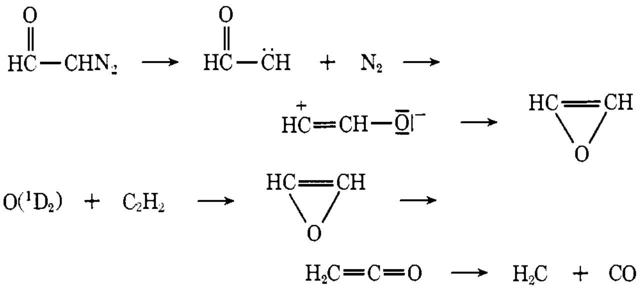
discussed above were examined using the computed orbital energy levels. The diazo ketones and the carbene and zwitterion intermediates have poor symmetry properties; the only symmetry element present is the plane of the NCCO or CCO skeleton of the molecule. Symmetry correlation diagrams have been constructed for the transformations, some of which are shown in Figures 11 and 12. All these processes are allowed and follow the lowest energy pathways. Interestingly the addition of $O(^1D_2)$ atoms to dimethylacetylene is forbidden (Figure 13), but the symmetry relations for the other processes are unaffected by methylation.



In conclusion it should also be mentioned that the present calculations on the four ketocarbenes, $HCO\ddot{C}H$, $CH_3CO\ddot{C}H$, $HCO\ddot{C}CH_3$, and $CH_3CO\ddot{C}CH_3$, and their zwitterion valence isomers, indicate a singlet ground state for these species. This prediction is based on Hoffmann's empirical rule[5,10] that when the optimum σ^2 configuration has an EHMO energy less than about 1.5 eV below the σp configuration at the same >C: angle, then the ground state is likely to be the triplet. From the data in Figures 1–3 it is seen that the first excited states of the species in question are all higher than the ground state, by at least 1.4 eV; this is consonant with accumulated laboratory experience on ketocarbenes concordantly pointing to the existence of a singlet ground state. Further *ab initio* MO studies are in progress.

Acknowledgments. We thank the National Research Council of Canada for financial support.

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(10) R. Hoffmann, G. D. Zeiss, and G. W. V. Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

Photochemistry of Nonconjugated Bichromophoric Systems.[1] Intramolecular Photocycloaddition of *N,N'*-Alkylenedimaleimides in Solution

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Abstract: The photochemical behavior of a series of *N,N'*-alkylenedimaleimides in solution is studied. Upon excitation, an intramolecular cycloaddition or an intermolecular polyaddition can occur. For compounds with chain lengths ranging from three to six methylene units, almost quantitative cyclomerization to a tetracycloadduct was observed. The quantum efficiencies vary from 0.42 for *N,N'*-hexamethylenedimaleimide to 0.62 for *N,N'*-trimethylenedimaleimide in dichloromethane. The absorption spectra of the bifunctional compounds are very similar to that of the monofunctional *N*-butylmaleimide; only a very slight hypochromism for the bichromophores with a shorter chain length is observed. No fluorescence, neither from the bifunctional nor from the monofunctional derivatives, could be detected. While the dimerization of *N*-butylmaleimide is found to proceed through the triplet excited state, the intramolecular cycloaddition occurs from the singlet state. It is proposed that the reaction proceeds through an excited state complex, formed upon excitation of one of the maleimide rings. Rate constants for exciplex formation are calculated and found to be of the order of 10^9 sec^{-1}, which is in the same range as the rate constants for intramolecular excimer formation, determined in other systems. It is suggested that the possibility of intramolecular exciplex formation is limited ultimately by the probability to obtain a favorable conformation, within the lifetime of the singlet excited state. The process is reversible and the equilibrium is shifted to the complex only if it is stabilized sufficiently, bond formation being the extreme.

During the last years, much attention has been paid to nonconjugated bichromophoric systems, since the photochemical properties of a chromophore may change appreciably, when two such groups are incorporated in the same molecule. In the bichromophoric molecule, processes may occur which do not take place, or only to a limited extent, in a solution of the monofunctional derivatives, even at high concentrations. The same possibility exists in polychromophoric systems. Bifunctional molecules are therefore good model compounds for the study of the photochemical behavior of macromolecules. The complicated photochemistry of biological polymers such as RNA and DNA could be explained to a certain extent, by the study of bichromophoric models.[4]

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(1) For previous papers in this series, see (a) F. C. De Schryver and J. Put, *Angew. Chem., Int. Ed. Engl.*, **8**, 213 (1969); (b) L. Leenders and F. C. De Schryver, *ibid.*, **10**, 338 (1971).

(2) (a) Nationaal Fonds voor Wetenschappelijk Onderzoek, predoctoral fellow, 1968–1972; (b) abstracted from the doctoral dissertation of J. Put, University of Leuven, Jan 1972; presented in part at the 6th International Photochemistry Conference in Bordeaux, Sept 1971.

(3) Address inquiries to this author.

(4) For a recent review of this photochemistry, see A. A. Lamola and J. Eisinger in "Excited States of Proteins and Nucleic Acids," R. F. Steiner and Y. Weinryb, Ed., Plenum Press, New York, N. Y., 1971.

Mainly four processes are studied in the photochemistry of nonconjugated bichromophoric systems, excimer and exciplex formation, intramolecular energy transfer, cyclomerization, and intermolecular photopolymerization. Intramolecular excimer formation in bifunctional molecules was first observed by Hirayama in a series of α,ω-diphenylalkanes.[5] On the basis of his observations, this author put forward the n = 3 rule which states that the intramolecular excimer formation is only possible in those systems in which the chromophores are separated by three methylene units. This rule was further confirmed in several other systems, *e.g.*, in biscarbazoles, bisnaphthalenes, and bisadenines.[6]

If there is a difference in the respective energy levels of the excited states of both chromophores, excitation transfer can occur from one chromophore to the other. This energy transfer can occur before as well as after intersystem crossing of the originally excited chromophore.[7]

If the two chromophores are suitably chosen, an intramolecular cycloaddition process can occur. The photochemical intramolecular cycloaddition of nonconjugated bisolefins has been known for quite some time and several review articles have been devoted to this subject.[8] Most of these cyclomerizations were studied mainly from the synthetic point of view. Either the cyclization occurred in competition with other photochemical processes, or the two reacting double bonds were held in close proximity, favorable for intramolecular reaction. During the last years, some intramolecular cyclomerizations with high yields were observed, between chromophores, which were linked together by flexible chains.[1,9] A mechanistic scheme which implies reaction from the singlet excited state, with intermediate complex formation (excimer or exciplex formation), was put forward by Chandross and Dempster[9h] for the cyclomerization in 1,3-(α-naphthyl)propane and by Morrison and coworkers[9l,m] for the reactions in 6-phenyl-2-hexene and 5-hepten-2-one. For other systems, an intramolecular reaction through the triplet excited state is proposed.[9k,n–q] In all cases mentioned, except in the biscinnamates[9k] and in the 1,7-diene studied by Scheffer,[9o,q] the intramolecular reaction was limited to systems in which the two functions were separated by three methylene units.

Intermolecular photopolyaddition of bichromophoric systems, in the solid phase[10a–l] as well as in solution,[10m–s] has been reported. In solution, three mechanisms are possible for this process; it can proceed through the singlet excited state as in bisanthracene derivatives,[10n] through the triplet excited state as is described for dimaleimides[10m,o] or through a reactive ground state which is formed by a photochemical process.[10p–s]

We studied the cyclomerization of a series of N,N'-alkylenedimaleimides and compared this reaction with the dimerization of N-butylmaleimide. Although photodimerizations of maleic anhydride and several maleimide derivatives were carried out by Schenck and coworkers,[11] no quenching experiments or kinetic data are available. We therefore made a more thorough study of the dimerization of N-butylmaleimide as a reference for the cyclomerization.

Results

A. Quenching of the Dimerization of N-Butylmaleimide. Since the rate of addition of an excited molecule of N-butylmaleimide (**1**) to a ground-state molecule, to form the dimer **2**,[12] is first order in maleimide concentration, the lifetime of the excited state depends on the maleimide concentration as described by eq 1, where k_d is the rate of unimolecular radiationless decay, and k_r is the rate constant for addition to a ground-state molecule. The lifetimes of the reacting excited state for different maleimide concentrations were determined by quenching with biacetyl.

$$\frac{1}{\tau} = k_d + k_r[M] \qquad (1)$$

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(5) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).

(6) For a recent review of the intramolecular excimer formation see W. Klöpffer, "Organic Molecular Photophysics," J. B. Birks, Ed., Wiley, New York, N. Y., in press. The authors thank Dr. W. Klöpffer for a preprint of this review.

(7) (a) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 2322 (1965); (b) D. E. Breen and R. A. Keller, *ibid.*, **90**, 1935 (1968); (c) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965); (d) R. A. Keller and L. J. Dolby, *ibid.*, **89**, 2768 (1967); (e) *ibid.*, **91**, 1293 (1969); (f) R. A. Keller, *ibid.*, **90**, 1940 (1968); (g) R. DeMember and N. Filipescu, *ibid.*, **90**, 6425 (1968); (h) A. A. Lamola, *ibid.*, **91**, 4786 (1969); (i) N. Filipescu, J. R. DeMember, and F. L. Minn, *ibid.*, **91**, 4169 (1969); (j) H. Morrison, *ibid.*, **87**, 932 (1965); (k) H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968); (l) P. A. Leermakers, J. P. Montillier, and R. D. Rauh, *Mol. Photochem.*, **1**, 57 (1969); (m) D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, **92**, 2153 (1970); **93**, 1153 (1971); (n) R. S. Cooke and G. S. Hammond, *ibid.*, **92**, 2739 (1970); (o) R. Brainard and H. Morrison, *ibid.*, **93**, 2685 (1971); (p) N. Filipescu and J. R. Bunting, *J. Chem. Soc. B*, 1498 (1970).

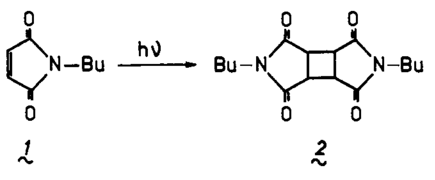
(8) (a) O. L. Chapman, *Advan. Photochem.*, **1**, 359 (1963); (b) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); (c) R. Huysgen, R. Grasley, and J. Sauer, "The Chemistry of Alkenes," Interscience, New York, N. Y., 1964, p 600; (d) P. de Mayo, *Advan. Org. Chem.*, **2**, 390 (1960); (e) P. De Mayo and S. T. Reid, *Quart. Rev., Chem. Soc.*, **15**, 408 (1961); (f) A. Mustafa, *Chem. Rev.*, **51**, 1 (1952); (g) J. Saltiel, *Surv. Progr. Chem.*, **2**, 265 (1964); (h) K. Schaffner, *Forschr. Chem. Org. Naturst.*, **22**, 81 (1964); (i) A. Schönberg, "Preparative Organische Photochemie," Springer-Verlag, West Berlin, 1958, p 2; (j) C. Walling, "Molecular Rearrangements," Part 1, Interscience, New York, N. Y., 1963, p 453; (k) W. J. Dilling, *Chem. Rev.*, **66**, 373 (1966); (l) H. Prinzbach, *Pure Appl. Chem.*, **16**, 17 (1968).

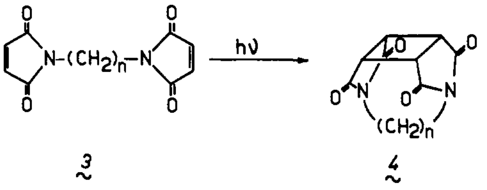
(9) (a) F. D. Greene, *Bull. Soc. Chim. Fr.*, 1356 (1960); (b) N. D. Weinschencker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (c) F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *ibid.*, **77**, 3852 (1958); (d) D. E. Applequist, M. A. Lintner, and R. Searle, *J. Org. Chem.*, **33**, 254 (1968); (e) J. H. Golden, *J. Chem. Soc.*, 3741 (1961); (f) R. Livingston and K. S. Wei, *J. Amer. Chem. Soc.*, **89**, 3098 (1967); (g) I. Roitt and W. Waters, *J. Chem. Soc.*, 2695 (1952); (h) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 703 (1970); (i) N. J. Leonard, K. Golanckiewicz, R. J. McCredie, S. M. Johnson, and I. C. Paul, *ibid.*, **91**, 5855 (1969); (j) K. T. Potts and E. Brugel, IUPAC International Symposium, Boston, Mass., 1971, Abstracts, p 94; (k) J. C. Doty, S. Y. Farid, D. Specht, and J. L. R. Williams, *ibid.*, Abstracts p 156; (l) W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971); (m) S. R. Kurowski and H. Morrison, *ibid.*, **94**, 507 (1972); (n) J. R. Scheffer and R. A. Wostradowski, *Chem. Commun.*, 144 (1971); (o) J. R. Scheffer and B. A. Boire, *J. Amer. Chem. Soc.*, **93**, 5490 (1971); (p) J. R. Scheffer, R. A. Wostradowski, and K. C. Dooley, *Chem. Commun.*, 1217 (1971); (q) J. R. Scheffer and B. A. Boire, *Tetrahedron Lett.*, 4741 (1970).

(10) (a) F. C. De Schryver and G. Smets in "Polymer Chemistry," J. Jenkins and A. Ledwith, Ed., in press; (b) F. C. De Schryver, N. Boens, and G. Smets, *J. Polym. Sci., Part A-1*, **10**, 1687 (1972); (c) F. C. De Schryver, L. Anand, G. Smets, and J. Switten, *J. Polym. Sci., Part B*, **9**, 777 (1971); (d) F. C. De Schryver, W. J. Feast, and G. Smets, *J. Polym. Sci., Part A-1*, **8**, 1939 (1970); (e) J. Higgins, A. H. Johannes, J. F. Jones, and R. Schutz, *ibid.*, **8**, 1987 (1970); (f) D. E. Pearson and P. D. Thiemann, *ibid.*, **8**, 2103 (1970); (g) F. C. De Schryver, T. Tran Van, and G. Smets, *J. Polym. Sci., Part B*, **9**, 425 (1971).

(11) G. O. Schenck and W. Hartmann, *Chem. Ber.*, **98**, 3854 (1965).

(12) In this dimerization, two isomers can be formed: one in which the two maleide rings lie at the same side of the cyclobutane ring (endo) and one in which the two rings lie at opposite sides (exo). Under the present reaction conditions, only the exo isomer is formed, as was confirmed by comparison of the signal of the cyclobutane protons in nmr of the dimer and the signal of the corresponding protons of the cyclomers of dimaleimides.





Degassed dichloromethane solutions, containing 0.4–10 × 10^{-3} *M* *N*-butylmaleimide and various concentrations of biacetyl, were irradiated in parallel at 350 nm. Relative quantum yields of disappearance of *N*-butylmaleimide were determined by uv analysis. Linear Stern–Volmer plots were obtained, indicating that, at these low concentrations, the photodimerization most probably occurs from one excited state.[13] This must be the triplet excited state, on the basis of the lifetimes determined by the Stern–Volmer equation (eq 2) and of sensitization experiments (*vide infra*).

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \qquad (2)$$

In Figure 1, representative Stern–Volmer plots for the quenching of the dimerization at different concentrations of *N*-butylmaleimide are given. The slopes are tabulated in Table I and the values of the lifetimes are calculated on the assumption that k_q equals 1.66 × 10^{10} M^{-1} $\sec^{-1}$ in dichloromethane at 30°, the temperature at which the reactions were carried out.[14] A plot of $1/\tau$ *vs.* *N*-butylmaleimide concentration gave a good straight line with a slope of 3.8 × 10^9 M^{-1} $\sec^{-1}$ (k_r) and an intercept at the ordinate of 1.01 × 10^7 $\sec^{-1}$ (k_d).

Table I. Quenching of the Photodimerization of *N*-Butylmaleimide with Biacetyl

[*N*-Butylmaleimide] × 10^{-3} M^a	$k_q\tau$, M^{-1}	$\tau \times 10^8$ $\sec^b$
10	335	2.02
5	560	3.37
1	1123	6.80
0.4	1480	8.91

^{a} Maximum conversion 10%. ^{b} See ref 14.

B. Quantum Yield of Dimerization. The absolute quantum yield of dimerization was measured by irradiation of a degassed solution of *N*-butylmaleimide in dichloromethane at a concentration of 10^{-3} *M*, with monochromatic light of 310 ± 5 nm. The intensity of the light was measured by actinometry with ferrioxalate.[15] The disappearance of the maleimide was followed by uv analysis. At 10^{-3} *M* a value of 0.12 was found for the product disappearance. The quantum yield for dimerization, Φ_{DIM}, therefore equals 0.06 at this concentration.

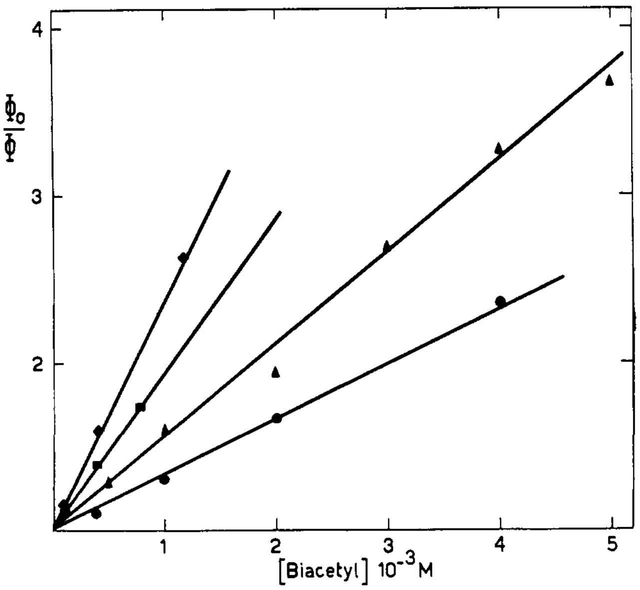


Figure 1. Stern–Volmer plots for quenching of the dimerization of *N*-butylmaleimide with biacetyl. at different concentrations of *N*-butylmaleimide: (◆) 4 × 10^{-4} *M*, (■) 1 × 10^{-3} *M*, (▲) 5 × 10^{-3} *M*, (●) 10^{-2} *M*.

C. Quantum Yield of Intersystem Crossing of *N*-Butylmaleimide. Since quenching by dienes, like 1,3-pentadiene, and by aromatic compounds, like stilbene, is prohibited, the determination of the intersystem crossing quantum yield by the conventional method, namely by cis–trans isomerization of the quencher, is not possible for maleimides. We measured the intersystem crossing efficiency by quenching with biacetyl and measuring the intensity of the phosphorescence of biacetyl at room temperature.[16] The intersystem crossing efficiency of the maleimide can be calculated by eq 3, where Φ_p is the quantum yield

$$\Phi_{\mathrm{isc}} = \frac{1}{\Phi_p}\frac{CI_p}{I_{\mathrm{abs}}} \qquad (3)$$

of phosphorescence of biacetyl at room temperature, *C* is a constant for the fluorometer, I_p is the phosphorescence intensity, and I_{abs} is the absorbed light intensity.

As several of these quantities are difficult to measure, Φ_{isc} was determined relative to benzophenone. Therefore, the phosphorescence intensity obtained with a sample of *N*-butylmaleimide was compared with the intensity obtained when a solution of biacetyl in the presence of benzophenone was irradiated. Care was taken that the same amount of light was absorbed in both experiments, by monitoring optical densities. For benzophenone, the difference between singlet and triplet lifetimes is large enough, so that the triplet is quenched selectively. In the case of the maleimide, care must be taken that no singlet quenching occurs. To avoid this, the concentration of biacetyl was kept low,[17] the amount of triplet quenched at that con-

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(13) The possibility to obtain linear Stern–Volmer plots while quenching more than one excited state has been discussed recently, see (a) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, 2, 133 (1970); (b) P. J. Wagner *ibid.*, 3, 23 (1971).

(14) k_q was calculated on the basis of the following equation: $k_q = 8RT/3000\eta$.

(15) For a description of the method, see (a) C. A. Parker, *Proc. Roy. Soc., Ser. A*, 220, 104 (1953); (b) C. E. Hatchard and C. A. Parker, *ibid.*, 235, 518 (1956); J. G. Calvert and W. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 783.

(16) For a discussion of the photochemical behavior of α diketones, see B. M. Moore, *Advan. Photochem.*, 8, 77 (1971), and references cited therein.

(17) The singlet lifetime of the maleimide could be determined using the rate constants of the photophysical processes, found for hexamethylenedimaleimide in the kinetic study of the cyclomerization reaction; see further in the text.

Table II. Cyclomerization of Dimaleimides

		3						4					
	R	Mp, °C	Ir,[a] γ, cm^{-1}				Nmr,[b] δ	Yield, %	Mp, °C	Ir,[a] γ, cm^{-1}	Nmr,[b] δ	M$^+$	Mol wt[d]
a	$-(CH_2)_2-$	196	3100	1580	830	695	*c*	0					
b	$-(CH_2)_3-$	174	3085	1585	830	680	6.73	100	350	3040	*c*	234	
c	$-(CH_2)_4-$	206	3094	1560	840	690	6.89	85	350	3020	3.80	248	
d	$-(CH_2)_5-$	107	3080	1585	835	695	6.95	98	349	3010	3.80	262	264
e	$-(CH_2)_6-$	144[e]	3090	1583	835	695	6.74	95	291	3000	3.80	276	280
f	$-(CH_2)_7-$	85	3080	1583	860	690	6.96	80	269	2980	3.80	290	
g	$-(CH_2)_8-$	121	3100	1585	826	689	6.72	10		2980	3.80	304	
h	$-(CH_2)_9-$	87	3080	1590	826	689	6.72	0					
j	$-(CH_2)_{10}-$	115	3100	1583	840	690	6.85	0					
i	$-(CH_2)_{12}-$	111	3095 3105	1590	842	700	6.95	0					
k	$-CH_2OCH_2-$	129.5[f]	3100	1585	840	698	6.81	100	320	3040	*c*	236	
l	*m*-Phenylene	203	3105	1590	245	690	7.17	0	dec				

[a] Infrared spectra were taken in a KBr pellet. [b] Signals of the four cyclobutane protons, all signals are singlets. All spectra recorded in $CDCl_3$ except **3c** and **4c**, which were recorded in DMSO-d_6. [c] **3a**, **4b**, and **4k** were not sufficiently soluble. [d] Molecular weights measured with a Mechrolab 301 A vapor-pressure osmometer in $CHCl_3$. [e] Mp 136–141°: R. J. Cotter, C. K. Sauers, and J. M. Whelan, *J. Org. Chem.*, **26**, 10 (1961). [f] Mp 128–132°: P. O. Tawney, R. H. Snyder, E. P. Conger, K. A. Leibrand, C. H. Stiteler, and A. R. Williams, *ibid.*, **26**, 15 (1961).

centration was calculated from the Stern–Volmer equation (2) and the measured phosphorescence intensity of biacetyl was extrapolated to total triplet quenching. A value for Φ_{isc} of 0.23 was found.

The value of Φ_{isc} was also determined by sensitization experiments. We could, however, find no sensitizer which absorbed selectively all the light, but experiments were carried out with benzophenone and corrections were made for the reaction caused by direct absorption of light by the maleimide. The value of Φ_{isc} found by this method was 0.24.

D. Cyclomerization of *N,N'*-Alkylenedimaleimides. Upon irradiation of dimaleimides **3b**–**g** (Table II) an intramolecular cycloaddition to tetracyclic compounds **4b**–**g** (Table II) occurs. The reactions were carried out in solution in CH_3CN or CH_2Cl_2 at a concentration of 10^{-2} *M*, using 310- or 350-nm light. Cyclomers were isolated from the oligomers by evaporating the solvent and treating the residue with ethyl acetate, in which the cyclomers are insoluble. The structure of the products is confirmed by the ir and nmr spectral data and especially by the mass spectra. The molecular ion peaks lie at *m/e* values that match exactly the molecular weights of the starting materials.[18]

The ultraviolet spectra of the products **4** show no absorption due to a –CH=CHCO system in the 300-nm region. The intramolecular character of the reaction is proved by mass spectrometry and by tonometry.

The influence of the chain length on the yield of cyclomerization and intermolecular oligomerization together with the spectral data for the cyclomers are shown in Table II. Almost quantitative yields of intramolecular reaction are obtained for dimaleimides with three or six methylene units between the rings and for the ether derivative **3k**. A quick drop in the cyclomer yield is observed, when going from seven (80%) to eight (10%) methylene units. For higher chain lengths, no cyclomerization is observed.

It should be pointed out that molecular models show that for dodecamethylenedimaleimide (**3j**), an intramolecular exo isomer is possible, while for shorter chains, an endo configuration of the cyclobutane ring is obliged, yet no cyclomerization is observed for **3j**, even at high dilution (10^{-4} *M*). Molecular models show further that a chain of two methylene units is too short to allow cyclomerization without implying very high strain. As expected, when the two maleimide moieties are joined by a rigid phenyl ring, as in *m*-phenylenedimaleimide, no intramolecular cyclization occurs but a polymeric material is formed.[19]

E. Influence of the Concentration on the Cyclomerization. Since decamethylenedimaleimide did not react intramolecularly at a concentration of 10^{-2} *M*, experiments were carried out at lower concentrations, but even at 10^{-4} *M*, no cyclomerization could be detected, indicating that the intramolecular reaction is no mere consequence of a concentration effect. The influence on the yield of cyclomer for hexamethylenedimaleimide in the range of 10^{-3} *M* to 10^{-1} *M* is small (see Table III).

Table III. Influence of Concentration on Cyclomerization of Hexamethylenedimaleimide

Concn, *M*	Cyclomerization	Oligomerization
10^{-3}	100	0
10^{-2}	95	5
5×10^{-2}	90	10
10^{-1}	80	20

F. Uv Spectra of Maleimides and Dimaleimides. The intramolecular cycloaddition could eventually be explained by an interaction or an association between the two chromophores in the ground state. Such an interaction should distort the uv spectrum of a dimaleimide appreciably with respect to that of a monofunctional derivative. In Figure 2 the spectra of hexamethylenedimaleimide and *N*-butylmaleimide, in dichloromethane, are shown. The maxima of the absorption band in the 300–400-nm region for the series of dimaleimides **3b**–**e**, and for *N*-butylmaleimide, lie at the same wavelength. On shortening

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(18) For a complete study of the mass spectra of dimaleimides and their cyclomers, see W. J. Feast, J. Put, F. C. De Schryver, and F. C. Compernolle, *Org. Mass. Spectrom.*, 3, 507 (1970).

(19) F. C. De Schryver and N. Boens, unpublished results.

Table IV. Kinetic Data for the Cyclomerizations of *N*,*N'*-Alkylenedimaleimides

Compd	Solvent	Φ_c, 300 nm[a]	Φ_{isc}	$k_q\tau$, M^{-1}	$\tau \times 10^{10}$, sec
3b	CH_2Cl_2	0.62 ± 0.02	0.025 ± 0.005	6.69	4.03
3c	CH_2Cl_2	0.42 ± 0.02	0.045 ± 0.01	12.20	7.35
3d	CH_2Cl_2	0.54 ± 0.02	0.045 ± 0.01	12.79	7.7
3c	CH_2Cl_2	0.42 ± 0.02	0.12 ± 0.02	14.59	8.8
3e	CH_3CN	0.34 ± 0.02	0.04 ± 0.01	9.39	5.66
3f	CH_2Cl_2	0.15 ± 0.02	0.15 ± 0.02		

[a] Initial concentration of dimaleimide 10^{-2} *M*; less than 10% conversion.

the chain, a small hypochromism is observed. The molar extinction coefficient of trimethylenedimaleimide is 8% hypochromic with respect to that of *N*-butylmaleimide. The same effect is found, when going from a less polar (CH_2Cl_2) to a more polar solvent (CH_3CN).

The deviations are very small and do not give any evidence for a strong ground-state interaction between the two chromophores.

G. Quantum Yield for Cyclomerization. The quantum yields for intramolecular reaction were determined by irradiating samples of the dimaleimides in CH_2Cl_2 or CH_3CN at a concentration of 10^{-2} *M*, with monochromatic light of 300 ± 5 nm. The light intensity was measured by actinometry with ferrioxalate.[15] The disappearance of the dimaleimides was followed by uv analysis. The course of the reaction was linear as long as light absorption was complete, as expected. Quantum yields for the different chain lengths are tabulated in Table IV.[20] Whereas the chemical yields, for compounds with three to six units, were almost the same, and very high, the quantum yields vary appreciably with the chain length.

H. Influence of the Solvent, Excitation Wavelength, and Temperature on the Quantum Yield. Samples of hexamethylenedimaleimide and trimethylenedimaleimide in different solvents were irradiated at the same time. However the choice of solvents is limited. The quantum yields are shown in Table V. The more polar the solvent, the lower are the quantum yields, while the chemical yields remain the same, indicating that deactivation processes, which do not lead to product, must be accelerated in polar solvents.[21,22]

Table V. Influence of the Solvent on the Cyclomerization Quantum Yield

	Φ_c[a]		
	Hexane/CH_2Cl_2 3/2 Vol %	CH_2Cl_2	CH_3CN
3b	0.70	0.62	0.48
3e	0.50	0.42	0.34

[a] Initial concentration of dimaleimide 10^{-2} *M*, with less than 10% conversion.

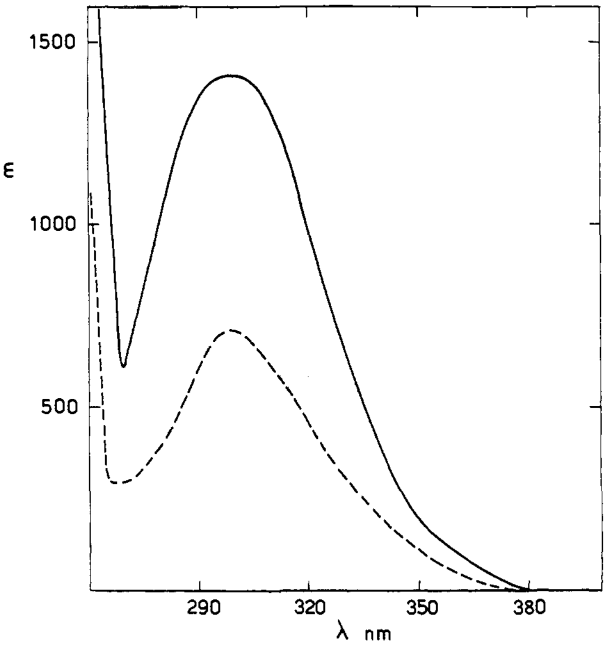

Figure 2. Uv spectra of *N*-butylmaleimide (- - -) and hexamethylenedimaleimide (—) in CH_2Cl_2.

The quantum yield of cyclomerization is independent of the wavelength of excitation in the region 300–350 nm. This means that vibrational relaxation to the lowest vibrational level of the first excited singlet state is very fast, and no vibrationally excited singlet state is involved in the reaction. No influence of the temperature on the quantum yields in the region 15–55° was observed.

I. Quenching of the Cyclomerization with Biacetyl. Biacetyl, which was found to be a good quencher for the dimerization of monofunctional maleimides, was also used to quench the intramolecular reaction. Linear Stern–Volmer slopes were obtained for dimaleimides with chain lengths from three to six methylene units. Much higher concentrations of biacetyl than for the intermolecular dimerization were needed to obtain quenching, indicating that the lifetime of the reacting excited state is much shorter. In Figure 3, Stern–Volmer plots for the quenching of the cyclomerization of dimaleimides with different chain lengths are represented.

The cyclomerization of hexamethylenedimaleimide was quenched in dichloromethane and in acetonitrile. A shorter lifetime was found in the latter solvent. The slopes of the Stern–Volmer plots are tabulated in Table IV and the values of the lifetimes are calculated on the assumption that k_q equals 1.66×10^{10} M^{-1} sec^{-1}.

J. Quantum Yield of Intersystem Crossing in Dimaleimides. The intersystem crossing efficiency of

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(20) Quantum yields for cyclomerization were obtained from quantum yields of product disappearance taking into account the small percentage of intermolecular reaction.

(21) Differences in viscosity of the solvents used cannot account for the change in quantum yield observed, since, at 30°, acetonitrile is less viscous than dichloromethane.

(22) Such an additional deactivation after irradiation was found for uracil and thymine dimerization and led to the proposal of triplet excimers in those compounds; see P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **92**, 181 (1969).

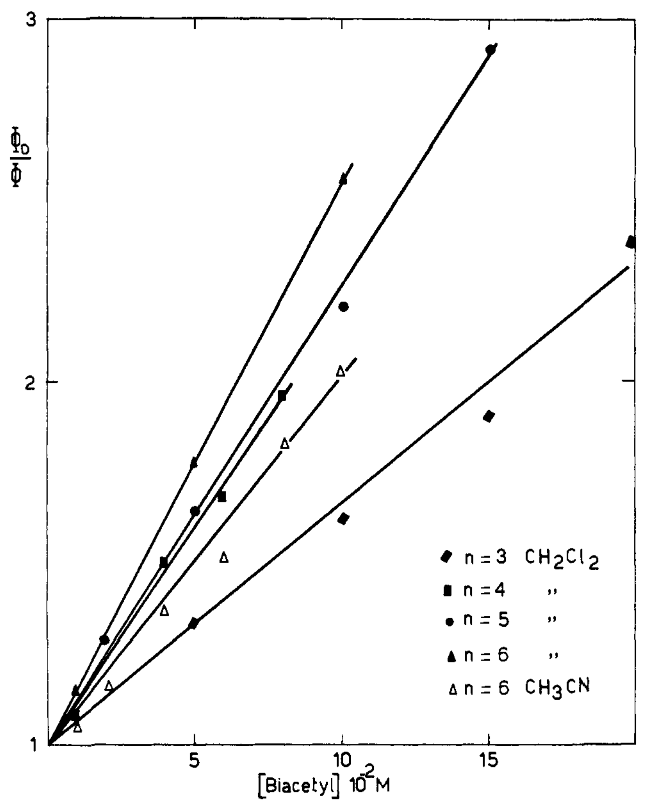

Figure 3. Quenching of the cyclomerization of dimaleimides in CH_2Cl_2 and in acetonitrile with biacetyl.

dimaleimides was measured by the quenching method with biacetyl, in the same way as described for *N*-butylmaleimide. The phosphorescence intensity of biacetyl at room temperature was measured and compared with that obtained with a sample, in which benzophenone was the sensitizer. The concentration of biacetyl was kept at 10^{-3} *M*, to avoid singlet quenching.

It is, however, possible that the triplet lifetime is seriously reduced, owing to intramolecular reaction, and in that case, measurement of the intersystem crossing efficiency would be very difficult. Arguments to the contrary will be presented in the Discussion. The values of Φ_{isc}, found for different chain lengths, are shown in Table IV.

K. Fluorescence Measurements. The fluorescence of maleimides and dimaleimides, which carry no substituents at the double bonds, is very weak in solution at room temperature. Attempts were made to record the spectrum, but a very weak structureless band was obtained, which cannot be attributed with certainty to the maleimide ring. In any case, the quantum yield of fluorescence is very low and fluorescence is a minor deactivation process of the singlet excited state of the maleimide ring.

Discussion

A. Dimerization of *N*-Butylmaleimide. The dimerization of *N*-butylmaleimide at relatively low concentrations (10^{-2} to 10^{-4} *M*) occurs from one excited state, which is apparently the triplet state. Scheme I can be written for the photochemical processes, occurring in this system. The quantum yield for dimerization then equals

$$\Phi_{DIM} = \Phi_{isc}\frac{k_r[M]}{k_r[M] + k_d} \qquad (4)$$

Scheme I

$M^0 \xrightarrow{h\nu} M^1$	light absorption
$M^1 \xrightarrow{k_s} M^0$	radiationless deactivation
$M^1 \xrightarrow{k_f} M^0$	fluorescence
$M^1 \xrightarrow{k_{isc}} M^3$	intersystem crossing
$M^3 \xrightarrow{k_d} M^0$	radiationless decay of triplet
$M^3 + M \xrightarrow{k_r} \text{dimer}$	addition

A value can be calculated for a concentration of 10^{-3} *M*, using the constants determined by quenching experiments, and the value of Φ_{isc}, found for this compound. The calculated value 0.062 lies close to the experimental one at this concentration, 0.06 (*vide supra*). This confirms the mechanism and indicates that there is no additional deactivation after addition of the triplet to a ground-state molecule.[22]

It is possible that at higher concentrations, dimerization from the singlet excited state occurs, but this could not be verified for the nonsubstituted *N*-butylmaleimide, because at higher concentrations, vinyl polymerization occurs as a side reaction and obscures the results.

B. Cyclomerization of Dimaleimides. On irradiation of *N*,*N'*-alkylenedimaleimides, almost quantitative intramolecular reaction is observed for chain lengths going from three to seven methylene units. There is a very sudden drop in the yield of cyclomer, when going from seven to nine methylene units. From this observation, from quenching experiments, and quantum yield measurements, one can conclude that the reaction proceeds through the singlet excited state. The following arguments can be put forward to substantiate this statement.

The intersystem crossing efficiency of *N*-butylmaleimide is 0.23, which is much smaller than the cyclomerization quantum yields of the dimaleimides. Thus, the cyclomerization must, at least partly, proceed through the singlet excited state.

The quenching experiments with biacetyl gave linear Stern–Volmer plots, indicating that most probably only one excited state reacts intramolecularly.[13]

We could not sensitize the reaction selectively, but irradiation of hexamethylenedimaleimide in the presence of benzophenone led to a drop in the cyclomer yield and an enhancement of the intermolecular reaction.

The intersystem crossing efficiencies of the dimaleimides decrease with decreasing chain length and thus with increasing cyclomerization quantum yields. It can be noticed further that a change of one order of magnitude in the intersystem crossing efficiencies is accompanied by only a small change in Φ_c.

At low concentrations of biacetyl (10^{-3} *M*) no quenching of the cyclomerization occurred, although a definite phosphorescence intensity from biacetyl at room temperature was measured, which could result only from energy transfer from the maleimide triplet to biacetyl.

One could explain then the sudden drop in the yield of cyclomer when going from hepta- to nonamethylenedimaleimide as follows. For the cyclomerization to occur, the molecule has to take a conformation, in which the chromophores come close together. This conformation is unfavorable for enthalpy and entropy reasons. Furthermore, the molecule must reach this conformation within the singlet lifetime. As the total number of possible conformations increases rapidly with increasing chain length, the probability that the molecule can take a conformation, favorable for intramolecular reaction, within the singlet lifetime, decreases very rapidly with lengthening the chain.[23]

The stabilization through excited state complex formation could make it possible to overcome the unfavorable enthalpy and entropy factors. The lack of intramolecular reaction from triplet manifold could be explained by the absence of such a stabilization for triplet excited state in this system. It can however not be excluded that a small amount of triplet reacts intramolecularly. It should be pointed out that intramolecular triplet reaction, if it occurs, must be possible at longer chain lengths, as the triplet lifetime is longer. We never observed cyclomers at irradiation of dimaleimide with a chain longer than eight methylene units, not even on sensitization and not even with dodecamethylenedimaleimide, where an intramolecular adduct with exo configuration is possible.[24]

Such reactions through singlet excited state complexes have been reported recently by other authors.[9h,l,m] We found in our laboratory a striking analogy between the cyclomerizations of dimaleimides and those of biscoumarine.[1b,25]

On the basis of these considerations, Scheme II can be written for the photochemical processes, taking place on excitation of a dimaleimide. M–M is a dimaleimide in the ground state, M–M¹ the localized singlet excited state, (M–M)¹ the excited state complex, and M–M³ the localized triplet state. The quantum yield of cyclomerization can then be expressed as shown in eq 5.

$$\Phi_c = \frac{k_r[(\mathrm{M{-}M})^1]}{I_{abs}} = \frac{k_r k_e}{(k_f' + k_s' + k_r + k_{-e})(k_f + k_s + k_{isc}) + (k_f' + k_s' + k_r)k_e} \quad (5)$$

Scheme II

$\mathrm{M{-}M} \xrightarrow{h\nu} \mathrm{M{-}M}^{1*}$	light absorption
$\mathrm{M{-}M}^{1*} \xrightarrow{k_v} \mathrm{M{-}M}^1$	vibrational relaxation
$\mathrm{M{-}M}^1 \xrightarrow{k_s} \mathrm{M{-}M}$	radiationless decay
$\mathrm{M{-}M}^1 \xrightarrow{k_f} \mathrm{M{-}M}$	fluorescence from the singlet
$\mathrm{M{-}M}^1 \xrightarrow{k_{isc}} \mathrm{M{-}M}^3$	intersystem crossing
$\mathrm{M{-}M}^1 \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} (\mathrm{M{-}M})^1$	complex formation and dissociation
$(\mathrm{M{-}M})^1 \xrightarrow{k_s'} \mathrm{M{-}M}$	radiationless decay
$(\mathrm{M{-}M})^1 \xrightarrow{k_f'} \mathrm{M{-}M}$	fluorescence from the complex
$(\mathrm{M{-}M})^1 \xrightarrow{k_r} \text{cyclomer}$	cyclomerization
$\mathrm{M{-}M}^3 \xrightarrow{k_d} \mathrm{M{-}M}$	radiationless decay
$\mathrm{M{-}M}^3 \xrightarrow{k_p} \text{polymer}$	intermolecular addition

In the case that the excited-state complex can collapse to a cyclomer, as in the dimaleimides, the rate of dissociation of the complex will be small with respect to the rate of formation and the equilibrium will be shifted completely to the complex: $k_{-e} \ll k_e$. The expression for the quantum yield can then be written as eq 6,

$$\Phi_c = \frac{k_e k_r}{(k_f + k_s + k_{isc} + k_e)(k_f' + k_s' + k_r)} = \Phi_e \Phi_r \quad (6)$$

where Φ_e is the quantum yield of complex formation and Φ_r the efficiency of the reaction from the complex.

We now assume that the radiationless deactivation and the fluorescence from the complex are very small, as compared to the reaction, which means that Φ_r will be close to unity: k_f' and $k_s' \ll k_r$. Since there is no fluorescence from the complex observed at room temperature, this assumption is correct, as far as fluorescence is concerned. The assumption for the radiationless deactivation will have to be checked.

One can wonder then, if there is any sense in proposing a complex as an intermediate. Although there are several arguments that point in the direction of complex formation (*vide supra*), in the case of dimaleimides at room temperature this will be only a shallow minimum at the reaction coordinate. This might be converted into a longer living intermediate by lowering the temperature, as the reaction will have a small but definite activation energy. In other systems, this complex can be a longer living intermediate at room temperature (**9h**), but in general, when a reaction is possible from the complex, it will be the main deactivation process, causing an appreciable shortening of the lifetime of this complex.

From eq 7 and 8, one can calculate the values of

$$\Phi_c = k_e/(k_e + k_f + k_s + k_{isc}) = k_e\tau_s \quad (7)$$

$$\Phi_{isc} = k_{isc}\tau_s \quad (8)$$

k_e and k_{isc}. Since the values of k_e and k_{isc} are known, the sum $k_f + k_s$ can be calculated from the reciprocal of the lifetime of the singlet excited state. It was already pointed out that k_f has to be low as compared to

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(23) This conclusion is confirmed by other systems, which have a longer singlet lifetime than dimaleimides, *e.g.*, biscoumarines, and which indeed react intramolecularly at much longer chain lengths (see ref 1b).

(24) One of the referees suggested that a small yield of intramolecular dimer from triplet might not be observed in yield measurements but might greatly change the triplet lifetime. We think that the amount of intramolecular triplet reaction, if there is any, must be very small and that this process will not change the triplet lifetime substantially. One can calculate from the rate constants of the intermolecular dimerization that, even if the intramolecular reaction should be ten times slower because of geometrical restrictions, this process would have still a quantum yield that almost equals the intersystem crossing quantum yield, *i.e.*, 0.12 for 3 e. This should be sufficiently high to be seen in yield measurements. Furthermore, we obtained appreciable triplet quenching in the dimaleimides at low biacetyl concentrations (10^{-3} *M*), indicating that the triplet lifetime is not greatly changed with respect to the monofunctional derivative. We therefore conclude that the intramolecular triplet reaction must be a minor process, although it cannot be excluded completely. It should be pointed out also that the rate constants derived from the proposed mechanism, without triplet cyclomerization, lead to a meaningful value for Φ_{isc} of *N*-butylmaleimide.

(25) For biscoumarines, the cyclomerization occurs at longer chain lengths, where the formation of an intramolecular endo or exo structure is possible. Only the endo product is formed (see L. Leenders and F. C. De Schryver, in press). This is attributed to the intermediate formation of a singlet excited state complex.

k_s, since there is no fluorescence at room temperature, from the maleimide ring.

The values obtained for the different constants are tabulated in Table VI. The values of k_e increase with the shortening of the chain. The value for tetramethylenedimaleimide is lower than one would expect, indicating that the butane chain undergoes strong hydrogen repulsion interactions in the exciplex configuration.

Table VI. Rate Constants for the Photochemical Processes in Dimaleimides

Compd	Solvent	k_e, sec^{-1}	k_{isc}, sec^{-1}	$k_s + k_f$, sec^{-1}
3b	CH_2Cl_2	1.5×10^9	5.7×10^7	0.9×10^9
3c	CH_2Cl_2	0.6×10^9	6.0×10^7	0.7×10^9
3d	CH_2Cl_2	0.7×10^9	5.7×10^7	0.5×10^9
3e	CH_2Cl_2	0.5×10^9	1.36×10^8	0.5×10^9
1	CH_2Cl_2		(1.36×10^8)	(0.5×10^9)
3e	CH_3CN	0.6×10^9	7.1×10^7	1.1×10^9

The radiationless deactivation is an important process, and the values of k_s increase with decreasing chain length, although they should remain constant. The same effect is seen when going from a less polar to a more polar solvent. This explains the lower quantum yield of the cyclomerization in CH_3CN. One must conclude that the two chromophores are not completely independent and that, at shorter chain lengths, the rates of the photophysical processes may differ from those of the isolated chromophores.

At longer chain lengths, however, the deviation will be small and we may assume that the rate constants for **3e** will be close to those of **1**. Based on this assumption, one can calculate the intersystem crossing efficiency of **1**, using the rate constants of **3e**. A value of 0.21 is obtained, which is close to the experimentally determined value 0.23, indicating that the assumption that Φ_r almost equals one is valid and that the rate constants of **3e** and **1** will be almost the same. If the calculation of Φ_{isc} is done with the rate constants of **3b**, there is an appreciable deviation from the experimental value, due to the change in k_s relative to **3e**. The assumption, made by Klöpffer,[26] that the rate constants of the photophysical processes in a trimethylenebiscarbazole and in *N*-isopropylcarbazole are the same, is consequently not necessarily correct.

Conclusion

The intramolecular cycloadditions described until now were limited to systems in which the chromophores were separated by two or three carbon atoms, or in which the chromophores were held in a favorable conformation. *N*,*N*-Alkylenedimaleimides, however, react intramolecularly through an excited state complex for much longer chain lengths. This would mean that the so-called $n = 3$ rule is not generally applicable. We would formulate this rule in a more general way: *the possibility of intramolecular complex formation is limited by the probability to reach, within the lifetime of the excited state involved, a favorable conformation and by the extent of stabilization in the complex, covalent bond formation being the extreme.* The complex formation is then an equilibrium, which will be shifted in the direction of the complex, only if this state provides sufficient stabilization to overcome the entropy increase and the interactions in the folded chain, or if this complex can collapse to a cyclomer.

This cyclomerization from the complex occurs with very high efficiency in the case of the dimaleimides. Rate constants for exciplex formation are found which depend on the chain length and which are of the order of 10^9 sec^{-1}. The same order of magnitude is found by Klöpffer[26] and Hirayama[5] for intramolecular excimer formation in biscarbazolylpropane and diphenylpropane.

The study of this and analogous systems may contribute to the understanding of the nonradiative deactivation processes. The complex may be the second minimum on the energy surface of the first excited state, from which crossing to the ground state of the product occurs in a diabatic process, as proposed recently by Dougherty.[27]

Experimental Section

Instrumentation. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. The uv analysis, to determine the conversions, was done on a Hitachi Perkin-Elmer spectrophotometer, Type 139. Infrared spectra were taken in KBr pellets on a Perkin-Elmer Model 521 apparatus or a Perkin-Elmer Model 235. Nuclear magnetic resonance spectra were taken on a Varian A-60 or a Varian XL-100. The mass spectra were recorded on an AEI-MS-12 instrument. The ionization energy was 70 eV and the samples were injected directly at a temperature between 100 and 200°. Fluorescence and phosphorescence measurements were carried out on the Fica 55 differential absolute fluorimeter. Melting points were determined with a melting point microscope Leitz Wetzlar 1146, and were not corrected. The preparative irradiations were done in a Rayonet RS preparative photochemical reactor equipped with RUL 3500 or RUL 3100-Å lamps, while in the kinetic experiments a Bausch and Lomb monochromator with super high-pressure mercury light source was used.

Preparation of *N*-Butylmaleimide and Dimaleimides. Nonsubstituted *N*-butylmaleimide (**1**) and the dimaleimides **3a**-**l** can be synthesized by a method described by Searle[28] or by the method of Martin, Dickinson, and Roland.[29] The dimaleimides obtained by either of these two methods are purified with chromatography. The crude products were dissolved in $CHCl_3$ and brought on a column which contained Florisil (60–100 mesh Fluka) as absorbents. The columns were 3 cm in diameter and 30 cm high. The products were eluted with $CHCl_3$. This procedure is repeated if necessary. The purified dimaleimides can be recrystallized from ethanol. The compounds used in the kinetic experiments were further purified by sublimation.

Good elementary analyses were obtained for all the dimaleimides, *e.g.*, for trimethylenedimaleimide [*Anal.* Calcd: C, 56.61; H, 4.25; O, 27.22; N, 11.92. Found: C, 56.70; H, 4.45; O, 26.65; N, 12.00] and for hexamethylenedimaleimide [*Anal.* Calcd: C, 60.86; H, 5.54; O, 23.16; N, 10.14. Found: C, 60.60; H, 5.92; O,23.13; N, 10.13].

Quantum Yield of the Dimerization of *N*-Butylmaleimide. A $10^{-3}M$ solution (3 ml) of *N*-butylmaleimide (**1**) in dichloromethane was degassed by four freeze–thaw cycles at a high vacuum line. The solution was then poured into a quartz cell, which was connected to the degassing flask. The cell was placed in a thermostated block at 20° in front of the monochromator, in a fixed position. The solution was stirred by means of a magnetic stirrer. The solution was irradiated with light of 300 ± 5 nm until ±10% conversion. The extent of conversion was determined by measuring the optical density at 300 nm. The amount of light absorbed was calculated from the optical densities. The incident light intensity was measured by actinometry with ferrioxalate.[15]

Quenching of the Dimerization. Different samples (10 ml) with

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(26) W. Klöpffer and W. Liptay, *Z. Naturforsch. A*, **25**, 1091 (1970).

(27) R. C. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971).

(28) N. E. Searle, U. S. Patent 2,444,536 (1948); *Chem. Abstr.*, **42**, 7340 (1948).

(29) E. L. Martin, C. L. Dickinson, and J. R. Rolands, *J. Org. Chem.*, **26**, 2032 (1961).

a given concentration of *N*-butylmaleimide (**1**), but with varying biacetyl concentrations, were degassed with three freeze–thaw cycles. The samples were then irradiated at the same time in a turntable in a preparative reactor equipped with lamps that have a maximum intensity at 350 nm (band width 40 nm). Biacetyl absorbed less than 2% of the light. The conversion in each sample was determined by measurement of the optical density. The change in optical density in each sample was compared with the change in optical density in the reference sample containing no biacetyl. Such a quenching was carried out for four different maleimide concentrations from 4×10^{-4} to 1×10^{-2} *M*. Care was taken that the maximum conversion was 10%. The irradiation was carried out at 350 nm to avoid complete absorption and front effect.

Preparative Cyclomerizations. Dimaleimide (1 g) was dissolved in the necessary amount of dichloromethane or acetonitrile to obtain a concentration of 10^{-2} *M*. The solutions were saturated with dry nitrogen during 1 hr and then irradiated in a preparative photochemical reactor equipped with lamps (RUL 3000 or RUL 3500 Å). The temperature in the reactor lies between 30 and 40°. The irradiation time was about 4 hr. After the reaction, the solvent was evaporated under reduced pressure. The residue was treated with ethyl acetate. The tetracyclo adducts are very slightly soluble in this solvent, while the eventually formed oligomers are very soluble, provided that the irradiation time was not too long, since at long irradiation times, cross-linking reactions occur.

Good elementary analyses were obtained for the cyclomers, as can be seen in Table VII. The products sublime between 200 and 220°, which provides a good method for further purification of these cyclomers.

Table VII. Elementary Analyses of Cyclomers of Dimaleimides

	Calcd, %				Found, %			
Compd	C	H	O	N	C	H	O	N
4b	56.61	4.25	27.22	11.91	56.45	4.45	27.20	12.15
4c	57.89	4.83	25.10	11.51	58.06	4.84	25.81	11.29
4d	59.54	5.38	24.40	10.66	59.51	5.48	24.55	10.57
4e	60.88	5.66	23.35	9.99	60.87	5.79	23.19	10.14
4f	62.05	6.25	22.04	9.65	61.99	6.13	22.26	9.50

Quantum Yields of Cyclomerization. The quantum yields of the cyclomerization were determined by irradiation of 3 ml of a 10^{-2} *M* solution of the dimaleimide in dichloromethane or acetonitrile. It was checked that the course of the reaction is linear as long as light absorption is complete. As the cyclomerizations are monomolecular reactions, no front effect exists, and one can work under conditions where all the light is absorbed. Monochromatic light of 300 ± 5 nm was used.

The solutions were not degassed, as one experiment showed that degassing had no measurable influence on the reaction. The cell was put in a fixed position in a thermostating block, thermostated at 20°. The light intensity was measured by irradiating ferrioxalate as an actinometer in the same cell.[15] The conversion was determined by measuring the optical density at 360 nm. Care was taken that the conversion did not exceed 10%. The influence of the temperature on the quantum yield was measured by irradiating samples of hexamethylenedimaleimide at 15, 25, 35, 45, and 55°. The cell was thermostated during 15 min before irradiation. To determine the influence of the excitation wavelength, the intensity of the monochromator was determined with ferrioxalate at 300, 330, and 350 nm and the samples of hexamethylenedimaleimide were irradiated at these wavelengths.

Quenching of the Cyclomerization. Quenching of the cyclomerization with biacetyl was carried out with a monochromatic light of 316 ± 5 nm. Solutions (10^{-2} *M*) of dimaleimides in dichloromethane or CH_3CN containing concentrations of biacetyl varying from 1 to 10×10^{-2} were thermostated at 21° and irradiated for 10 min. Biacetyl does not absorb any light under these conditions. The solutions were stirred vigorously by means of a magnetic stirrer and placed under the thermostating block. The conversion was determined by measuring the optical density at 360 nm. The difference in optical density before and after irradiation of each sample was compared with the difference in a reference sample without biacetyl, which gave directly the value of Φ_0/Φ.

Intersystem Crossing Efficiency. (a) Sensitizing Method. A 10^{-2} *M* solution of *N*-butylmaleimide (**1**) in dichloromethane was degassed and irradiated at 350 nm until ±10% (1 hr) conversion, as determined by measuring the optical density at 350 nm. The amount of light absorbed was calculated from these optical densities. The solution was stirred during irradiation. Another sample, containing 10^{-2} *M* *N*-butylmaleimide and 10^{-1} *M* benzophenone, was degassed and irradiated at 350 nm in the same cell, while stirring. Under these conditions, benzophenone absorbs 90% of the light and *N*-butylmaleimide 10%. The conversion was determined by measuring the OD at 300 nm after a $^1/_{10}$ dilution. The conversion was corrected for the amount of direct reaction. The ratio of the changes in optical density in these two experiments gives the value of Φ_{isc}

$$\frac{\Delta OD_d}{\Delta OD_s} = \frac{\Phi_d}{\Phi_s} = \frac{\Phi_{isc}\Phi_a}{\Phi_a} = \Phi_{isc}$$

where d means direct, s means sensitized; Φ_a is the efficiency of reaction from the triplet.

(b) Quenching Method. Solutions containing *N*-butylmaleimide, a dimaleimide, or benzophenone in such a concentration as to make optical density at 350 nm equal to 2, and containing 1×10^{-3} *M* biacetyl, were made. A 4-ml portion of this solution was then poured into a fluorescence cell connected to the degassing flask, and degassed by five freeze–thaw cycles under high vacuum. The intensity of the phosphorescence of biacetyl at room temperature was measured. The area under the peak between 490 and 560 nm was taken as a measure of the intensity. The measured intensities were corrected for total triplet quenching. From the Stern–Volmer equation, one can calculate the amount of triplet quenched at the given concentrations of biacetyl. Since the triplet lifetime is known (see Table I) the corrected intensity obtained for each sample is then compared with the one obtained with benzophenone, which gives the value of Φ_{isc} for each compound. For benzophenone, total triplet quenching occurs at the given biacetyl concentration, while the singlet is not at all quenched. At this low biacetyl concentration, the amount of singlet quenched in *N*-butylmaleimide and the dimaleimides is very small, as can be calculated too from the Stern–Volmer equation, using the singlet lifetimes obtained by quenching.

To check whether the cyclization is quenched at this concentration of biacetyl, two samples of hexamethylenedimaleimide, one without biacetyl and one containing 10^{-3} *M* biacetyl, were irradiated with monochromatic light. The conversions were measured and found to be the same in the two samples.

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