most stable form. Importantly no **5f** was obtained from this reaction in accord with expectations since the NMP, **1f** pair has a large negative ΔG_{ET} (Table I). Identical results are obtained in all cases where ΔG_{ET} is negative; cyclohexene and 2-methyl-2-butene afford only the alcohol-trapped product **4** and photoreduction products but none of the $\pi^2 + \sigma^2$ addition product **5**.



4f **6**

Apparently electron transfer is the dominant process in these cases. Further evidence for the course of these reactions comes from analysis of the regiochemistry of the addition product. Alcohol addition to the radical cation would be expected to take place to give the most stable radical **7** as is observed in other cases.[11] Coupling of **7** with the protonated NMP radical anion would afford the observed product **4e**.



4e

In addition to the two extremes of large positive and negative ΔG_{ET} values there are several alkene–NMP pairs which predict small positive ΔG_{ET} values. In these cases irradiation of the alkenes **1b** and **1c** with NMP in methanol gives a pair of products. Thus irradiation of NMP with 2-methylpropene in methanol afforded a 15% yield of **4b** and a 60% yield of **5b**. Similarly NMP with 2-butene gave a 12% yield of **4c** and a 20% yield of **5C**.

We thus have three basic situations: (1) electron transfer is strongly endothermic ($\Delta G_{ET} > 5$ kcal) resulting in only $\pi^2 + \sigma^2$ additions products; (2) electron transfer is slightly endothermic. Here the $\pi^2 + \sigma^2$ addition process can effectively compete with electron transfer, and we obtain both addition products **5** and trapped radical ion pairs **4**. It is important to note here that the structure of the alkene not only effects the ΔG_{ET} value and thus the rate constant for electron transfer but also probably effects the rate of the $\pi^2 + \sigma^2$ reaction via electronic and steric effects;[2d] (3) electron transfer is exothermic and we observe trapped radical ion pairs **4** in addition to photoreduction products (eq 2). The fact that one only observes photoreduction products (eq 2) when ΔG_{ET} is negative is interesting especially since these products and **4** both arise via electron transfer. We propose that these products arise from different radical ion pairs (contact and solvent separated, respectively), and we are presently in the process of gathering experimental evidence substantiating this proposition.

Experimental Section

Melting points were measured on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Dr. Franz Kasler of the University of Maryland. IR spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer and were calibrated with the 1601-cm^{-1} absorption band of polystyrene. NMR spectra were recorded on a Varian XL-100 or EM-360 or an IBM WP-200 spectrometer. Analytical HPLC determinations were performed on a Varian Model 5000 liquid chromatograph interfaced to a HP 18850-A printer/plotter. Chromatographic separations were carried out on silica gel (13–24 μm) on a medium-pressure system. Mass spectra were recorded on a Du Pont 492 spectrometer. Irradiations were carried out in test tubes or large photochemical reactors with a 450-W Hanovia medium-pressure mercury lamp.

Photolysis of NMP in the Presence of Alkenes. General Procedure. A solution containing 0.2 g (0.0012 mol) of NMP, 0.006 mol of the appropriate alkene, and 28 mL of reagent grade methanol was irradiated for a period of 3 h in a serum-capped quartz tube at 0 °C (ice bath). The light source was a Hanovia 450-W mercury lamp in a quartz jacket. The solution was outgassed by bubbling nitrogen through it for a period of 10 min prior to irradiation. Solvent was removed in vacuo and the residue separated by preparative TLC (silica gel, petroleum ether–ether, 1:3). Spectral and analytical characteristics of the products isolated are given for the individual alkenes.

2-Methylpropene. Workup afforded 17 mg (8%) of NMP, 112 mg (47%) of **5b**,[2d] 36 mg (13%) of the oxetane derived from 2-methylpropene addition to **5b**[2d] and 40 mg (15%) of the alcohol-trapped product **4b** as an oil: IR ($CHCl_3$) 3400, 1690 cm^{-1}, NMR ($CDCl_3$) δ 0.82 (s, 3 H), 1.09 (s, 3 H) 3.10 (s, 3 H), 3.45 (s, 2 H), 3.50 (s, 3 H), 5.50 (s, 1 H), 7.32–7.96 (m , 4 H); mass spectrum, *m/e* (relative intensity) 163 (12), 162 (100), 147 (5), 146 (8), 133 (8), 77 (8), 56 (27). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.32; H, 7.46; N, 5.83.

2-Butene. Workup afforded 54 mg (27%) of NMP, 43 mg (22%) of **5c**,[2d] and 26 mg (12%) of **4c** as an oil: IR ($CHCl_3$) 3360, 1695 cm^{-1}; NMR ($CDCl_3$) δ 0.43 (d, J = 7 Hz, 3 H), 1.81 (d, J = 7 Hz, 3 H), 2.00–2.78 (m, 1 H), 2.98 (s, 3 H), 3.45–3.88 (m, 1 H), 3.58 (s, 3 H), 6.30 (s, 1 H), 7.29–7.93 (m, 4 H); mass spectrum, *m/e* (relative intensity) 162 (100), 147 (6), 77 (6), 59 (18), 56 (25). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.78; H, 7.39; N, 5.86.

Cyclohexene. Workup gave 83 mg (41%) of NMP and 50 mg (25%) of **4d** as a pair of diastereoisomers in approximately equal amounts which were separable by TLC. One isomer of **4d** (mp 179–180 °C) showed: IR ($CHCl_3$) 3340, 1696 cm^{-1}; NMR ($CDCl_3$) δ 0.6–2.68 (m, 10 H), 3.11 (s, 3 H), 3.58 (s, 3 H), 7.00 (s, 1 H), 7.32–7.82 (m, 4 H); mass spectrum, *m/e* (relative intensity) 164 (16), 162 (100), 85 (66), 83 (13), 82 (13), 67 (21). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H,7.69; N, 5.05. Found: C, 69.51; H, 6.32; N, 5.25. The other isomer, an oil, showed: IR ($CHCl_3$) 3360, 1698 cm^{-1}; NMR ($CDCl_3$) δ 0.75–2.73 (m, 10 H), 2.98 (s, 3 H), 3.70 (s, 3 H), 6.32 (s, 1 H), 7.80–7.90 (m, 4 H); mass spectrum, *m/e* (relative intensity) 163 (100), 85 (5), 83 (8), 82 (10), 67 (15). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.05. Found: C, 69.97; H, 7.86; N, 5.41. When either of these diastereoisomers were separated and allowed to stand in $CDCl_3$ at room temperature overnight, a ~1:1 mixture of diastereoisomers resulted.

2-Methyl-2-butene. Workup gave 93 mg (47%) of NMP and 84mg (51%) of **4e** as a mixture of isomers in a 5:3 ratio which were separated by preparative TLC. One of the isomers, mp 133–134 °C, showed: IR ($CHCl_3$) 3340, 1685 cm^{-1}; NMR ($CDCl_3$) δ 0.42 (s, 3 H), 1.18 (d, J = 7 Hz, 3 H), 1.26 (s, 3 H), 3.12 (s, 3 H), 3.43 (s, 3 H), 3.82 (q, J = 7 Hz, 3 H), 6.60 (s, 1 H), 7.26–7.90 (m, 4 H);

mass spectrum, *m/e* (relative intensity) 187 (5), 171 (5), 173 (5), 163 (10), 162 (100), 132 (8), 76 (7), 58 (10). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. Found: C, 68.22; H, 7.80; N, 5.66. The other diastereoisomer of **4e**, mp 154-155 °C; showed: IR ($CHCl_3$) 3360, 1700 cm^{-1}; NMR ($CDCl_3$) δ 0.50 (s, 3 H), 1.16 (d, J = 7 Hz, 3 H), 1.37 (s, 3 H), 3.11 (s, 3 H), 3.58 (s, 3 H), 3.81 (q, J = 7 Hz, 1 H), 5.80 (s, 1 H), 7.30-7.92 (m, 4 H); mass spectrum, *m/e* (relative intensity) 187 (6), 172 (6), 163 (13), 162 (100), 133 (6), 70 (5), 59 (10), 55 (13). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. Found: C, 68.53; H, 8.36; N, 5.15.

2,3-Dimethyl-2-butene. Workup gave 53 mg (26%) of NMP and 100 mg (42%) of **6**, mp 105-106 °C, along with two isomeric photoreduction products (eq 2). Compound **6** showed: IR ($CHCl_3$) 3460, 1688, 1672 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (s, 6 H), 1.28 (s, 6 H), 2.87 (d, J = 5 Hz, 3 H), 3.28 (s, 3 H), 6.00-6.50 (b s, 1 H), 7.00-7.80 (m, 4 H); mass spectrum, *m/e* (relative intensity) 173 (7), 163 (13), 162 (100), 85 (13), 74 (27), 72 (7), 69 (8). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 69.31; H, 8.30; N, 5.05. Found: C, 68.97; H, 8.21; N, 5.27.

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Registry No. **4b**, 70113-70-1; **4c**, 70113-71-2; **4d**, 70113-69-8; **4e** (isomer 1), 70113-66-5; **4e** (isomer 2), 70113-67-6; **5b**, 67177-35-9; **5c**, 69656-56-0; **6**, 70113-68-7; NMP, 550-44-7; $CH_2{=}C(CH_3)CH_3$, 115-11-7; $CH_3CH{=}CHCH_3$, 107-01-7; $CH_3C(CH_3){=}CHCH_3$, 513-35-9; $CH_3C(CH_3){=}C(CH_3)CH_3$, 563-79-1; cyclohexene, 110-83-8.

Theoretical Determination of Molecular Structure and Conformation. 14. Is Bicyclo[6.2.0]decapentaene Aromatic or Antiaromatic?

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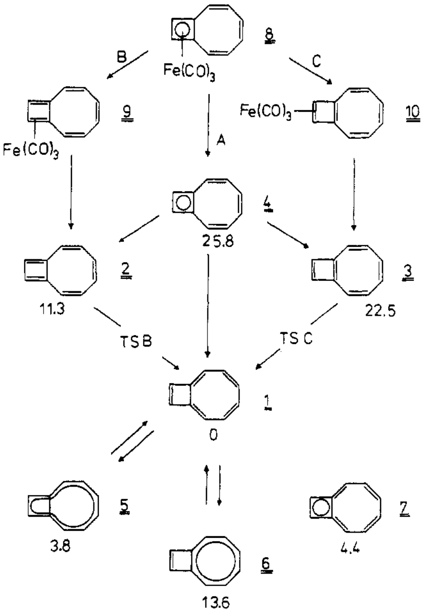
Ab initio HF/STO-3G and MNDOC calculations on bicyclo[6.2.0]decapentaene (1) suggest that 1 possesses a slightly puckered equilibrium structure with C_1 symmetry. The barrier to planarity is, however, lower than room temperature, i.e., 1 is at room temperature T essentially planar. According to theory, there is some peripheral delocalization of π electrons leading to weak aromaticity of 1. The calculated resonance energy of 1 is 4 kcal/mol. There exist two valence tautomers of 1 which are 11 and 23 kcal/mol less stable than 1. MNDOC calculations indicate that both forms easily undergo bond shifting and, therefore, are hardly detectable if not stabilized by benzoannelation.

The electronic nature of bicyclo[6.2.0]decapentaenes has attracted considerable interest by both experimentalists[1] and theoreticians,[2,3] in particular after the first successful synthesis of the parent compound (1, see Scheme I) by Oda and co-workers.[4,5] 1 contains in its periphery $(4n + 2)$ π electrons which should lead to some aromatic stabilization. This electronic stabilization, however, may be compensated by potential antiaromatic character of the component rings of 1 which are $4n$ π electron systems. Destabilization will increase if forms 2 and 3 (Scheme I) contribute substantially to the electronic structure of 1. Simple HMO or graph theoretical considerations predict a preponderance of the antiaromatic character of the component rings of 1.[2] These predictions have recently been supported by results of an elaborate MMP2 force field investigation of 1 carried out by Allinger and Yuh.[6] By making an as-

Scheme I



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