equal to those of solutions 21-C-7·3 and 21-C-7·4.

^{13}C NMR Studies. Samples were prepared by stirring the arenediazonium salt (0.5 mmol) with the appropriate amount of crown ether in $CDCl_3$ until solution occurred. ^{13}C NMR spectra were recorded on a Varian XL-100 NMR spectrophotometer in the ^{1}H fully decoupled mode. $CDCl_3$ provided an internal deuterium lock.

Acknowledgment. We warmly thank the National Institutes of Health for support of this work through Grants GM-26990, GM-29150, and GM-29610.

Registry No. 4-Methylbenzenediazonium tetrafluoroborate, 459-44-9; 4-methoxybenzenediazonium tetrafluoroborate, 459-64-3; 4-*tert*-butylbenzenediazonium tetrafluoroborate, 52436-75-6; 4-butoxybenzenediazonium tetrafluoroborate, 76832-54-7; 21-crown-7/4-methylbenzenediazonium tetrafluoroborate complex, 85048-77-7; 24-crown-8/4-methylbenzenediazonium tetrafluoroborate complex, 85048-78-8; 21-crown-7/4-methoxybenzenediazonium tetrafluoroborate complex, 80440-74-0; 24-crown-8/4-methoxybenzenediazonium tetrafluoroborate complex, 85048-79-9; 18-crown-6/4-*tert*-butylbenzenediazonium tetrafluoroborate complex, 65791-39-1; 21-crown-7/4-*tert*-butylbenzenediazonium tetrafluoroborate complex, 85048-80-2; 24-crown-8/4-*tert*-butylbenzenediazonium tetrafluoroborate complex, 85048-81-3; 18-crown-6/4-butoxybenzenediazonium tetrafluoroborate complex, 85048-82-4; 21-crown-7/4-butoxybenzenediazonium tetrafluoroborate complex, 85048-83-5; 18-crown-6/4-methylbenzenediazonium tetrafluoroborate complex, 63281-55-0; 18-crown-6/4-methoxybenzenediazonium tetrafluoroborate complex, 74317-32-1; 24-crown-8/4-butoxybenzenediazonium tetrafluoroborate complex, 85048-84-6; tetraethylene glycol, 112-60-7; triethylene glycol ditosylate, 19249-03-7; tetraethylene glycol ditosylate, 37860-51-8.

Structural Effects in Photoepoxidation Sensitized by α-Diketones

Edward L. Clennan,*[1a] David R. Speth,[1b] and Paul D. Bartlett*[1c]

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071, and Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Received August 6, 1982

A series of α-diketones and benzils were examined for their effectiveness as sensitizers in the photoepoxidation reaction. The reduction potentials of these α-diketones were also determined at a hanging-mercury-drop electrode. The reduction potentials of the *p,p'*-disubstituted-benzils were successfully correlated to the sum of the Hammett σ values. No evidence could be found that electron transfer plays an important role in the epoxidation mechanism. The mechanistic possibilities are briefly discussed. Studies of the photoepoxidation reaction in a variety of solvents have also shown that the reaction is very insensitive to solvent effects.

In 1976, Bartlett and Shimizu[2] reported an α-diketone-photosensitized epoxidation reaction. Prior to their report, several examples[3] of photooxidations, which resulted in concurrent formation of epoxides and singlet oxygen-like products, had appeared in the literature. The α-dicarbonyl-sensitized reaction produces high yields of epoxides and is a preparatively useful photoepoxidation. Despite the high yield of epoxides, this reaction suffers from competing processes that include (a) energy transfer to oxygen, resulting in excited singlet oxygen, (b) energy transfer to the olefin, leading to isomerization, (c) direct oxidation of the α-diketone, and (d) addition of excited ketone to the olefin to form an oxetane. The plurality of these competing reactions has made it difficult to isolate the photoepoxidation reaction for a mechanistic study.

Two attractive mechanistic hypotheses, which take advantage of the unique chemical and physical properties of α-diketones to explain the efficiency of these photoepoxidation sensitizers, are (1) single-oxygen-atom donation to the carbon-carbon double bond of olefins by acylperoxy or aroylperoxy radicals, which are easily formed from α-diketones,[4] and (2) a photoepoxidation initiated by electron transfer to the α-diketone to produce the easily formed semidione.[5] The second mechanism is attractive in view of the demonstrated importance of electron transfer[6,7] in the initiation of photooxidation under conditions close to those of singlet-oxygen formation.

In this report we describe the electrochemical and spectral properties of a series of *p,p'*-disubstituted-benzils and the Leonard series of tetramethylated α-diketones.[8] We also present qualitative and quantitative data on the use of these α-diketones in the photoepoxidation reaction and discuss our results in light of the two mechanisms presented above.

Electrochemistry

The one-electron-reduced products of α-diketones, the semidiones, have been examined extensively by ESR.[9] These semidiones can be easily produced by a variety of methods including electrochemical and chemical reduction of α-diketones. Surprisingly, the electrochemical studies of this interesting redox couple are quite limited. The

---

[1] (a) University of Wyoming. (b) Dow Chemical Company, Midland, MI. (c) Texas Christian University.

[2] Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193.

[3] (a) Bartlett, P. D.; Ho, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 627. (b) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1977**, *60*, 2673. (c) Bartlett, P. D. *Chem. Soc. Rev.* **1976**, *5*, 154.

[4] (a) Gream, G. E.; Paice, J. C.; Ramsay, C. C. R. *Aust. J. Chem.* **1969**, *22*, 1229. (b) Gream, G. E.; Paice, J. C. *Ibid.* **1969**, *22*, 1249.

[5] Russell, G. A.; Osuch, C. E.; Sentore, G.; Mouta, T.; Yomashito, M. *J. Org. Chem.* **1979**, *44*, 2780.

[6] (a) Eriksen, J. Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. (b) Spada, L. T.; Foote, C. S. *Ibid.* **1980**, *102*, 391. (c) Manning, L. E.; Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 4275. (d) Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083.

[7] (a) Barton, D. H. R.; Leclerc, G.; Magnus, P. D.; Nenzies, I. D. *J. Chem. Soc., Chem. Commun.* **1972**, 447. (b) Brown-Wensley, D. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162. (c) Schaap, A. P.; Zaklika, K. A.; Kaskar, B.; Fung, L. W.-M. *Ibid.* **1980**, *102*, 389. (d) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 457. (e) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1982**, *104*, 1454.

[8] Leonard, N. J.; Latinen, H. A.; Mottus, E. H. *J. Am. Chem. Soc.* **1953**, *75*, 3300.

[9] Russell, G. A.; Ballenegger, M.; Malkus, H. L. *J. Am. Chem. Soc.* **1975**, *97*, 1900 and references therein.

0022-3263/83/1948-1246$01.50/0

Table I. Properties of Substituted Benzils

	compound						
	P	P′	mp, °C	σ_p	$E_{1/2}$[a,b]	λ_{max}[c]	ϵ[d]
1	NMe_2	NMe_2	202.5–205	−1.20	−1.514	374	15000
2	OMe	OMe	132–134	−0.54	−1.303	392	82
3	OMe	Me	103–104.5	−0.44	−1.248	380	102
4	Me	Me	102–103	−0.34	−1.256	396	51
5	OMe	H	57.5–59	−0.27	−1.211	382	91
6	OMe	Cl	126.5–127	−0.04	−1.154	391	65
7	H	H	93.5–94	0.0	−1.168	391	56
8	H	Cl	74.5–75	+0.23	−1.091	387	100
9	Cl	Cl	197–198	+0.46	−1.028	385	74
10	OMe	NO_2	154.5–156	+0.51	−0.769, −1.135	375	262
11	NO_2	NO_2	210–212	+1.56	−0.695, −0.917, −1.198	357	401
12	decafluoro			+2.64[e]	−0.502		

[a] In CH_3CN reported in volts vs. the SCE. [b] $E_{1/2}$ is determined from cyclic voltammetry by taking the average of the cathodic and anodic peak potentials. [c] In benzene. [d] Extinction coefficient at λ_{max}. [e] Calculated with $\sigma_o = +0.29$, $\sigma_m = +0.06$, and $\sigma_p = +0.34$.[11]

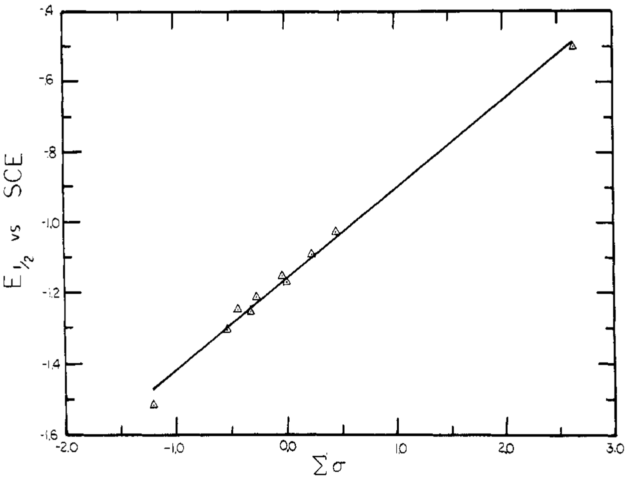


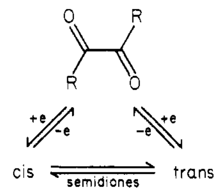
Figure 1. Half-wave reduction potentials of *p,p′*-disubstituted-benzils plotted vs. the sum of the σ constants.

majority of electrochemical studies have focused on the two-electron reduction process in protic media leading to the isomeric stilbenediols.[10,11]

We have examined the cyclic voltammetric behavior of 12 substituted benzils at a hanging-mercury-drop electrode and report these data along with other physical properties of the α-diketones in Table I. The 12 substituted benzils exhibited electrochemically quasi-reversible and chemically reversible cyclic voltammetric behavior from which half-wave reduction potentials could be obtained. All of the cyclic voltammetric data in Table I were collected in the presence of activated alumina, which improved the appearance of the data without changing the reduction potentials. The peak to peak separation on mercury covered a range from 59 to 70 mV but was much larger on platinum (70–140 mV) and very dependent on the condition of the platinum surface.

A plot of the reduction potentials of benzils **1–9** and **12** vs. the sum of the Hammett σ constants[12] gives an excellent correlation ($r = 0.9934$) as shown in Figure 1. The slope of this plot, +0.287, is very similar to the value obtained for the reduction of substituted benzophenones (+0.26).[13]

Scheme I



The observation of an excellent linear correlation suggests that all of the α-diketones are reduced by the same mechanism.[14] The reduction of benzils **10** and **11** with one and two nitro groups, however, exhibits first-reduction potentials that are more positive than expected on the basis of the sum of the Hammett σ constants and must certainly be reduced by a different mechanism. These benzils also exhibit two and three reversible redox couples in contrast to the one reversible couple observed for the other benzils in Table I. These data suggest that the first electron in the reduction of both compounds is placed into a molecular orbital that is more heavily weighted on the nitro than on the α-diketo groups.

A mechanistic scheme for the reduction of benzils uncomplicated by the presence of nitro groups is shown in Scheme I. A coulometry study of *p,p′*-dimethoxybenzil and benzil itself verifies that the cyclic voltammetry curves correspond to one-electron reductions. This reduction in all cases can lead to two distinct species, the cis and trans semidiones,[15] which are not in rapid equilibrium. The couple that is experimentally observed is the one that exhibits the fastest rate of electron transfer.[16] The decreased steric interaction and increased thermodynamic stability of the trans semidione as compared to the cis isomer suggests that it has the more favorable rate of electron transfer and is the experimentally observed redox couple.[17]

We have also examined the cyclic voltammetric behavior of the Leonard[8] α-diketones, and these data are reported in Table II. As Leonard noted previously from a po-

---

(10) Johnson, D. C.; Gaines, D. R. *Anal. Chem.* **1973**, *45*, 1670.

(11) (a) Stapelfeldt, H. E.; Perone, S. P. *Anal. Chem.* **1969**, *41*, 623. (b) Vincenz-Chodkowska, A.; Grabowski, Z. R. *Electrochim. Acta* **1964**, *9*, 789.

(12) (a) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191. (b) Tribble, M. T.; Trayham, J. G. *J. Am. Chem. Soc.* **1969**, *91*, 379. (c) "Advances in Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London and New York, 1972; p 106.

(13) Brockman, R. W.; Pearson, D. E. *J. Am. Chem. Soc.* **1952**, *74*, 4128.

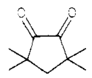
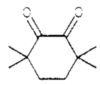
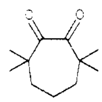
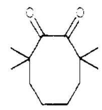
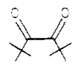
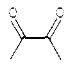
(14) (a) "The Elucidation of Organic Electrode Processes"; Zuman, P., Ed.; Academic Press: New York, 1969. (b) "Topics in Organic Polarography"; Zuman, P., Ed.; Plenum Press: New York, 1970.

(15) Bauld, N. L. *J. Am. Chem. Soc.* **1965**, *87*, 4788.

(16) (a) Heyrovsky, J.; Kuta, J. "Principles of Polarography"; Academic Press: New York, 1966. (b) Bockris, J. O. M.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum Press: New York, 1970; Vol. I and II.

(17) The cis semidione is formed to a greater extent than the trans isomer when they are produced via dissolving metal reduction. It has been suggested[14] that this reflects the stabilization of the cis isomer by complexation of both oxygens with the counterion.

Table II. Properties of Photoepoxidation Sensitizers[a]

	sensitizer	dihedral angle[7]	λ_{max}	$E_{1/2}$	% in 20 min reaction[b]	 epoxide	% epoxide/ % reaction
13		0-10	495,[c] 508	-1.164	35	3.8	0.109
14		30-60	380	-1.294	112	22	0.196
15		90-110	337	-1.826	45	3.9	0.087
16		100-140	343	-1.842	3	0	0
17		90	365	-1.645	83	25	0.301
18		90-180	440	-1.398	195	66	0.338

[a] Concentrations: $(\text{sens})_0 = (\beta\text{-methylstyrene})_0 = 0.001$, in CH_2Cl_2. [b] Total consumption of sensitizer and β-methylstyrene as % of initial concentration of β-methylstyrene. [c] Sandris, C.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1956**, 958.

larography study, increases in the dihedral angle between carbonyls are reflected in increasingly negative reduction potentials.

Photoepoxidation

The effectiveness of the benzils and the Leonard α-diketones as epoxidation sensitizers covers a remarkably wide range. The *p,p'*-bis(dimethylamino)benzil **1** and 3,3,8,8-tetramethylcyclooctanedione (**16**) produce no epoxide upon extended irradiation, whereas benzil **7** produces 1.8 mol of epoxide for each mole of α-diketone consumed.[18] Despite this wide range of reactivity, a correlation between reduction potential and effectiveness as a photoepxodiation sensitizer has not been observed. The photoepoxidation properties of the Leonard α-diketones in CH_2Cl_2 have been extensively investigated to look for such a correlation, and these data are presented in Table II. No attempt was made to measure the rate constants of these reactions, but the consumption of diketone and of β-methylstyrene and the formation of epoxide were followed at a series of times. Table II shows the results after 20 min; similar observations with pivalil and biacetyl are included for comparison. In this series there is no reason to invoke electron transfer as the initiating step in photoepoxidation. The ease of reduction decreases with increasing ring size, but the rate and epoxide yield are at a maximum with the six-membered ring. Consideration of the intercarbonyl dihedral angle, as estimated by Leonard, suggests that angular mobility in the dione is more important to its sensitizer activity than its half-wave potential; this is in accord with the superiority of both the acyclic diones as sensitizers. One trend in these data is worth noting; the most active sensitizers are also the most prone to decomposition. Apparently those features that make an α-diketone a good sensitizer also make it subject to oxidative destruction, or alternatively its destruction is a necessary prerequisite for epoxidation.

The photoepoxidation reaction utilizing these α-diketones is very insensitive to solvent effects. There seems to be a general-yield advantage in the order CH_2Cl_2 > $CHCl_3$ > CCl_4, but there is little to choose among ether, benzene, acetonitrile, dimethylformamide, dimethyl sulfoxide, methanol, and ethanol, covering a range of solvent parameter E_T from 34.5 to 55.5.

Conclusions

Examination of a wide variety of α-diketones has not provided any evidence for electron transfer to form semidiones as the initiating step in photoepoxidation. The reported photooxidative degradation of α-diketones, the observation that those α-diketones that undergo the most rapid photodegradation are the best photoepoxidation sensitizers, and the reported propensity of aroylperoxy and acylperoxy radicals to epoxidize olefins[19] suggests that single-oxygen-atom donation from aroylperoxy or acylperoxy radicals is the best description of the mechanism of this reaction.

From a practical viewpoint we have also demonstrated that there is no yield or substantial rate advantage in utilizing any system other than benzil or biacetyl in CH_2Cl_2 for photoepoxidation.

Experimental Section

NMR measurements were obtained for ^{13}C spectra (see Table III) on a JEOL FX60 (SW = 4000 Hz, RF = 15.03 MHz) and the ^1H spectra on a JEOL MH-100. The ^{13}C chemical shifts were assigned with the aid of off-resonance decoupling.

Benzil, biacetyl, and *p,p'*-dimethoxybenzil were all obtained commercially. The unsymmetrically substituted benzils were made by method A (see below) and the symmetrically substituted benzils, except for **1**, by method B.

Preparation of Unsymmetrically Substituted Benzils (Method A). The procedure for the *p*-nitro-*p'*-methoxybenzil was adapted for all the unsymmetrical benzils.

In a 250-mL flask, 10.5 g (55 mmol) of (*p*-nitrophenyl)acetic acid was warmed with 30 mL of of $SOCl_2$ until a clear solution resulted (about 30 min). Excess $SOCl_2$ was then removed on a rotary evaporator under high vacuum. The oily acid chloride was diluted with 75 mL of CS_2, and 6.5 g (60 mmol) of anisole was added. After cooling the solution to 5 °C, 9.0 g (67 mmol) of $AlCl_3$

---

[18] Bartlett, P. D.; Roof, A. A. M.; Shimizu, N. *J. Am. Chem. Soc.* **1982**, *104*, 3130.

[19] Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2049.

Table III. ^{13}C NMR Absorptions of Substituted Benzils[c] (Formular Numbers as in Table I)

	X				X′							
	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4	C=O	OCH_3	$ArCH_3$	NMe
1	121.43	132.09	110.72	154.12					193.88			39.89
2	126.37	130.88	114.64	164.90					193.55	55.62		
3	130.86	129.69[b]	130.08[b]	145.93	126.31	132.35	114.35	164.97	194.59 193.36	55.62	21.90	
4	130.60	129.95[b]	129.62[b]	145.99					194.46		21.90	
5	133.26	129.88[b]	128.97[b]	134.69	126.11	132.35[b]	114.42	165.03	194.85 193.17	55.62		
6	125.85	131.18[b]	114.42	165.16	131.57	132.42[b]	129.36[b]	141.38	193.36 192.38	55.61		
7	133.00	129.88[b]	129.04[b]	134.89					194.53			
8	132.73	129.95	129.10[b]	135.08	*a*	131.25[b]	129.43[b]	141.58	193.88 193.03			
9	*a*	131.18	129.44	141.70					190.25			
10	137.61	130.92	124.03	151.13	125.46	132.61	114.61	165.49	192.32 191.28			
11	136.71	130.78	124.24	151.52					190.30			

[a] Not observed. [b] Assignments may be interchanged. [c] Solvent $CDCl_3$, reference Me_4Si.

was added slowly in portions over a period of 30 min. Foaming resulted, and HCl was liberated during addition. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Excess CS_2 was removed by decanting, and ice and water were added to hydrolyze the $AlCl_3$ complex. The resulting solid was recovered by filtration (or ether extraction and washing).

For conversion of the desoxybenzoin to the benzil, 6.67 g (25 mmol) was dissolved in 50 mL of 70% acetic acid containing 2.8 g (28 mmol) of SeO_2 and refluxed overnight. After cooling, the mixture was filtered through Celite to remove Se metal and poured into three times its volume of water. The water was extracted with ether and the ether washed three times with water, twice with saturated Na_2CO_3, and once with brine and then dried with $MgSO_4$. The residue remaining after removal of the solvent was recrystallized from methanol to give an overall yield of about 40%. (Other benzils were recrystallized from methanol, ethanol, 95% ethanol, or hexane for the H/MeO compound.)

Preparation of Symmetrically Substituted Benzils (Method B). A solution of 200 mmol of *p*-substituted-benzaldehyde (*p*-chloro or *p*-methyl) was dissolved in 60 mL of 95% ethanol and 20 mL of water along with 10.0 g of NaCN. After the solution was refluxed overnight, the reaction mixture was poured into water. The aqueous solution was saturated with salt and extracted several times with ether. The ether was washed with brine and dried with $MgSO_4$. After removal of the ether, the oily residue was dissolved in pyridine along with 27.0 g of $CuSO_4$. After the solution was refluxed overnight, the reaction mixture was cooled and poured over ice. The crude benzil was isolated by filtration and recrystallized from acetic acid (*p*-chloro) or 95% ethanol (*p*-methyl). Yields were 45–50% overall.

***p,p*′-Bis(dimethylamino)benzil** (synthesized by the method of Becker:[20] NMR ($CDCl_3$) δ 6.56 (m, 4 H), 7.80 (m, 4 H), 3.02 (s, 12 H); mp 202.5–205 °C (lit.[20] 202–203 °C).

***p,p*′-Dimethylbenzil** (synthesized by the method of Clarke and Dreger):[21] ^1H NMR ($CDCl_3$) δ 7.44 (dd, 8 H), 2.38 (s, 3 H); mp 102–103 °C (lit.[22] mp 102–104 °C).

***p*-Chloro-*p*′-methoxybenzil:** ^1H NMR ($CDCl_3$) δ 7.88 (m, 4 H), 7.44 (m, 2 H), 6.95 (m, 2 H), 3.88 (s, 3 H); mp 126.5–127 °C (lit.[23] 129.5 °C).

***p*-Chlorobenzil:** ^1H NMR ($CDCl_3$) δ 7.84–8.36 (m, 4 H), 7.32–7.80 (m, 5 H); mp 74.5–75 °C (lit.[24] 73 °C).

***p*-Methoxy-*p*′-nitrobenzil:** ^1H NMR ($CDCl_3$) δ 8.20 (m, 4 H), 7.95 (m, 2 H), 6.94 (m, 2 H), 3.88 (s, 3 H); mp 154.5–156 °C (lit.[25] 156 °C).

***p,p*′-Dinitrobenzil:** mp 210–212 °C (lit.[26] 210–212 °C).

***p,p*′-Dimethoxybenzil:** ^1H NMR ($CDCl_3$) δ 6.80 (m, 4 H), 7.70 (m, 4 H), 3.76 (s, 6 H); mp 132–134 °C.

Decafluorobenzil: mp 326–329 °C (lit.[27] 328–329 °C).

***p,p*′-Dichlorobenzil:** ^1H NMR ($CDCl_3$) δ 7.60 (dd, 8 H); mp 197–198 °C (lit.[28] 195–196 °C).

***p*-Methoxybenzil:** ^1H NMR ($CDCl_3$) δ 7.80–8.00 (m, 4 H), 7.28–7.72 (m, 3 H), 6.96 (m, 2 H), 3.84 (s, 3 H); mp 57.5–59 °C (lit.[29] 63 °C).

***p*-Methyl-*p*′-methoxybenzil:** ^1H NMR ($CDCl_3$) δ 7.72 (m, 4 H), 6.96 (m, 2 H), 3.80 (s, 3 H), 2.40 (s, 3 H).

Pivalil: bp 80 °C (50 mmHg) (lit.[29] bp 59–62 °C (14 mm)).

3,3,6,6-Tetramethyl-1,2-cyclohexanedione: ^1H NMR ($CDCl_3$) δ 1.14 (s, 12 H), 1.25 (s, 4 H); mp 111–113 °C (lit.[29] 114.2–114.8 °C).

3,3,7,7-Tetramethyl-1,2-cycloheptanedione: ^1H NMR ($CDCl_3$) δ 1.14 (s, 12 H), 1.65–1.75 (m, 6 H); bp 60–63 °C (2 mmHg) (lit.[29] 87–91 °C (6 mm)).

3,3,8,8-Tetramethyl-1,2-cyclooctanedione:[28] ^1H NMR ($CDCl_3$) δ 1.65–2.20 (br s, 8 H), 1.44 (m, 9 H); bp 68 °C (0.2 mmHg).

3,3,5,5-Tetramethyl-1,2-cyclopentanedione: ^1H NMR ($CDCl_3$) δ 1.20 (s, 12 H), 2.00 (s, 2 H); mp 89–92 °C (lit.[30] 93.5–94 °C).

Electrochemical Technique. A Model 9323 PAR hanging-mercury-drop electrode was utilized for cyclic voltammetry along with a PAR Model 175 Universal Programmer and a Model 173 potentiostat/galvanostat. A varian *X–Y* recorder was used for scan rates less than 500 mV/s and a Tektronix oscilloscope for faster scans.

A CV sample in Burdick and Jackson distilled acetonitrile or in purified DMF 2×10^{-3} M in electroactive substrate and 0.1 in supporting electrolyte (n-Bu_4NClO_4) was utilized for this study. The samples were deoxygenated by bubbling purified N_2 through the sample prior to data collection. All numbers are reported relative to the saturated calomel electrode.

Epoxidation Procedure. A 450-W medium-pressure Hanovia mercury vapor lamp, in a water-cooled Pyrex jacket, was immersed in an isopropyl alcohol cooling bath in a 6-L beaker. The bath, surrounded by aluminum foil, was stirred magnetically and maintained within ±1° of the reaction temperature, which in each case was between 12 and 15 °C. The epoxidations were run in a 10 × 2.5 cm round cell with a glass frit at the bottom through which oxygen was bubbled at 35–40 mL/min. Under this arrangement the oxygen passing through the solution in a typical irradiation time of 15 min amounted to 26 times that required for complete epoxidation. The reacting solutions were 0.05 M

---

[20] Tuzun, C.; Ogliaruso, M.; Becker, E. I. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, 111.

[21] Clarke, H. T.; Dreger, E. E. "Organic Syntheses"; Wiley: New York, 1941; Collect. Vol. I, 87.

[22] Ekecrntz, S.; Ahlquist, A. *Chem. Zentralbl.* **1908**, 1689; *Beilstein 7*, 774.

[23] Jenkins, S. S. *J. Am. Chem. Soc.* **1934**, *56*, 1137.

[24] Corey, E. J.; Schaefer, J. P. *J. Am. Chem. Soc.* **1960**, *82*, 918.

[25] Kanno, S.; Suzuki, S. *J. Pharm. Soc. Jpn.* **1951**, *71*, 1247; *Chem. Abstr.* **1952**, 6115.

[26] (a) Es, T. van; Backeberg, O. G. *J. Chem. Soc.* **1963**, 1371. (b) Es, T. van; Backeberg, O. G. *Ibid.* **1963**, 1363.

[27] Chambers, R. D.; Clark, M.; Spring, D. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2464.

[28] Gomberg, M.; Van Nalta, F. J. *J. Am. Chem. Soc.* **1929**, *51*, 2238.

[29] Leonard, N. J.; Mader, P. M. *J. Am. Chem. Soc.* **1950**, *72*, 5388.

[30] Hesse, G.; Beyer, P. *Justus Liebigs Ann. Chem.* **1971**, *747*, 84–97.

in sensitizer and 0.10 M in *trans*-β-methylstyrene; ethylbenzene (0.04 M) was present as an internal VPC standard.

Aliquots were taken from the reacting solution at various times during 15 min and analyzed by VPC on a 2 ft × $^1/_8$ in. 5% SE-30 column, temperature 95 °C for 7 min, then rising to 120 °C.

Acknowledgment. We thank the Robert A Welch Foundation, the National Science Foundation, the National Institutes of Health, and Research Corp. for support of this research.

Registry No. 1, 17078-27-2; 2, 1226-42-2; 3, 33425-19-3; 4, 3457-48-5; 5, 22711-21-3; 6, 54945-17-4; 7, 134-81-6; 8, 22711-23-5; 9, 3457-46-3; 10, 2387-74-8; 11, 6067-45-4; 12, 19555-07-8; 13, 20633-06-1; 14, 20651-89-2; 15, 68347-39-7; 16, 81578-43-0; 17, 4388-88-9; 18, 431-03-8; β-methylstyrene, 637-50-3.

Stereochemically Specific Diels–Alder Additions to Norbornyl- and Norbornenyl-Fused Fulvene Systems[1]

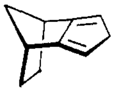
Leo A. Paquette,*[2a] Tina M. Kravetz,[2a] Michael C. Böhm,[2b] and Rolf Gleiter*[2b]

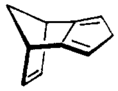
Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, and the Institut für Organische Chemie der Universität Heidelberg, D-6900 Heidelberg, West Germany

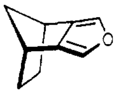
Received July 14, 1982

The title fulvenes **9** and **10** were prepared and shown to enter into stereocontrolled below-plane Diels–Alder cycloaddition with a range of dienophiles. The photoelectron spectra of **9** and **10** were also recorded and analyzed by semiempirical MO calculations. Although σ/π coupling in the two (three) highest canonical orbitals of **9** (**10**) is seen to be unimportant, the lowest canonical "π" linear combinations are coupled so strongly that pronounced rotation of the π lobes in these orbitals is seen. The extent to which this phenomenon and other factors may contribute to overall stereoselection is discussed.

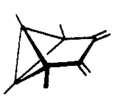
On the assumption that electronic influences inherent in norbornyl and norbornenyl frameworks should be observable at more remote sites, we[3] and others[4–6] have examined cycloadditions to exocyclic dienes such as **1**–**3**.

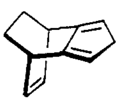

1


2


3

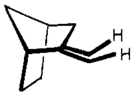

4


5

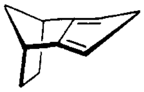

6

The expectation of pronounced π-facial stereoselectivity was founded in part upon earlier studies involving **4** and **5** where electronic effects contribute in a major way to an appreciable reactivity difference.[7] In fact, condensation of **1**–**3** with a variety of dienophiles proceeds from below the diene plane (as drawn) in virtually all cases.[3–6] This behavior contrasts in general with that exhibited by **6** which lacks norbornene character and consequently possesses lessened electronic directive influences.[3a,b,e]

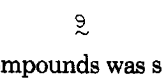
A number of rationalizations have been applied to these observations. Our view, which has its foundations in molecular orbital theory and is supported by photoelectron spectroscopy, focuses on the evident mixing of the bicyclic σ orbital framework with the diene π_s orbital. The resulting strong interaction effects a disrotatory tilt of the π orbitals at C_1 and C_4 of the butadiene moiety such that frontier electron density is enhanced syn to the methano bridge. Antibonding interaction between the π_s orbital of the exocyclic butadiene system and the HOMO of the dienophile is consequently smaller for attack from below (Figure 1). More recently, Houk has indicated by means of calculations that π pyrmaidalization of the exocyclic double bond in **7** is such that the terminal hydrogen atoms are bent in the exo direction.[8] The obvious relationship of **7** to **1** (see **8**) was cited as a possible reason for preferential approach of the dienophile from the ethano face.

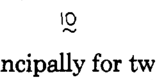


7


8

Clearly, the question of whether simple geometric distortion is a factor in the π-facial stereoselective cycloadditons to **1**–**3** had to be resolved. Accordingly, we have proceeded to examine the Diels–Alder behavior of the norbornyl-fused dimethylfulvene systems **9** and **10**. This pair of compounds was selected principally for two reasons. First, X-ray crystallographic[9] and electron diffraction studies[10] of 6,6-dimethylfulvene (and related molecules[11])


9


10

---

[1] Electronic Control of Stereoselectivity. Part 13. For part 12, see: Paquette, L. A.; Charumilind, P. *J. Am. Chem. Soc.* **1982**, *104*, 3749.

[2] (a) Columbus. (b) Heidelberg.

[3] (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *Ibid.* **1980**, *102*, 7218. (c) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907. (d) Paquette, L. A.; Bellamy, F.; Böhm, M. C.; Gleiter, R. *Ibid.* **1980**, *45*, 4913. (e) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *Ibid.* **1980**, *45*, 4922.

[4] Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

[5] Sugimoto, T.; Kobuke, Y.; Furukawa, J. *J. Org. Chem.* **1976**, *41*, 1457.

[6] (a) Avenati, M.; Hagenbuch, J.-P.; Mahaim, C.; Vogel, P. *Tetrahedron Lett.* **1980**, *3167*. (b) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1819.

[7] (a) Jorgensen, W. L. *J. Am. Chem. Soc.* **1975**, *97*, 3082. (b) Jorgensen, W. L.; Borden, W. T. *Tetrahedron Lett.* **1975**, 223. (c) van Duijnen, P. T.; van der Ploeg, P.; Hogeveen, H.; Buurdeman, W. F. J. *Ibid.* **1975**, 573. (d) Hogeveen, H.; Huurdeman, W. F. J. *J. Am. Chem. Soc.* **1978**, *100*, 860. (e) Hogeveen, H.; Huurdeman, W. F. J.; Kok, D. M. *Ibid.* **1978**, *100*, 871.

[8] Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436.

[9] Norman, N.; Post, B. *Acta Crystallogr.* **1961**, *14*, 503.

[10] Chiang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 261.