(22) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).
(23) R. Roger, *J. Chem. Soc.*, 2168 (1932), reported $[\alpha]^{20}_D$ −154.5° (*c* 2.8, EtOH) for pure mandelic acid.
(24) (a) N. B. Lorette and J. H. Brown, *J. Org. Chem.*, **24**, 261 (1959); (b) N. S. Radin, A. K. Hajma, and Y. Akahori, *J. Lipid Res.*, **1**, 250 (1960).
(25) J. Dale and H. S. Mosher, *J. Org. Chem.*, **35**, 4002 (1970).

Photochemical Studies. 16.[1] Irradiation Induced Transformations of 1,2-Dihydrophthalimides and Related Compounds

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Norbornen-7-one-5,6-dicarboximides (**6a–c**) decarbonylate thermally and photochemically to the corresponding 1,2-dihydrophthalimides (**5**). The latter undergo the following wavelength and substitution dependent photochemical transformations via singlet excited states: fragmentation to benzene and benzamides (**7**), electrocyclic closure to *anti*-bicyclo[2.2.0]hex-2-ene-5,6-dicarboximides (**8**), a 1,2-acyl shift to bicyclo[3.1.0]hex-3-ene-2,6-dicarboximides (**10**), and a degenerate 1,5 shift which leaves **5** structurally unchanged. The triplet excited states, reached both by direct irradiation or sensitization, lead only to photodimers. A mechanism involving α cleavage via diradical intermediates is invoked for those photochemical processes in which the imide moiety takes active part.

We have recently embarked upon a detailed study[1,2] of the photochemical behavior of β,γ,δ,ε-unsaturated carbonyl compounds. This was spurred by our earlier findings on substituted 1,2-dihydrophthalic anhydrides[3] and imides[4] and by the recent upsurge in β,γ-unsaturated carbonyl photochemistry.[5]

After having dealt with 1,2-dihydrophthalic anhydride (**1**),[1] we wish now to report results to date of our investigation of the photochemistry of 1,2-dihydrophthalimide (**5a**) and some closely related compounds.[2]

A limited amount of information on some substituted 1,2-dihydrophthalimides was available at the start of this work. Thus, while irradiation of the 1,2,4,5-tetramethyl derivative (**5d**) had been said to cause (to an unspecified extent) electrocyclic closure accompanied by some fragmentation to durene,[6] no fragmentation was observed with the N-substituted derivatives[6] (**5e,f**) and no reaction at all with the tetraphenyl derivatives (**5g,h**).[4] On the other hand, the well delineated photochemical behavior of **1**[1] (Scheme I), fragmentation being the main and most efficient process, compelled us to examine similar systems, with the imides being first on the list.[2]

Results and Discussion

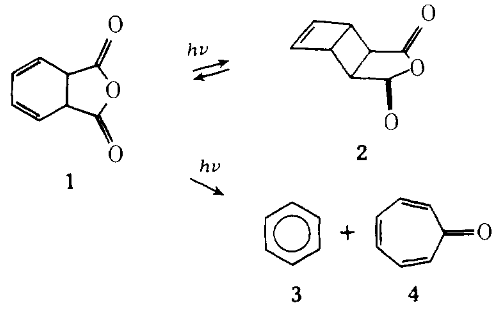
The precursors in this work were the norbornen-7-one-2,3-dicarboximides (**6**) obtained by cycloaddition of the corresponding maleimides to cyclopentadienone diethyl ketal.[1,7] Pyrolysis of **6** readily provided the 1,2-dihydrophthalimides (**5a–c**).

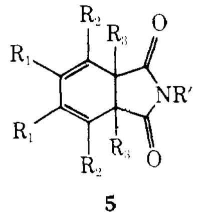
Exhaustive photolysis of the parent compound **5a** at 254 nm gave an unexpectedly variegated mixture of products (Scheme II), four of which were readily identified as benzene (**3**), benzamide (**7a**), *anti*-bicyclo[2.2.0]hexene-5,6-dicarboximide (**8a**), and phthalimide (**9a**). A fifth product was isolated and, following careful NMR analysis (^{1}H and ^{13}C) as elaborated below, was shown to be bicyclo[3.1.0]hex-3-ene-2,6-dicarboximide (**10a**). The respective yields at this and other wavelengths and irradiation conditions are given in Table I. The formation of an additional dimeric product was observed at higher wavelength or by sensitization and was suppressed by diene triplet quenching.

Irradiation with monochromatic light to low conversion of **5a** led to the following quantum yields for benzene formation: 0.016 (230 nm), 0.009 (257 nm) and 0.002 (284 nm). The product distribution was, in all cases, wavelength dependent as can be clearly deduced also from Tables I and II. The latter lists the yields of products from irradiation of **5c** in a variety of conditions. Furthermore, we present in Table III average yields of photoproducts obtained by irradiation of the various precursors **6** at 254 nm. We expected these data to be instructive and so they were, insofar as they showed **5** to be the key compound in the sequence leading, by further irradiation, to all other products, as depicted in Scheme II.

The efficient photodecarbonylation of **6** (e.g., $\phi_{6a}{}^{257} = 0.7$) resembles that of its anhydride analogue which has been discussed, and we shall not dwell on it. We focus our interest on the phototransformations of **5**. First the fragmentation processes. Using product isolation criteria alone and judging from the parallelism observed between benzene (**3**) and benzamide (**7**) yields, it is obvious that bond cleavage occurs as the primary step. One should recall that, of the scant literature on imide photochemistry, saturated imides were found

Scheme I





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	a	b	c	d	e	f	g	h
R_1	H	H	H	Me	Me	Me	Ph	Ph
R_2	H	H	H	H	H	H	Ph	Ph
R_3	H	H	H	Me	Me	Me	H	H
R′	H	Et	Ph	H	C_6H_{11}	*n*-Bu	H	Ph

Scheme II

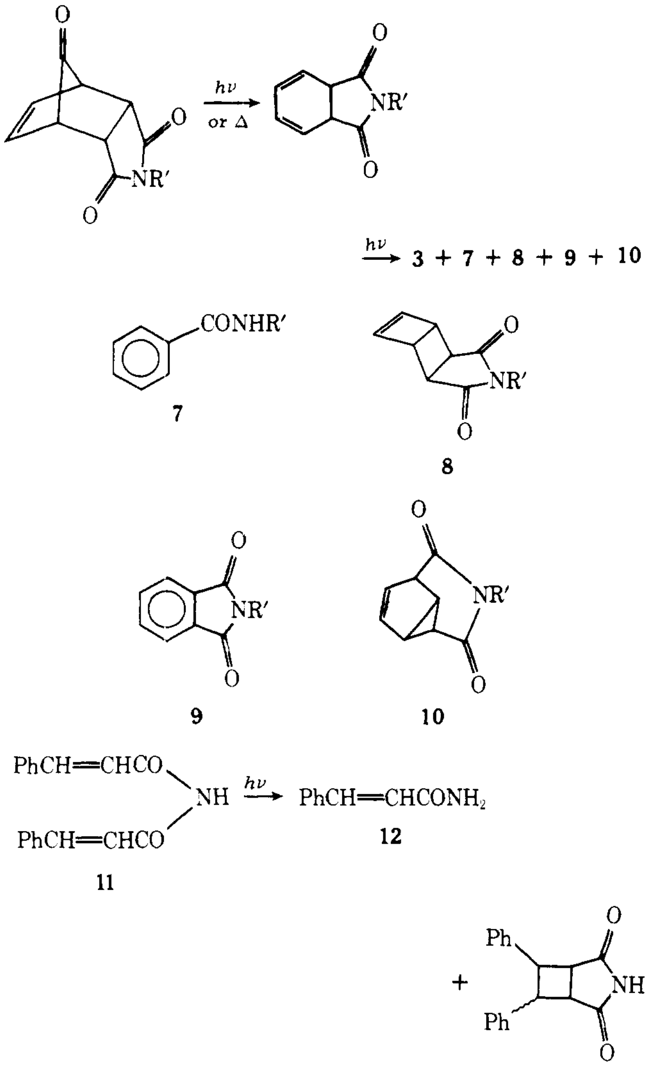


Table I. Average Yields (%) of Irradiation Products from 5a at Various Conditions[a] (Cf. Scheme I)

λ, nm	3	7a	8a	9a	10a	dimer
254	16	28	4	<1	24	
>270	<1	9	6		9	12
>310			5			80
>310 (acetone)[b]						85
>310 (acetophenone)[b]						70
>310 (cyclohexadiene)[c]			3			

[a] In acetonitrile or dioxane until disappearance of the starting material. [b] Sensitization experiments. [c] Quenching experiment.

Table II. Average Yields (%) of Irradiation Products from 5c at Various Conditions[a] (Cf. Scheme I)

λ, nm	3	8c	9c	10c	dimer
254	3	13	2	30	10
>270		22	5	11	30
>310		19	3		70[d]
>330			8		82
>310 (thioxanthone)[b]			2		66
>310 (chrysene)[b]			2		74
>310 (cyclohexadiene)[c]		14	2		

[a] In acetonitrile or dioxane, to maximum conversion. [b] Sensitization experiments. [c] Quenching experiment. [d] Two dimers were detected: 67% A (identical with that obtained in all other cases) + 3% B (identical with the thermal dimer from **5c**; see text).

Table III. Average Yields (%) of Irradiation Products from 6 at 254 nm[a]

R	5	3	7	8	9	10	dimer
H	4	10	22	3	1	18	
Et[b]	11	<1	6	10	3	30	
Ph	12	<1		9	4	9	7

[a] In acetonitrile, to maximum conversion. [b] Similar results were obtained with R = Me.

to undergo photofragmentation only in the gas phase[8] and cinnamimide (**11**) yielded in solution cinnamamide (**12**) besides undergoing internal cycloaddition.[9] Of all of the analogous cases to ours,[4,6,10-12] only **5d** was reported to undergo some (?) photofragmentation to durene.[6] Furthermore, benzamides were also never reported.

An additional feature that is worthy of mention at this point is the β,γ-unsaturated carbonyl character of the 1,2-dihydrophthalimides (**5**). This should express itself photochemically as well as spectroscopically.[5] The latter is indeed seen in Figure 1, where the electronic absorption spectrum of **5a** is compared to cyclohexadiene and hexahydrophthalimide. The additional red-shifted (CT) band is clearly observed.[5]

We feel compelled to explain the photofragmentation of **5a** and **5b** invoking an α cleavage to a diradical (Scheme III) followed by CO loss, with the resulting diradical undergoing a 1,3-hydrogen shift to yield the corresponding benzamide. Contrary to the photolysis of **1**,[1] no tropone (**4**) was detected, which we take as an indication that the initial diradical does not lose the R'NCO unit (vide infra) but only CO *in the primary step*, as postulated in Scheme III. This in fact brings us to another point, namely, the decrease of the fragmentation mode with increasing wavelength as well as with N-substitution. Indeed, from Table II one can see that *N*-phenylbenzamide was never isolated, not even at 254 nm when small yields of benzene are still observed. We attribute this to an increased

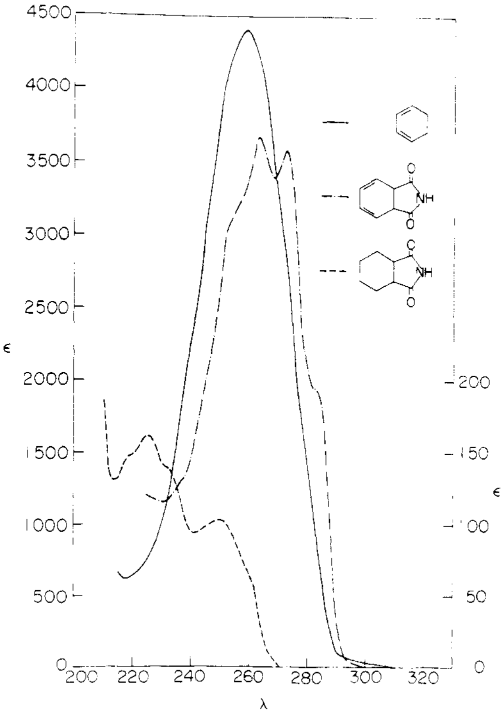
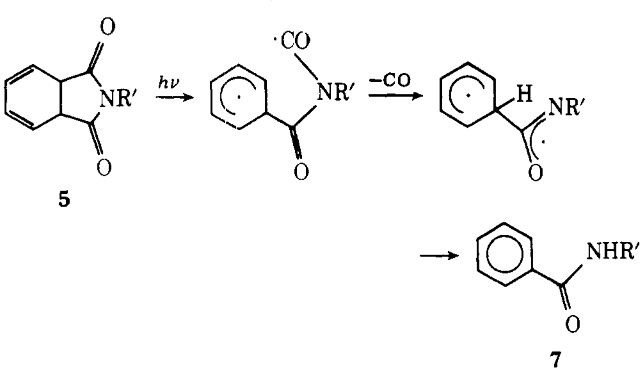


Figure 1. Electronic absorption spectra of 1,2-dihydrophthalimide and, for the sake of comparison, 1,3-cyclohexadiene and perhydrophthalimide (the spectrum of the latter saturated compound follows the ε scale on the right).

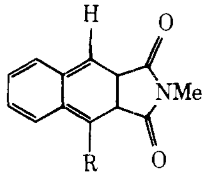
Scheme III



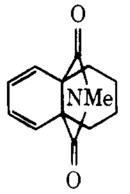
delocalization of the radical when the nitrogen is substituted, especially with a phenyl group. This presumably suppresses hydrogen migration vs. cleavage or recombination (vide infra). Finally, the fact that in all of the known literature cases[6,10–12] which dealt with UV irradiation of imides substituted at both angular positions no benzamides were reported provides circumstantial support to our postulation of an intramolecular 1,3-hydrogen shift (Scheme III).

We may proceed now to the next transformation, namely, electrocyclic closure of **5** to *anti*-bicyclo[2.2.0]hex-2-ene-5,6-dicarboximide (**8**). The process per se is well documented,[13] and its first photochemical version in dihydrophthalic derivatives was reported by van Tamelen et al.,[14] who obtained **2** by irradiation of **1**. The subsequent course of events was recently reviewed and discussed.[1] To return to our case, carefully monitored photolysis to low conversion showed that while at 230 nm no bicyclo[2.2.0]hexene product **8a** was formed, at 257 nm the ratio of **8a**/**7a** was 1 and became 3 at 284 nm. This again resembles the observations made in the anhydride series,[1] where the analogous bicyclo[2.2.0]hexene product **2** also accumulated at higher wavelength due to its increasing transparency in that irradiation range. On the other hand, due to the reversibility of the electrocyclic transformation **5** $\rightleftarrows$ **8**, low wavelength irradiation of **8a** leads inevitably to the formation of the other products, notably to **10a**, which is largely photostable.

One further point of interest is the stereochemistry of this process. There are two possible modes of disrotatory closure of **5** to give accordingly the *syn*- and *anti*-bicyclo[2.2.0]hexene products. In the case of the anhydride **1**, exclusive formation of the anti product **2** was proven[14b] and confirmed.[1] Subsequently, however, irradiation of **5d–f**,[6] **13a**,[11] and **14**[12] led in each case to mixtures of *syn*- and *anti*-bicyclo[2.2.0]hexene derivatives. We had therefore to provide both proof and rationalization of our results.



13a, R = H
b, R = Ph



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The first was done by both chemical and physical means. Treatment of the anhydride **2** with aniline gave, after thermal imide closure, a product identical in all respects with **8c**, proving its anti configuration. Moreover, a comparative physical study was performed since some data for the syn isomer of **8c** were available from a previous independent synthesis.[15] Thus, the melting point of **8c** is 152 °C, while that of the syn isomer was reported[15] to be 136 °C. NMR chemical shift data are given in Table IV, and their consistency with the above assignment speaks for itself. The rationale for this behavior is, it seems to us, of purely steric origin. Thus, in the absence of angular substitution the anti isomers **8** are clearly preferred, whereas the presence of angular substituents as in **5d–f**, **13a**, and **14** introduces torsional strain in the anti form, and this apparently brings about a more even-handed distribution of syn and anti isomers.[6,11,12]

Table IV. Chemical Shifts (δ) of Protons in 8 (Cf. Scheme I)

	R	config	$H_{1,4}$	$H_{2,3}$	$H_{5,6}$	ref
	Ph	syn	3.79	3.51	6.36	15
8c	Ph	anti	3.59	3.25	6.42	*b*
8a	H	anti	3.57	3.17	6.43	*b*
8b	Et	anti	*a*	3.02	6.45	*b*

[a] Overlaps with CH_2. [b] This work.

We consider the most interesting transformation of **5** to be that leading to bicyclo[3.1.0]hex-3-ene-2,6-dicarboximide (**10**). The structure proof was not simple and was reached by painstaking ^1H NMR studies involving extensive double irradiations (Figure 2) as well as ^{13}C NMR measurements (Figure 3) of **10c**. At this point we had to rationalize the formation of **10**, and the most likely hypothesis to start with was an oxadi-π-methane type mechanism.[5,16] This, however, was

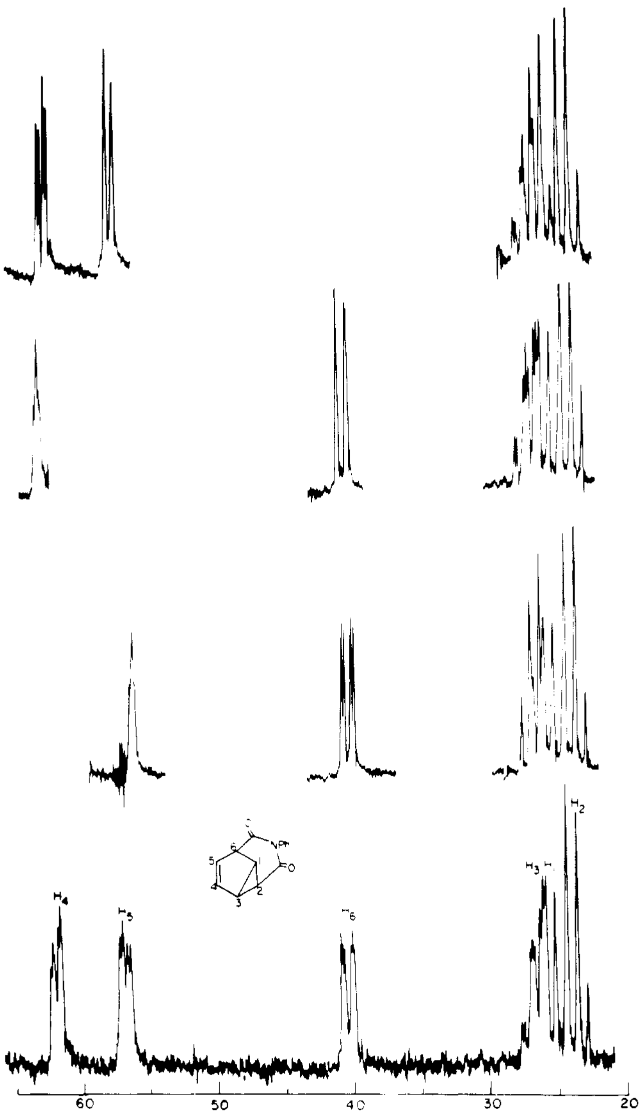


Figure 2. ^1H NMR spectrum (at the bottom) of **10c**, including proton assignments as derived from the three upper double irradiation spectra at the frequencies of H-4, H-5, and H-6, respectively.

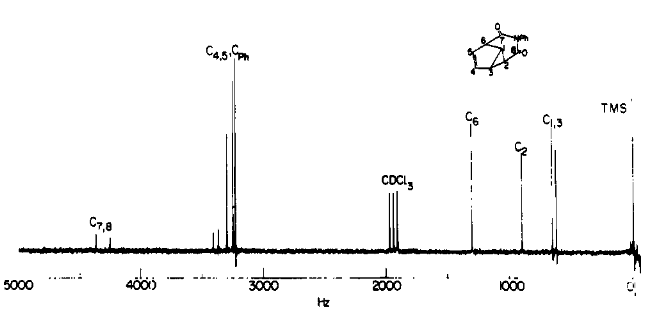
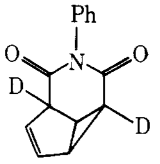


Figure 3. ^{13}C NMR spectrum of **10c**.

formally possible in two modes of bonding accompanying the 1,2 shift (Scheme IV): (a) 1,5 bonding in a "classic" oxadi-π-methane rearrangement,[5,16] and (b) 1,3 bonding in a vinylogous one, i.e., involving the entire diene moiety. Interestingly, both modes provide *structurally* identical products. Deuterium labeling was considered as an adequate probe for this problem since the protons in **10** had well-resolved and reliably assigned proton magnetic resonances (vide supra and Figure 2). Hence, base-catalyzed deuteration of **5c** readily gave **15**, which was irradiated at 254 nm. The 1,2-shift product was isolated and unequivocally proven to be **16** to the extent of ~70%; the remaining 30% had the deuteria scrambled over all of the possible positions in the molecule, and we shall return to this point later. We found the first mentioned result rewarding insofar as it provided a clear indication that mode "β" (Scheme IV) obtains.

In fact, this type of shift was without precedent apart from two contemporary and independent cases, namely, the photoconversion of **13** to **17**[11] and of **14** to **18**.[12] However, in each of these starting materials there is substitution which may be suspected to introduce bias in its behavior. Thus, in the transformation **13** → **17**,[11] the ensuing aromatization is bound to play a crucial role in directing the cyclopropane closure in 1,3 and not 1,5 fashion (as would be required by a classic oxadi-π-methane rearrangement). Our labeling experiment definitively settles this question in the simplest and therefore most general case of the parent compound **5**, **15**. Moreover, the position of the labels in **16** rules out unequivocally sundry other hypothetical possibilities of bicyclo[3.1.0]hexene formation such as by $_{\pi}2_s + {}_{\pi}4_a$ closure of a cyclohexadiene → hexatriene type product (**19**).[12] This would require the labels



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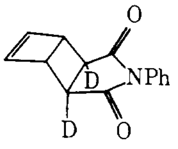

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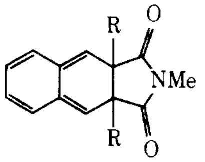


22, R = -CH$_3$; -(CH$_2$)$_4$-

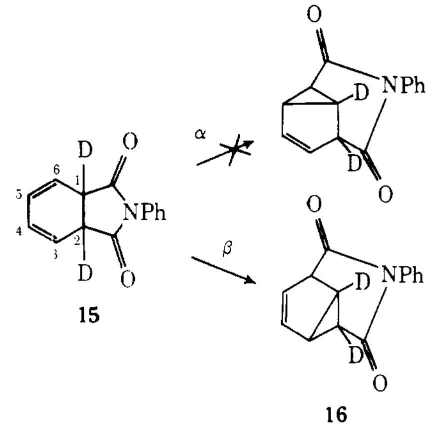
as in **20**, contrary to the experimental results. In fact, we strongly endorse the postulate that such a conrotatory opening of cyclohexadiene is highly improbable when an imide ring, as in **5**, **15**, or an anhydride ring, as in **1**,[14] is fused to it, and to our knowledge there is only one claimed violation of this postulate.[12]

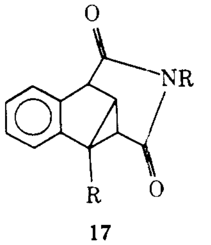
We return now to the above-mentioned 30% scrambling of the deuterium labels around the system in **16**. We proceeded to examine two further compounds from the irradiation mixture, namely, the starting material **15** and the bicyclo[2.2.0]hexene derivative **21**. Both exhibited the deuterium labels in the α positions (to the carbonyls) to the same extent of 70% as in **16**, the rest being dispersed in *all* other possible positions.

Our only explanation to this finding is that an additional photoinduced process is taking place, a degenerate imide rearrangement around the six-membered ring in **5**. This can be thought of formally as a series of 1,5 shifts, although consecutive 1,3 shifts could also be invoked (Scheme V). Interestingly, a *thermal* 1,5 shift had been reported in some related compounds (**22**).[11] To check this point, **15** was heated at 120 °C for 20 h. No structural changes and no deuterium scrambling in the starting material were detected. On prolonged heating the only product was a dimer, identical with photodimer B (cf. Table II).

Concerning the mechanisms of these two, viz., 1,2 and 1,5 rearrangements (cf. Schemes IV and V), the main question is, of course, whether they occur in concerted fashion or via diradical intermediates as invoked in the fragmentation processes (vide supra). Attempts to probe into this problem were made by irradiation of **5c** in the presence of tri-*n*-butylstannum hydride. Only **8c** was isolated, of the various irradiation products described in Scheme II. The rest was a mixture of ill-defined tin-containing compounds, but none

Scheme IV





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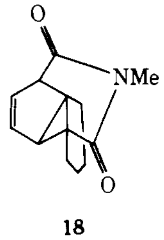

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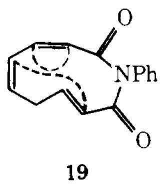

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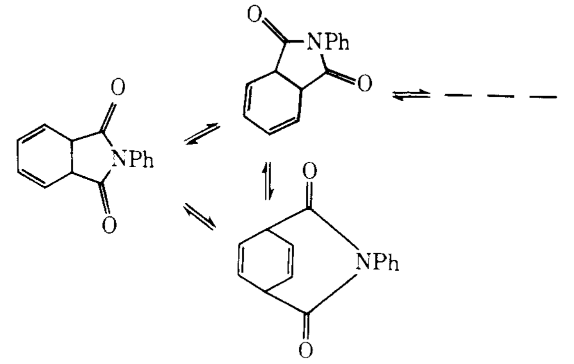
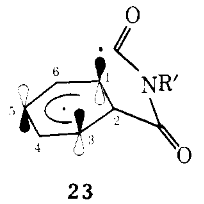
Scheme V





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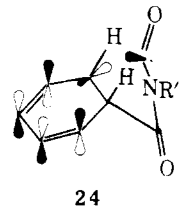

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Table V. Average Yields (%) of Irradiation Products from 5c at 254 nm in Different Solvents[a]

	product			
solvent	8c	10c	dimer A	other products[b]
isooctane	2	9	36	
acetonitrile	13	30	10	
methanol	26	30	<1[c]	8[d]

[a] In Rayonet photoreactors, 22 h. [b] In all cases, *N*-phenylphthalimide and starting material were isolated in up to 5 and 10%, respectively. [c] Could be increased by prolonged irradiation, whereby the yields of 8c and 10c diminished considerably and ill-defined decomposition byproducts were formed. [d] *N*-Phenylmethylurethane (up to 13%[c]).

of the expected radical reduction products. Still, the suppression of the rearrangement to **10** along with the fragmentation to benzene is taken to suggest that α cleavage occurs in both processes.

Although this is by no means a definitive assignment, a few words of theoretical backing are in order. The rejection of an allyl radical as an intermediate in the classic oxadi-π-methane rearrangement[5,16] was mainly based on the fact that its conversion to a cyclopropyl radical is thermodynamically largely unfavorable.[25] However, the pentadienyl radical is 14 kcal/mol less stable than the cyclopentenyl radical.[17] Moreover, the activation energy for the opening of the latter (38 kcal/mol) is substantially higher than that for the ring closure (24 kcal/mol).

While we deal with the more strained bicyclo[3.1.0]hexene system,[18] the latter is no stranger though to the organic photochemist. It is readily formed in cycloaddition reactions,[19] in ring closure of conjugated trienes,[13b,20] in di-π-methane rearrangements,[21] and of course, cyclohexadienone rearrangements.[22-24] In several such cases, diradical intermediates were proven or suggested, and for our case of invocation of α cleavage as a primary step in the 1,2 rearrangement, some circumstantial evidence is obtained from the interesting parallelism observed between the yields of **10a** and **10c** and the appropriate fragmentation products (benzene and benzamide) (cf. Table I). Still in this context and going back to the closing mode discussed above, the compulsory disrotatory bicyclo[3.1.0]hexene closure is readily envisaged from the HOMO (SOMO) **23** as a 1,3- rather than a 1,5-bond formation (cf. Scheme IV). To be sure, such a mechanism could be probed into by studying the 1,2 photorearrangement of an optically active substrate in order to establish whether bond formation is indeed accompanied by racemization at position 1. A concerted formal cycloaddition process would be of the $_{\pi}4_s + {}_{\sigma}2_a$ type and would involve inversion at position 1 in **24**. This problem is now under scrutiny.[26]

A recent refinement in the theory of photochemical reactions[27] seems to provide additional support to our interpretation involving the intermediacy of diradicals since the relevant species in our study embody considerable chemical dissymmetry between the two odd electron sites, which is bound to bring about a large charge separation.[27] A tetratopic reaction[28] then obtains, and a pronounced solvent effect was indeed observed (Table V). In the case of methanol, the enhanced photofragmentation is unmistakably proven by the isolation of up to 13% of *N*-phenylmethylurethane.

As to the multiplicity of the excited states, we take the results of our sensitization and quenching experiments as a clear indication that the photofragmentation and -rearrangement processes occur via n,π^* singlet excited states. On the other hand, the evidence at hand suggests that the excited states leading to the various photodimers are π,π^* triplets, the trends being enhanced intersystem crossing and lower triplet energies with N-substitution in **5**. We prefer, however, to wait for a further accumulation of spectroscopic data, now underway, before making definitive assignments.

Experimental Section

Spectrometric work was performed on the following instruments: UV, Cary-17; IR, Perkin-Elmer 257 and 177; ^{1}H NMR, Jeol-JNM-C-60 HL and Varian HA-100; ^{13}C NMR, Brucker WH-90; MS, Du-Pont 21-491 B.

Preparative photolyses were carried out in Rayonet reactors using 254-, 300-, and 350-nm lamps. Monochromatic irradiations were performed at 230, 257, and 284 nm, and quantum yield determinations were done using a Jasco CRM-FA Spectro-Irradiator equipped with a 2-kW Xenon lamp, monochromator, and electronic integrator. The latter was periodically calibrated by potassium ferrioxalate actinometry. Samples were deoxygenated prior to irradiation by purging the solution with nitrogen or argon.

Elemental analyses were carried out by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Materials. Norborn-5-en-7-one-2,3-dicarboximide (6a). A solution of maleimide in acetone was added to an equimolar solution of cyclopentadienone diethyl ketal in petroleum ether,[1,7] and the mixture was stirred overnight at room temperature. The solvents were removed under reduced pressure, and the residue was triturated with a mixture of cyclohexane–ether. Recrystallization from the same solvents gave the adduct, i.e., the diethyl ketal of **6a** (60–70%): mp 116–117 °C; IR (KBr) 1710, 1780 cm^{-1} (CO); ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 1–1.3 (6 H, 2t), 3.2–3.65 (8 H, m), 6.15 (2 H, m), 8.7 (1 H, s); MS *m/e* 251 (M$^+$). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.2; H, 6.76; N, 5.58. Found: C, 62.35; H, 6.87; N, 5.60.

Deketalization was accomplished by refluxing a solution of the above adduct (3 g) and BF$_3$ etherate (1 mL) in acetone (100 mL) for 3 h. After evaporation of the solvent, the residue was triturated with and then recrystallized from ether to give the keto imide **6a** (90–100%): mp 168–169 °C; IR (KBr) 1700, 1780, 1815 cm^{-1} (CO); UV (MeCN) (ϵ) 274 (30), 253 (130) nm; ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 3.5 (4 H, m), 6.6 (2 H, m); MS *m/e* 177 (M$^+$). Anal. Calcd for $C_9H_7NO_3$: C, 61.01; H, 3.96; N, 7.91. Found: C, 60.60; H, 4.11; N, 7.92.

Norborn-5-en-7-one-2,3-dicarbox-*N*-ethylimide (6b) was prepared along the same lines as above, starting with *N*-ethylmaleimide. The ketone **6b** was finally recrystallized from ether: mp 110–112 °C; IR (KBr) 1710, 1800, 1850 cm^{-1} (CO); UV (MeCN) (ϵ) 270 sh (35), 250 (180) nm; ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 1.0 (3 H, t), 3.26–3.6 (6 H, m), 6.45 (2 H, m); MS *m/e* 205 (M$^+$).

Norborn-5-en-7-one-2,3-dicarbox-*N*-phenylimide (6c) was obtained as above, starting with *N*-phenylmaleimide. The keto imide **6c** was recrystallized from acetone (overall yield 70%): mp 164 °C dec; IR (CHCl$_3$) 1710, 1790, 1830 cm^{-1} (CO); UV (MeCN) (ϵ) 280 sh (80), 255 (580) nm;^{1} NMR (CDCl$_3$) δ_{Me_4Si} 3.6 (4 H, m), 6.6 (2 H, m), 7.75 (5 H, m); MS *m/e* 253 (M$^+$). Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.15; H, 4.35. Found: C, 71.15; H, 4.40.

1,2-Dihydrophthalimide (5a). A solution of **6a** in xylene (100 mL) was refluxed under nitrogen for 2 h. The solvent was removed in vacuo at room temperature and the residue crystallized from ether (75%): mp 128 °C; IR (KBr) 1700, 1765 cm^{-1} (CO); UV (MeCN) (ϵ) 271 (3570), 262 (3670) nm; ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 3.78 (2 H, m), 5.9 (4 H, m), 9.3 (1 H, s); MS *m/e* 149 (M$^+$). Anal. Calcd for $C_5H_7NO_2$: C, 64.43; H, 4.70. Found: C, 64.13; H, 4.81.

***N*-Ethyl-1,2-dihydrophthalimide (5b)** was prepared along the same lines as above (oil): IR (neat) 1700, 1775 cm^{-1} (CO); ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 1.1 (3 H, t), 3.35–4.65 (4 H, m), 5.9 (4 H, m); MS *m/e* 177 (M$^+$).

***N*-Phenyl-1,2-dihydrophthalimide (5c)** was obtained as above: mp 115 °C (ether); IR (CHCl$_3$) 1710, 1785 cm^{-1} (CO); UV (MeCN) (ϵ) 271.5 (3500), 262 (3850) nm; ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 3.9 (2 H, m), 6.0 (4 H, m), 7.3 (5 H, m); MS *m/e* 225 (M$^+$).

***N*-Phenyl-1,2-dideuteriophthalimide (15).** A mixture of **5c** (350 mg), D_2O (3 mL), and anhydrous K_2CO_3 (55 mg) was homogenized by adding dry dioxane and stirred overnight at room temperature. Dry NaCl was added, and the mixture was thoroughly extracted with benzene. The organic solution was washed with deuterium oxide and dried. After evaporation and recrystallization from ether, the dideuterio derivative **15** was obtained (43%), mp 115 °C. ^{1}H NMR and MS showed virtually complete deuteration in the angular positions.

Photolyses. Quantum and chemical yields of benzene were determined by irradiation of the imide in MeCN followed by passing the solution over a short column of basic alumina (activity I).[1] Only benzene was eluted and determined quantitatively by UV spectroscopy (cf. text and Tables I–III).

All other photoproducts were determined by quantitative isolation using mainly chromatographic resolution followed by structural analysis. Yields are given in Tables I–III.

Irradiation of the Keto Imides 6. The keto imide **6a** (500 mg) in MeCN (130 mL) was photolyzed at 254 nm until maximum conversion (~24 h), as monitored by measuring periodically the characteristic IR absorption of the bridge carbonyl. The solvent was removed under reduced pressure, and the residue was resolved using preparative thin-layer chromatography on silica gel plates (Merck) by repeated elution with $CHCl_3$. The following consecutive bands were scraped off and extracted ($CHCl_3$): (1) phthalimide (**9a**), mp 238 °C, identical with an authentic sample; (2) bicyclo[3.1.0]hex-3-ene-2,6-dicarboximide (**10a**) [mp 156–158 °C (acetone); IR (KBr) 1680, 1715 cm^{-1} (six-membered imide carbonyl); ^{1}H NMR ($CDCl_3$) δ_{Me_4Si} 2–2.8 (3 H, m), 3.86 (1 H, d), 5.65 (1 H, dd), 6.1 (1 H, dd), 8.6 (1 H, s); MS *m/e* 149 (M$^+$)]; (3) two compounds were isolated after rechromatographing this band, 1,2-dihydrophthalimide (**5a**), identical with an authentic sample, and *anti*-bicyclo[2.2.0]hex-2-ene-5,6-dicarboximide (**8a**) [mp 200 °C (acetone); IR (KBr) 1740, 1790 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ_{Me_4Si} 3.17 (2 H, m), 3.57 (2 H, m), 6.45 (2 H, m); MS *m/e* 149 (M$^+$). Anal. Calcd for $C_8H_7NO_2$: C, 64.43; H, 4.70. Found: C, 64.34; H, 4.78.]; (4) this last band provided, after rechromatography, starting material and benzamide (**7a**), mp 130 °C, identical with an authentic sample.

The keto imides **6b** and **6c** were irradiated at 254 nm and worked up along similar lines as above (elution was done using benzene–chloroform mixtures). The photoproducts of **6b** were in the following order: *N*-ethylphthalimide (**9b**), mp 67–70 °C, identical with an authentic sample; *N*-ethyl-1,2-dihydrophthalimide (**5b**), identical with an authentic sample (vide supra); *N*-ethyl-*anti*-bicyclo[2.2.0]hex-2-ene-5,6-dicarboximide (**8b**) [^{1}H NMR (CCl_4) δ_{Me_4Si} 1.0 (3 H, t), 3.02 (2 H, m), 3.3–3.8 (4 H, m), 6.45 (2 H, m); MS *m/e* 177 (M$^+$)]; *N*-ethylbicyclo[3.1.0]hex-3-ene-2,6-dicarboximide (**10b**) [^{1}H NMR (CCl_4) δ_{Me_4Si} 1.1 (3 H, t), 2.0–2.8 (3 H, m), 3.3–3.9 (3 H, m), 5.45 (1 H, m), 6.05 (1 H, m); MS *m/e* 177 (M$^+$)]; starting material and finally *N*-ethylbenzamide (**7b**) were isolated.

Irradiation of **6c** gave the following: *N*-phenylphthalimide (**9c**) and *N*-phenyl-1,2-dihydrophthalimide (**5c**), identical with their respective authentic samples; *N*-phenyl-*anti*-bicyclo[2.2.0]hex-2-ene-5,6-dicarboximide (**8c**) [mp 151 °C (ether); IR (KBr) 1700, 1770 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ_{Me_4Si} 3.25 (2 H, m), 3.59 (2 H, m), 6.42 (2 H, m), 7.6 (5 H, m); MS *m/e* 225 (M$^+$)]; *N*-phenylbicyclo[3.1.0]hex-3-ene-2,6-dicarboximide (**10c**) [mp 192 °C (acetone); IR (KBr) 1675, 1720 cm^{-1} (CO six-membered imide); ^{1}H NMR ($CDCl_3$) δ_{Me_4Si} 2.3–2.8 (3 H, m), 4.05 (1 H, md), 5.7 (1 H, dd), 6.2 (1 H, md), 7.0–7.4 (5 H, m); also cf. Figure 2 for spectrum and double irradiations; MS *m/e* 225 (M$^+$). Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.66; H, 4.89. Found: C, 74.35; H, 4.94.]; starting material came next and finally a higher molecular weight product which turned out to be a dimer of **5c** (A) (vide infra and Table II) [mp 278 °C (benzene); IR (KBr) 1710, 1775 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ_{Me_4Si} 2.5–2.7 (8 H, m), 6.0 (2 H, m), 6.5 (2 H, m), 7.1–7.5 (10 H, m); MS *m/e* 450 (M$^+$), 225 (M/2$^+$)].

Irradiations of the 1,2-Dihydrophthalimides 5a and 5c (Cf. Tables I and II). Similar procedures to those described above were followed for the corresponding ketones **6a** and **6c**, using UV spectroscopy as the monitoring technique, and the same products were obtained except that an additional photodimeric product was obtained from the irradiation of **5a** at $\lambda > 270$ nm: mp 280 °C (acetone–benzene); IR (KBr) 1700, 1780 cm^{-1} (CO); ^{1}H NMR (acetone-d_6) δ_{Me_4Si} 2.8–3.8 (8 H, m), 5.85 (2 H, m), 6.3 (2 H, m); MS *m/e* 298 (M$^+$), 149 (M/2$^+$). The same dimer was exclusively obtained on sensitized irradiation of **5a**.

Similarly, irradiation of **5c** provided the same products as in the above described photolysis of **6c**, but in different wavelength dependent yields. In addition to that, at 310 ± 20 nm the dimeric fraction contained, besides the known dimer A (vide supra and Table II), a small amount of a second dimer B: mp 325 °C; IR (KBr) 1710, 1770 cm^{-1} (CO); MS *m/e* 459 (M$^+$), 225 (M/2$^+$). However, all sensitized irradiations provided only the dimer A.

Irradiations of **5c** were performed in two additional solvents (Table V). In methanol this resulted in a notable increase in the yield of **8c** and **10c** with only traces of dimer, but with formation of phenylurethane in 8% yield, identical with an authentic sample obtained by treatment of phenyl isocyanate with methanol. In isooctane a sharp increase in dimer yield was observed with a parallel decrease in that of the rearrangement products **8c** and **10c** (Table V).

It should be noted that, as ascertained in blank experiments, small amounts of phthalimides (~2%) are formed in the course of the workup from the starting dihydrophthalimides.

To end this chapter, we mention that the photolysis of the dideuterated derivative of **5c** (**15**) was conducted entirely analogously to that described above and followed by careful ^{1}H NMR analysis of the residual starting material and products **16** and **21**. A 30% deuterium scrambling was observed, 70% being retained in the shown positions in **15**, **16**, and **21**.

Conversion of *anti*-Bicyclo[2.2.0]hex-2-ene-5,6-dicarboxylic Anhydride (2) to 8c. A mixture of the anhydride **2** (33 mg) and aniline (4 mL) was heated in a nitrogen atmosphere for 20 h. The solvent was removed in vacuo, and the residue was purified by preparative thin-layer chromatography. The only product was identical with the photoproduct **8c** obtained by irradiation of **5c** and **6c**.

Thermal Treatment of 15. A solution of the dideuterio derivative **15** (47 mg) in $C_2D_2Cl_4$ (0.6 mL) in an NMR tube was deoxygenated by sweeping it with helium and subsequently heating at 120 °C for 20 h. No deuterium scrambling was detected in its ^{1}H NMR spectrum. After a week at this temperature, a dimer was formed (50%), mp 325 °C, identical with photodimer B described above.

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Registry No.—**2,** 68366-13-2; **3,** 71-43-2; **5a,** 4436-48-0; **5b,** 68307-70-0; **5c,** 68307-71-1; **6a,** 68307-74-4; **6a** diethyl ketal, 68307-75-5; **6b,** 68307-76-6; **6c,** 68307-77-7; **7a,** 55-21-0; **7b,** 614-17-5; **8a,** 68366-11-0; **8b,** 68307-72-2; **8c,** 68366-12-1; **9a,** 85-41-6; **9b,** 5022-29-7; **9c,** 520-03-6; **10a,** 68307-68-6; **10b,** 68307-73-3; **10c,** 68307-69-7; **15,** 68307-78-8; aniline, 62-53-3; maleimide, 541-59-3; cyclopentadienone diethyl ketal, 2931-32-0; *N*-ethylmaleimide, 128-53-0; *N*-phenylmaleimide, 941-69-5; *N*-phenylmethylurethane, 2621-79-6.

References and Notes

(1) Part 15: B. Fuchs and G. Scharf, *Isr. J. Chem.*, **16,** 335 (1977), and references cited therein.

(2) (a) Part of this work was reported in preliminary form: G. Scharf and B. Fuchs, *J. Chem. Soc., Chem. Commun.*, 244 (1975). (b) Taken in part from the Ph.D. Thesis of G. Scharf, Tel-Aviv University, 1975.

(3) B. Fuchs, *J. Chem. Soc. C*, 68 (1968); *Isr. J. Chem.*, **3,** 44 (1965).

(4) B. Fuchs, *Isr. J. Chem.*, **6,** 517 (1968).

(5) (a) W. G. Dauben, G. Lodder, and J. Ipaktschi, *Top. Curr. Chem.*, **54,** 73 (1975); (b) K. M. Houk, *Chem. Rev.*, **76,** 1 (1976).

(6) J. B. Bremner and R. N. Warrener, *Chem. Commun.*, 926 (1967).

(7) P. E. Eaton and R. H. Hudson, *J. Am. Chem. Soc.*, **87,** 2769 (1965).

(8) G. Choudhary, A. M. Cameron, and R. A. Back, *J. Phys. Chem.*, **72,** 2289 (1968).

(9) R. T. Lalonde and C. B. Davis, *Can. J. Chem.*, **47,** 3250 (1969).

(10) D. W. Jones and G. Kneen, *J. Chem. Soc., Chem. Commun.*, 1038 (1972); *J. Chem. Soc., Perkin Trans. 1*, 175 (1975).

(11) D. W. Jones and G. Kneen, *Chem. Commun.*, 1356 (1971); *J. Chem. Soc., Perkin Trans. 1*, 171 (1975).

(12) J. M. Ben-Bassat and D. Ginsburg, *Tetrahedron*, **30,** 483 (1974).

(13) (a) G. B. Gill and M. R. Willis, "Pericyclic Reactions", Chapman and Hall, London 1974; (b) W. G. Dauben, M. S, Kellog, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33,** 197 (1973); (c) P. Courtot, "Elements de Photochimie Avancée", Hermann, Paris, 1972, p 187.

(14) (a) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85,** 3296 (1963); (b) E. E. van Tamelen, S. P. Pappas, and K. L. Kirk. *ibid.*, **93,** 6092 (1971).

(15) E. K. G. Schmidt, L. Bremner, and R. Pettit, *J. Am. Chem. Soc.*, **92,** 3240 (1970).

(16) S. S. Hixson, P. S. Mariano, and E. H. Zimmerman, *Chem. Rev.*, **73,** 531 (1973).

(17) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88,** 241 (1966).

(18) R. Sustmann and F. Lübbe, *Chem. Ber.*, **109,** 444 (1976); *Tetrahedron Lett.*, 2831 (1974).

(19) S. Boué and R. Srinivasan, *Mol. Photochem.*, **4,** 93 (1972).

(20) A. Padwa and S. Clough, *J. Am. Chem. Soc.*, **92,** 5803 (1970).

(21) (a) H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schroder, *J. Am. Chem. Soc.*, **93,** 3653 (1971); (b) J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *ibid.*, **93,** 4804 (1971).

(22) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8,** 1 (1969).

(23) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sontag, *J. Am. Chem. Soc.*, **90,** 2990 (1968).

(24) J. Griffiths and H. Hart, *J. Am. Chem. Soc.*, **90,** 3297, 5296 (1968).

(25) O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46,** 1317 (1968).

(26) For a recent discussion and leading references on the "methane carbon" stereochemistry in the classic oxadi-α-methane rearrangement, see W. G. Dauben, G. Lodder, and J. D. Robbins, *J. Am. Chem. Soc.*, **98,** 3030 (1976).

(27) L. Salem, *Science*, **191,** 822 (1976).

(28) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8,** 41 (1975).