

# Photochemistry of Nonconjugated Bichromophoric Systems. Photopolymerization of *N,N*-Alkylenebis(dimethylmaleimides)

F. C. De Schryver,\* N. Boens, and G. Smets

Contribution from the Department of Chemistry, Universiteit Leuven,  
Celestijnenlaan 200 F, B-3030 Heverlee, Belgium. Received February 20, 1974

**Abstract:** The term photopolymerization is defined as a polymerization process in which every chain propagating step involves the absorption of a photon. A kinetic analysis for the type a photopolymerization of a bichromophoric system A-A where the two chromophores react independently is presented. This type of photopolymerization is exemplified by the photopolymerization of *N,N'*-polymethylenebis(dimethylmaleimides). Quantum yield determinations and kinetic analysis clearly indicate that this photopolymerization is a multistep reaction. The rate constants for deactivation,  $k_d^T$ , and reaction,  $k_r^T$ , of the excited chromophore in the photopolymerization of *N,N'*-polymethylenebis(dimethylmaleimides) are determined by quenching experiments and are compared with those of the model system, *N*-butyldimethylmaleimide.

Recently<sup>1</sup> the term photopolymerization was defined as a polymerization process in which every propagation step involves a photochemical reaction. From this statement follows that a photopolymerization should be considered as a multistep reaction, in contrast to the photoinitiated polymerization.<sup>2</sup>

Photopolymerization can in principle be divided into two classes: the type a photopolymerization<sup>1b,c,e</sup> in which an excited state, singlet and/or triplet, is involved in each propagation reaction; and the type b photopolymerization in which each propagation occurs by reaction of a ground state species formed in a prior photochemical reaction.<sup>1f</sup>

Up to now attention has been focused on the synthetic aspects of this process, and only preliminary data of the kinetics involved have been reported.<sup>1a,d</sup> The aim of this paper is to stress the intimate relation between the type a photopolymerization and the photoaddition reaction as exemplified by the photopolymerization of *N,N*-alkylenebis(dimethylmaleimides). Noninteracting bichromophoric systems<sup>3</sup> are indeed most suitable for this type of study if the factors that influence the choice between intra- and intermolecular reaction of a system are known.

If one considers a type a photopolymerization of a bichromophoric system A-A, where the two chromophores react independently, and excludes the probability of exciting simultaneously the two chromophores, a general reaction scheme can be proposed (Scheme I).

The overall reaction rate for the disappearance of chromophore A<sup>0</sup> in the absence of quencher is given by eq 1. Assuming steady-state conditions and total light absorption, eq 2 is obtained on integration of eq 1 between time  $t$  and  $t_0$ . The concentrations are

$$-\frac{d[A^0]}{dt} = I_{\text{abs}} + k_r^s[A^0][A^1] + k_r^t[A^0][A^3] - k_d^s[A^1] - k_d^t[A^3] \quad (1)$$

respectively  $[A^0]_0(1 - p)$ , where  $[A^0]_0$  is the initial concentration and  $p$  the degree of conversion, and  $[A^0]_0$ .

$$2.303 \frac{K}{M} \log \frac{1}{1 - p} + 2.303 \frac{L(M - K)N}{MN} \log \frac{M + N[A^0]_0}{M + N[A^0]_0(1 - p)} + p[A^0]_0 = 2I_0(t - t_0) \quad (2)$$

In this equation  $K = k_d^T(k_d^s + k_{ST})$ ,  $L = k_d^s k_r^T$ ,  $M = k_r^s k_d^T + k_r^T k_{ST}$ , and  $N = k_r^s k_r^T$ .

If it is further assumed that only one excited state reacts, eq 3 and eq 4, in which  $\Phi_{isc}$  is the intersystem

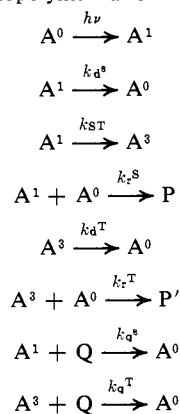
$$2.303 \frac{k_d^s + k_{ST}}{k_r^s[A^0]_0} \log \frac{1}{1 - p} + p = \frac{2I_0}{[A^0]_0} (t - t_0) \quad (3)$$

$$2.303 \frac{k_d^T}{k_r^T[A^0]_0} \log \frac{1}{1 - p} + p = \frac{2I_0}{[A^0]_0} \Phi_{isc}(t - t_0) \quad (4)$$

crossing efficiency, are obtained respectively for singlet and triplet reaction.

Furthermore, if the proposed idea is correct, it is possible to express the rate of polymerization as a

## Scheme I. Type I Photopolymerization



(1) (a) F. C. De Schryver, *Verh. Kon. Vlaam. Acad. Wetensch., Lett. Schone Kunsten Belg., Kl. Wetensch.*, **33**, 120 (1971); (b) F. C. De Schryver, J. Feast, and G. Smets, *J. Polym. Sci., Part A-1*, **8**, 1939 (1970); (c) F. C. De Schryver, N. Boens, and G. Smets, *ibid.*, **10**, 1687 (1972); (d) F. C. De Schryver, *Pure Appl. Chem.*, **34**, 213 (1973), and references cited therein. (e) For a recent survey on solid-state, four-center-type photopolymerizations, see M. Hasegawa, Y. Suzuki, H. Nakanishi, and F. Nakanishi, *Progr. Polym. Sci.*, **5**, 143 (1973); (f) F. C. De Schryver, T. Van Thien, and G. Smets, *J. Polym. Sci., Part B*, **9**, 425 (1971); (g) J. Higgins, A. M. Johannes, J. F. Jones, R. Schultz, D. A. McCombs, and C. S. Menon, *J. Polym. Sci. Part A-1*, **8**, 1987 (1970); (h) P. E. Pearson and P. D. Thieman, *ibid.*, **8**, 2103 (1970); (i) H. H. Böslér and R. C. Schulz, *Makromol. Chem.*, **158**, 113 (1972).

(2) G. Oster and N. L. Yang, *Chem. Rev.*, **68**, 125 (1968).

(3) For a previous report in this series, see J. Put and F. C. De Schryver, *J. Amer. Chem. Soc.*, **95**, 137 (1973).

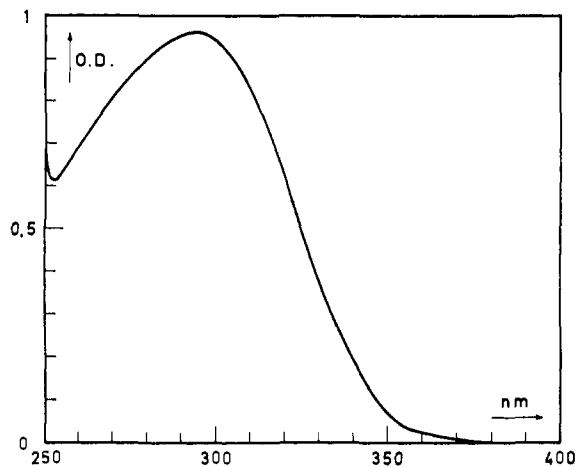
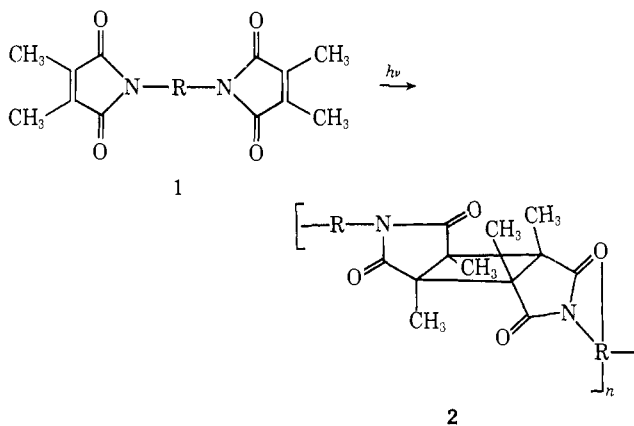


Figure 1. Optical density of **1c** as a function of wavelength in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$ : concentration  $5.37 \times 10^{-3} \text{ M}$ ;  $d = 1 \text{ cm}$ .

function of the degree of polymerization  $\bar{x}_n = 1/(1 - p)$ , which can be measured independently. Inspection of these equations shows the importance of the ratios of rate constants on the order of the reaction. It is therefore of prime importance to determine these rate constants and the nature of the excited state(s) involved in the reaction.

### Results and Discussion

On irradiation in the 300–350 nm region *N,N*-nonamethylene (**1a**) and *N,N*-undecamethylenebis(dimethylmaleimide) (**1b**) undergo cycloaddition<sup>4</sup> as does the model compound *N*-butyldimethylmaleimide (**1c**).



a,  $\text{R} = (\text{CH}_2)_9$ ; b,  $\text{R} = (\text{CH}_2)_{11}$ ; c,  $\text{R} = N\text{-}n\text{-butyl}$

**Ultraviolet Spectra of 1a, 1b and 1c.** The spectral appearance in the 250- to 400-nm region of the *N*-alkyldimethylmaleimide is presented in Figure 1. The fact

(4) The configuration of the cyclobutane ring in the polymer of **1b** is determined by comparative  $^{13}\text{C}$  and  $^1\text{H}$  nmr analysis of the dimer of **1c**, the polymer of **1b**, and the cyclomer of *N,N'*-trimethylenebis(dimethylmaleimide). The  $^{13}\text{C}$  and  $^1\text{H}$  absorptions of the dimer of **1c** and of poly-**1b** are identical; e.g., the protons of the methyl group on the cyclobutane ring absorb at 1.2 ppm in the dimer of **1c** and in poly-**1b** ( $\text{CDCl}_3\text{-TMS}$ ), and at 1.38 ppm in the cyclomer of *N,N'*-trimethylenebis(dimethylmaleimide) ( $\text{CDCl}_3\text{-TMS}$ ). The cyclobutane ring carbon atoms near the nitrogen atoms absorb at 49.6 ppm in the dimer and the carbonyl carbon atoms at 178.0 ppm; the methyl carbon atoms absorb at 13.0 ppm in the dimer and at 13.1 ppm in the polymer; the methylene carbon atoms near the nitrogen atoms absorb at 39.2 ppm in the dimer and at 39.4 ppm in the polymer ( $\text{CDCl}_3\text{-TMS}$ ). Since the dimer of **1c** has an exo configuration [R. N. Warrener and J. B. Bremner, *Res. Pure Appl. Chem.*, **16**, 117 (1966)], it can be concluded on the basis of nmr data that poly-**1b** has also the exo configuration.

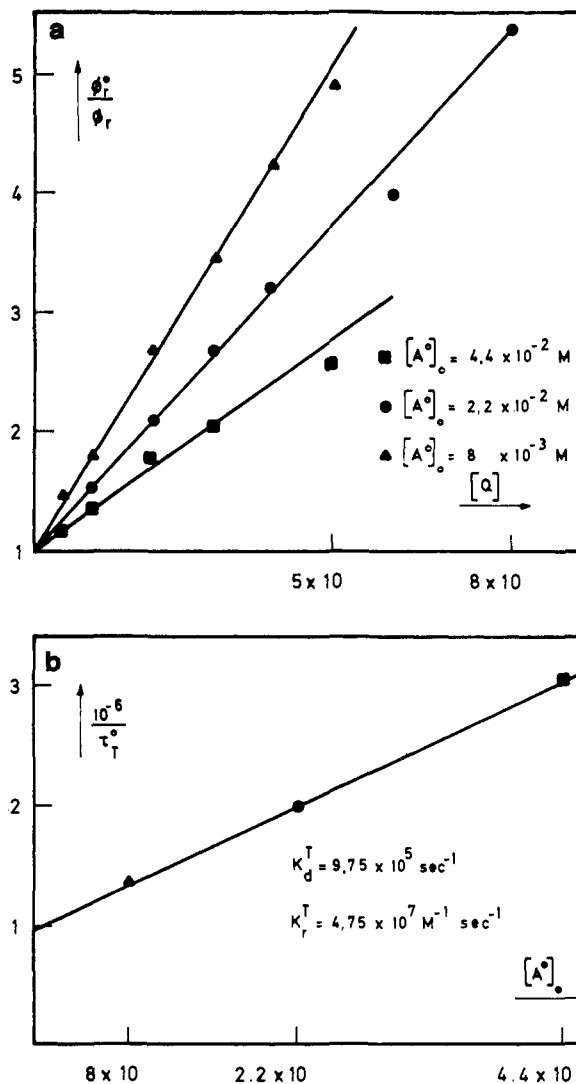


Figure 2. (a) Quenching of the photopolymerization of **1a** with 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide in  $\text{CH}_3\text{CN}$ . (b) Determination of  $k_d^T$  and  $k_r^T$  in the photopolymerization of **1b** in  $\text{CH}_3\text{CN}$ ;  $[\text{Q}] = 3,3,4,4\text{-tetramethyl-1,2-diazetidine 1,2-dioxide}$ .

that the molar extinction coefficient of **1a** and **1b** is within experimental error, equal to the double of that of **1c** at the same wavelength (Table I), indicates the

Table I. Molar Extinction Coefficients of **1a**, **1b**, and **1c**

	$\text{CH}_2\text{Cl}_2$		$\text{CH}_3\text{CN}$
	$\lambda = 293$	$\lambda = 350$	$\lambda = 292$
<b>1a</b>	355	27	343
<b>1b</b>	360	28	330
<b>1c</b>	182	14	172

absence of important interaction in the bichromophoric system in the ground state.

**Quenching of the Photopolymerization.** Degassed solutions of **1a**, **1b** or **1c** in  $\text{CH}_2\text{Cl}_2$  or in  $\text{CH}_3\text{CN}$  and containing various concentrations of a quencher were irradiated in parallel in a merry-go-round equipped with lamps with maximum intensity at 352 nm and a band width of 40 nm. The resulting Stern-Volmer plots are in all cases linear, e.g., Figure 2a. Linear Stern-Volmer

plots can be obtained if: (a) two states react and both are quenched,<sup>5a,b</sup> and if

$$k_q^s \tau_s^0 [1 + \Phi_r^{0T}/\Phi_r^{0s}] = k_q^T \tau_T^0 \quad (5)$$

where  $k_q^s$  and  $k_q^T$  equal the rate constant for respectively singlet and triplet quenching.  $\Phi_r^{0s}$  and  $\Phi_r^{0T}$  represent the quantum yield of respectively the singlet and triplet reaction in absence of quencher,  $\tau_s^0$  and  $\tau_T^0$  are the lifetimes of respectively the singlet and triplet excited state. The quantum yields and the lifetimes are dependent on the running chromophore concentration, e.g.

$$\tau_T^0 = 1/(k_d^T + k_r^T[A^0]) \quad (6)$$

Let us consider for which concentration(s) of  $[A^0]$  eq 5 is valid.

$$[A^0] = \frac{k_q^T k_r^s (k_d^s + k_{ST}) - k_q^s (k_r^s k_d^T + k_r^T k_{ST})}{k_r^s (k_r^T k_q^s - k_q^T k_r^s)} \quad (7)$$

Linear Stern–Volmer plots will be obtained for all concentrations of  $[A^0]$  if

$$k_r^T k_q^s = k_r^s k_q^T \quad (8)$$

$$k_d^s k_r^T = k_d^T k_r^s \quad (9)$$

and for only one concentration of  $[A^0]$  if the equalities in eq 8 and 9 do not hold. If eq 8 and 9 hold, and these values are substituted in the general Stern–Volmer equation, the general equation is simplified to a Stern–Volmer expression for reaction and quenching of the triplet state only (*vide infra*, eq 10).

In the dimethylmaleimide system the applicability of eq 8 and 9 is doubtful. From estimates of the singlet lifetime (*vide infra*) and in comparison with nonsubstituted maleimides,  $k_d^s$  should be of the order of  $10^9 \text{ sec}^{-1}$ . This would mean that, for  $k_q^T/k_d^T$  to be equal to  $k_q^s/k_d^s$ , (a)  $k_q^s$  should at least be 100 times faster than diffusion controlled. On this basis, this first assumption can be excluded. Other assumptions are the following.

(b) Singlet state is reactive; both states are quenched.

(c) Both states are reactive; only the singlet state is quenched.

(d) Singlet state reacts and is quenched.

In cases b, c, and d, the lifetime  $\tau_s^0$  could be calculated from the slope of the quenching curve assuming diffusion-controlled quenching. The lifetimes obtained, assuming a value of  $1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  in  $\text{CH}_3\text{CN}$ <sup>6</sup> and of  $1.66 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ <sup>3</sup> for the rate of quenching, are in the order of  $10^{-6}$ – $10^{-7}$  (Tables II–VII). The lifetimes of the singlet excited state, calcu-

**Table II.** Quenching of the Photopolymerization of **1a** in Acetonitrile with Ferrocene

$[A^0]_0, 10^{-3} \text{ M}$	$k_q^T \tau_T^0, \text{ M}^{-1}$	$\tau_T^0, 10^{-7} \text{ sec}$	$10^{-6}/\tau_T^0, \text{ sec}^{-1}$
4	9300	8.45	1.18
20	7400	6.72	1.48
50	5300	4.82	2.08

$$k_d^T = 1.10 \times 10^6 \text{ sec}^{-1}; k_r^T = 1.93 \times 10^7 \text{ sec}^{-1} \text{ M}^{-1}$$

(5) For an analogous treatment of a monomolecular photochemical reaction, see (a) P. J. Wagner in "Creation and Detection of the Excited State," A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, p 173; (b) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970).

(6) (a) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968); (b) P. J. Wagner and D. J. Bucheck, *ibid.*, **92**, 181 (1970).

**Table III.** Quenching of the Photopolymerization of **1b** in Acetonitrile with Ferrocene

$[A^0]_0, 10^{-3} \text{ M}$	$k_q^T \tau_T^0, \text{ M}^{-1}$	$\tau_T^0, 10^{-7} \text{ sec}$	$10^{-6}/\tau_T^0, \text{ sec}^{-1}$
4	7300	6.64	1.51
22	5800	5.27	1.90
50	4300	3.91	2.56

$$k_d^T = 1.42 \times 10^6 \text{ sec}^{-1}; k_r^T = 2.26 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$$

**Table IV.** Quenching of the Photodimerization of **1c** in Acetonitrile with Ferrocene

$[A^0]_0, 10^{-3} \text{ M}$	$k_q^T \tau_T^0, \text{ M}^{-1}$	$\tau_T^0, 10^{-7} \text{ sec}$	$10^{-6}/\tau_T^0, \text{ sec}^{-1}$
5.05	8900	8.09	1.24
26.3	5800	5.27	1.90
50	4600	4.18	2.39

$$k_d^T = 1.17 \times 10^6 \text{ sec}^{-1}; k_r^T = 2.55 \times 10^7 \text{ sec}^{-1} \text{ M}^{-1}$$

**Table V.** Quenching of the Photopolymerization of **1b** in Acetonitrile with 3,3,4,4-Tetramethyl-1,2-diazetene 1,2-Dioxide

$[A^0]_0, 10^{-3} \text{ M}$	$k_q^T \tau_T^0, \text{ M}^{-1}$	$\tau_T^0, 10^{-7} \text{ sec}$	$10^{-6}/\tau_T^0, \text{ sec}^{-1}$
8	8100	7.36	1.36
22	5480	4.98	2.01
44	3580	3.25	3.07

$$k_d^T = 9.75 \times 10^6 \text{ sec}^{-1}; k_r^T = 4.75 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$$

**Table VI.** Quenching of the Photopolymerization of **1a** in Dichloromethane with 3,3,4,4-Tetramethyl-1,2-diazetene 1,2-Dioxide

$[A^0]_0, 10^{-3} \text{ M}$	$k_q^T \tau_T^0, \text{ M}^{-1}$	$\tau_T^0, 10^{-6} \text{ sec}$	$10^{-5}/\tau_T^0, \text{ sec}^{-1}$
8	28200	1.70	5.89
22	18800	1.13	8.83
40	12700	0.76	13.07

$$k_d^T = 4.1 \times 10^6 \text{ sec}^{-1}; k_r^T = 2.2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$$

**Table VII.** Quenching of the Photopolymerization of **1b** in Dichloromethane with 3,3,4,4-Tetramethyl-1,2-diazetene 1,2-Dioxide

$[A^0]_0, 10^{-3} \text{ M}$	$k_q^T \tau_T^0, \text{ M}^{-1}$	$\tau_T^0, 10^{-6} \text{ sec}$	$10^{-5}/\tau_T^0, \text{ sec}^{-1}$
8	31,600	1.90	5.25
16	23,200	1.40	7.16
24	17,700	1.07	9.38

$$k_d^T = 3.2 \times 10^6 \text{ sec}^{-1}; k_r^T = 2.55 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$$

lated on the basis that no fluorescence is observed (indicating an upper limit of  $10^{-47}$  for the quantum yield of fluorescence and using the inherent singlet lifetime), should be in the subnanosecond range. This is much shorter than the values obtained by quenching. Furthermore, the reaction can be sensitized by acetophenone and benzophenone, indicating that the triplet state is also reactive. It is also highly improbable that triplet quenching does not occur since the triplet energy level of the quenchers used is lower than that of the chromophore ( $E_T^s$  of *N*-butyldimethylmaleimide =  $66 \pm 1 \text{ kcal mol}^{-1}$ ).

(7) The limit of detection of the fluorimeter Fica.

(8) Phosphorescence spectra measured in EPA at 77°K showed weak unstructured luminescence. The triplet energy is given at the emission maximum. Analogous results were obtained for *N*-alkylmaleimides by C. J. Seliskar and S. P. Mc Glynn, *J. Chem. Phys.*, **55**, 4337 (1971).

(e) Triplet state reacts; singlet state is quenched. In this case the Stern–Volmer plot is independent of the chromophore concentration. This is not found in this photopolymerization.

(f) The only possibility left is that the photopolymerization occurs from the triplet excited state of the chromophore, which is quenched. The Stern–Volmer equation is then given by

$$\Phi_r^0/\Phi_r = 1 + k_Q^T[Q]\tau_T^0 \quad (10)$$

In the quenching experiments the maximum conversion is usually small (<10%) and the running concentration in the expression of the lifetime (eq 6) can be replaced by  $[A^0]_0$ , the initial chromophore concentration.

Using the higher mentioned rate constants for diffusion-controlled quenching, we calculated the triplet lifetimes (Table II–VII). From the plot of  $1/\tau_T^0$  as a function of the initial chromophore concentration  $[A^0]_0$ , the rate constants  $k_d^T$  and  $k_r^T$  are obtained (Figure 2b, Tables II–VII).

**Quantum Yields.** The quantum yield for the disappearance of the dimethylmaleimide chromophore ( $\Phi_r^{0T}$ ) is given by eq 11. The quantum yields for the

$$\Phi_r^{0T} = 2\Phi_{ISC} \frac{k_r^T[A^0]}{k_d^T + k_r^T[A^0]} \quad (11)$$

disappearance of the dimethylmaleimide chromophore were measured by irradiation of a degassed solution of **1a**, **1b**, or **1c** in dichloromethane or acetonitrile with monochromatic light. The intensity of the incident light was measured by actinometry with *N,N'*-hexamethylenebismaleimide in dichloromethane.<sup>3</sup> Yields of the disappearance of the dimethylmaleimide chromophore were measured as usual by uv analysis. The results are compiled in Tables VIII and IX.

**Table VIII.** Quantum Yields for the Disappearance of the Dimethylmaleimide Chromophore in Acetonitrile

	$[A^0]_0,^a M$	$\lambda_{irr}, nm$	$\Phi_r^{0T}$	
<b>1b</b>	$4 \times 10^{-2}$	297	0.23	
		313	0.21	
		334	0.21	
<b>1a</b>	$2 \times 10^{-2}$	313	0.19	
		$4 \times 10^{-2}$	297	0.22
			313	0.24
334	0.23			
<b>1c</b>	$1 \times 10^{-1}$	313	0.30	
		$4 \times 10^{-2}$	313	0.24

<sup>a</sup> Initial dimethylmaleimide chromophore concentration is given.

**Table IX.** Quantum Yields for the Disappearance of the Dimethylmaleimide Chromophore in Dichloromethane

	$[A^0]_0,^a M$	$\lambda_{irr}, nm$	$\Phi_r^{0T}$	
<b>1a</b>	$2 \times 10^{-2}$	313	0.17	
		$4 \times 10^{-2}$	313	0.24
			334	0.23
<b>1c</b>	$2 \times 10^{-1}$	313	0.33	
		$4 \times 10^{-2}$	313	0.23

<sup>a</sup> Initial dimethylmaleimide chromophore concentration is given.

As can be seen from the data in Tables VIII and IX, the quantum yield at a certain chromophore concentration is practically independent of the wavelength and of the chain length between the two maleimide units. The small values indicate clearly that *this type of photo-*

*polymerization is not a chain process.* The quantum yields are dependent on the chromophore concentration, as follows from eq 11.  $1/\Phi$  as a function of  $1/[A^0]$  for the photopolymerization of **1a** in acetonitrile and dichloromethane gives a straight line, from which the values of  $\Phi_{ISC}$  and  $k_d^T/k_r^T$  can be calculated (Figure 3). The value  $k_d^T/k_r^T = 0.02 M$  in dichloromethane is in good agreement with the value obtained from quenching experiments ( $k_d^T/k_r^T = 0.019$ ; Table VI) with 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide as quencher.

The value  $k_d^T/k_r^T = 0.018$  in acetonitrile differs from that calculated from quenching experiments with ferrocene as quencher ( $k_d^T/k_r^T = 0.057$ ; Table II). The ratio  $k_d^T/k_r^T$  calculated from quenching experiments is generally greater in these experiments where ferrocene was used as a quencher (e.g., for **1b** in acetonitrile a value of  $k_d^T/k_r^T = 0.06$  (Table III) is found with ferrocene as quencher, and a value of  $k_d^T/k_r^T = 0.02$  is found with 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide (Table V)). This is due to an enhanced inter-system crossing from the triplet to the ground state ( $k_d^T$ ). An analogous effect is found in the crossing of the first excited singlet state to the triplet excited state. In the presence of ferrocene, the quantum yield of inter-system crossing for **1a** in acetonitrile equals 0.29, as compared to 0.18 in absence of ferrocene.

**Rate of Photopolymerization.** Degassed  $10^{-1} M$  solutions of **1a** or **1b** in  $CH_2Cl_2$  were irradiated in parallel with RUL 3500 Å lamps in the case of **1a** or RUL 3000 Å lamps in the case of **1b**. The temperature was controlled at 25°. All the incident light was absorbed by the system up to about 70–90% conversion. The solutions remained colorless during irradiation and no precipitate was formed. The reaction kinetics was followed by uv analysis at 290 or 300 nm. The long wavelength absorption disappeared completely in the polymer. The molecular weights of the formed polymers were measured as a function of the irradiation time. The intrinsic viscosities of the formed polymers were measured as a function of the degree of conversion.

**1. Kinetic Results of the Photopolymerization of 1a in  $CH_2Cl_2$ .** Irradiation with RUL 3500 Å Lamps,  $[A^0]_0 = 2 \times 10^{-2} M$ . The results for the photopolymerization of **1a** are given in Table X. The degree of conversion,  $p$ , equals  $(1 - A_t)/A_0$ , where  $A_0$  is the absorbance at time  $t_0$ ;  $A_t$  is the absorbance at time  $t$  and is calculated from the change in absorbance as a function of the irradiation time. As can be seen from the results in Table X, the degree of conversion and  $(\bar{x}_n - 1)/\bar{x}_n$ , obtained from the independently measured degree of polymerization,  $\bar{x}_n$ , are identical within experimental error. This result verifies the statement that in this type of polymerization,  $\bar{x}_n = 1/(1 - p)$ . Plots of the absorbance, the degree of conversion, or  $(\bar{x}_n - 1)/\bar{x}_n$  as a function of the irradiation time  $t$  give a straight line up to approximately 70% conversion (Figure 4). Deviations of linearity at higher conversions are due to the nontotal light absorption at the wavelength used (*vide infra*).<sup>9</sup> This indicates that the first

(9) If the amount of light absorbed is small, eq 1, assuming  $k_t^s = 0$  becomes on integration between time  $t$  and  $t_0$

$$\left[ \frac{k_d^T}{2.303k_r^T[A^0]} \right] \left[ \frac{p}{1-p} \right] + \log \frac{1}{1-p} = 2\Phi_{ISC}I_0\epsilon d(t - t_0)$$

In this equation  $\epsilon$  is the molar extinction coefficient of the chromophore and  $d$  the path length of the reaction vessel.

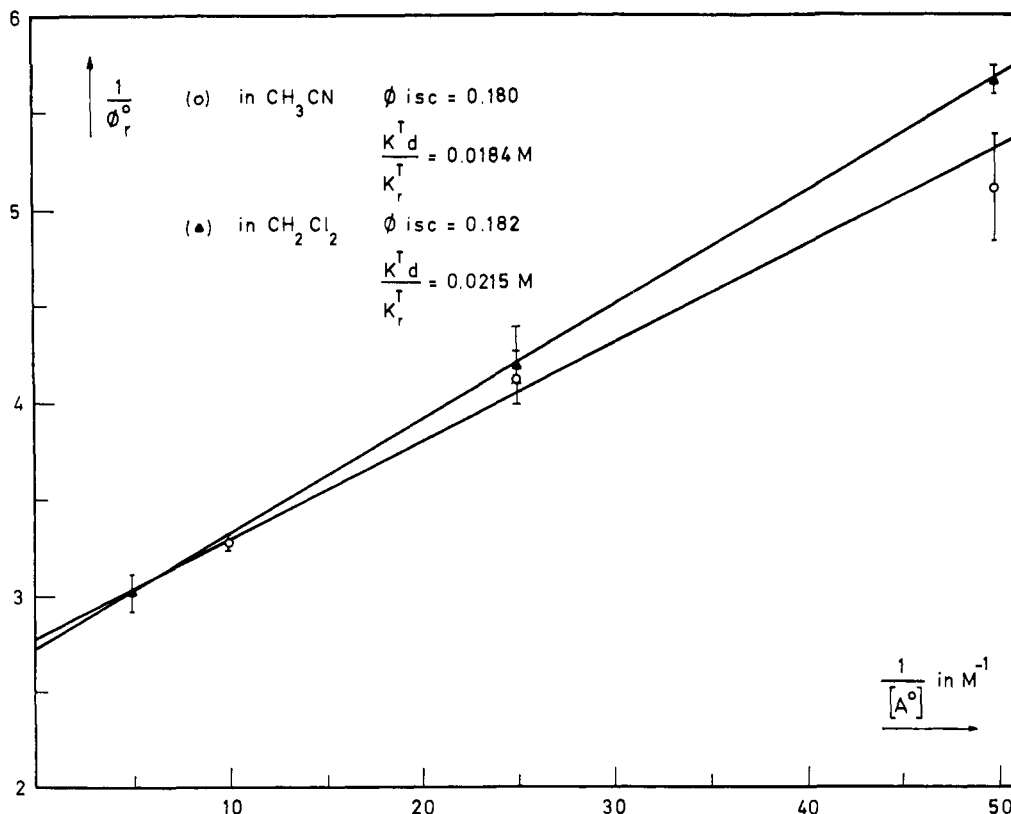


Figure 3.  $1/\Phi^{0T}$  as a function of  $1/[A^0]_0$  in the photopolymerization of **1a**,  $\lambda_{irr}$  313 nm.

Table X. Kinetic Results for the Photopolymerization of **1a** in  $CH_2Cl_2$ <sup>a</sup>

Irradiation time, <i>t</i> , hr	Absorbance, 300 nm <sup>b</sup>	Degree of conversion, <sup>c</sup> <i>p</i>	$1/(1-p)^c$	$0.215 \log [1/(1-p)] + p^c$	Mol wt	$\bar{x}_n^d$	$(\bar{x}_n - 1)/\bar{x}_n^d$	$0.215 \log \frac{\bar{x}_n + (\bar{x}_n - 1)}{\bar{x}_n^d}$	$[\eta]^e$
0	0.765	0	1	0	374	1	0	0	0.03
0.5	0.622	0.188	1.23	0.206	460	1.23	0.19	0.20	
1	0.480	0.373	1.59	0.416	590	1.58	0.37	0.41	
1.5	0.341	0.554	2.24	0.629	830	2.22	0.55	0.62	0.04
1.75	0.275	0.641	2.78	0.736	1000	2.68	0.63	0.71	
2	0.204	0.734	3.76	0.857	1320	3.54	0.71	0.83	0.09
2.5	0.085	0.889	9.42	1.094	2860	7.64	0.87	1.06	0.17
3.5	0.022	0.971	34.80	1.302					0.53
4.5	0.009	0.988	84.9	1.402					0.95
7.5	0.002	0.997	382.3	1.551					1.01

<sup>a</sup>  $[A^0]_0 = 2 \times 10^{-1} M$ ; irradiation with RUL 3500 Å lamps. <sup>b</sup> Dilution 50×. <sup>c</sup> Calculated from optical density measurements. <sup>d</sup> Calculated from molecular weight determinations by vapor pressure osmometry. <sup>e</sup> Measured at 20° in dichloromethane solution.

term in eq 4 or in eq 12, in which the rate of polymeriza-

$$2.303 \frac{k_d^T}{k_r^T[A^0]_0} \log \bar{x}_n + \frac{\bar{x}_n - 1}{\bar{x}_n} = \frac{2I_0\Phi_{ISC}}{[A^0]_0} (t - t_0) \quad (12)$$

tion is expressed by changes in the degree of polymerization as a function of reaction time, contributes only to a small extent to the total rate expression. Using values of  $k_d^T$  and  $k_r^T$ , determined by quenching experiments (see Table VI) in dichloromethane, and using the initial chromophore concentration  $[A^0]_0 = 2 \times 10^{-1} M$ , the total rate expression can be calculated. The data calculated on this basis are assembled in Table XI. The intrinsic viscosity as a function of the degree of conversion is a hyperbole.

**2. Kinetic Results of the Photopolymerization of 1b in Dichloromethane.**  $[A^0]_0 = 2 \times 10^{-1} M$ . Irradia-

**tion with RUL 3000 Å Lamps.** To substantiate the importance of total light absorption, irradiation of this system was performed at 300 nm where total light absorption is maintained to a much higher degree of conversion. The results for the photopolymerization of **1b** are given in Table XI. As in the case of **1a**, the absorbance of the solution, the degree of conversion, and  $(\bar{x}_n - 1)/\bar{x}_n$  vary linearly with the irradiation time, indicating that the first term in eq 4 or in eq 12 is small as compared to  $p$ . Using the absolute value of  $k_d^T$  and of  $k_r^T$ , obtained from quenching experiments in dichloromethane with 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide (Table VII), and the initial chromophore concentration  $[A^0]_0 = 2 \times 10^{-1} M$ , the total rate expression is calculated and reported in Table XI. A plot of the total rate expression as a function of time is presented in Figure 5.

Table XI. Kinetic Results for the Photopolymerization of *N,N*-Undecamethylenebis(dimethylmaleimide) in Dichloromethane<sup>a</sup>

Irradiation time, <i>t</i> , hr	Absorbance, 290 nm <sup>b</sup>	Degree of conversion, <i>p</i>	0.145 log		Mol wt	$\bar{x}_n^d$	$(\bar{x}_n - 1)/\bar{x}_n^d$	0.145 log $\bar{x}_n + (\bar{x}_n - 1)/\bar{x}_n$
			$1/(1-p)^c$	$[1/(1-p)] + p^c$				
0	0.752	0	1	0	402	1	0	0
0.33	0.717	0.046	1.05	0.049	450	1.12	0.10	0.11
0.83	0.636	0.154	1.18	0.164	500	1.24	0.20	0.21
1.33	0.565	0.249	1.33	0.267	580	1.44	0.30	0.33
2	0.482	0.359	1.56	0.387	690	1.72	0.42	0.45
2.66	0.392	0.478	1.92	0.519	820	2.05	0.51	0.55
3.33	0.276	0.633	2.73	0.696	1330	3.3	0.70	0.77
4	0.182	0.758	4.13	0.847	1750	4.3	0.77	0.86
4.66	0.083	0.890	9.06	1.028	3700	9.22	0.89	1.03

<sup>a</sup>  $[A^0]_0 = 2 \times 10^{-1} M$ ; irradiation with RUL 3000 Å Lamps. <sup>b</sup> Dilution 50×. <sup>c</sup> Calculated from optical density measurements. <sup>d</sup> Calculated from molecular weight determinations.

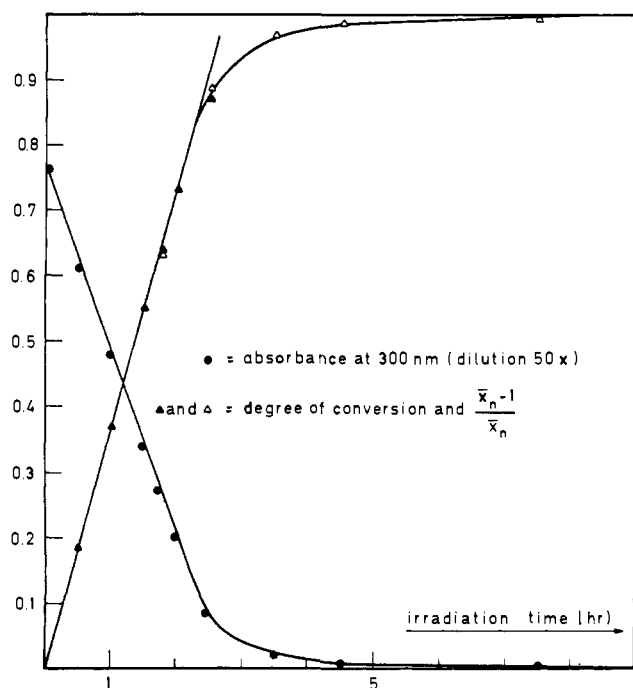


Figure 4. Photopolymerization of **1a** in  $CH_2Cl_2$  at 25° using RUL 3500 Å lamps.  $[A^0]_0 = 2 \times 10^{-1} M$ : (●) absorbance at 300 nm (dilution 50×), (Δ) degree of conversion, (▲)  $(\bar{x}_n - 1)/\bar{x}_n$ .

## Conclusion

The experimental data clearly illustrate the validity of the proposed scheme and the intimate relation between photoaddition and the type a photopolymerization. The photopolymerization kinetics under the condition of total light absorption are dependent on the rate constant of reaction, the deactivation of the triplet state, and the initial chromophore concentration, as could be expected from the derived equations. Other examples in which the first term of the rate expression (eq 4 or 12) contributes significantly will be reported in the near future.

## Experimental Section

**Chemicals.** Dichloromethane (Fluka Puriss; abfülldatum 30-11-1972) and acetonitrile (Baker reagent grade, Lot 5955) are used without further purification. Ferrocene (Baker Photosensitizer and Quencher Kit) was sublimed twice prior to use.

**Instrumentation.** Ultraviolet spectra were recorded on a Perkin-Elmer double beam spectrophotometer, Model 124. The uv analysis, to determine the conversions, was done on a Hitachi Perkin-Elmer spectrophotometer, Type 139, thermostated at 20°.

The viscosities of the polymers were measured with an Ostwald viscosimeter in dichloromethane solution at 20°. The molecular

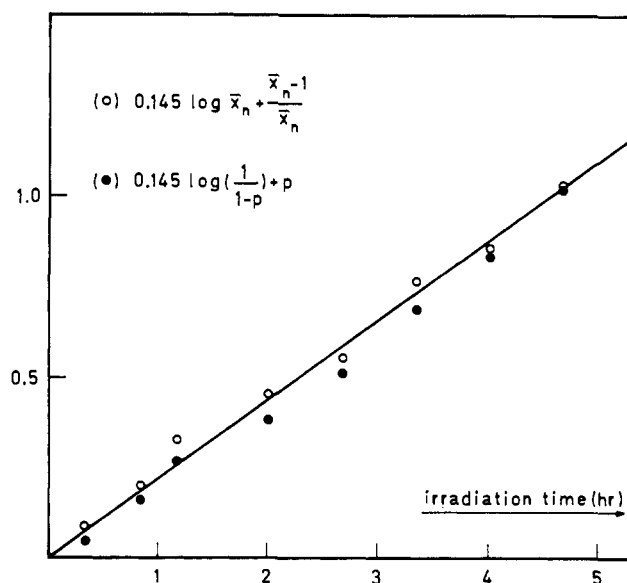


Figure 5. Photopolymerization of **1b** in  $CH_2Cl_2$  at 25° using RUL 3000 Å lamps.  $[A^0]_0 = 2 \times 10^{-1} M$ .

weights were determined in chloroform solution with a Mechrolab 301A vapor-pressure osmometer. The kinetic experiments were done in a Rayonet RS preparative photochemical reactor equipped with RUL 3500 Å or RUL 3000 Å lamps and a "merry-go-round" apparatus. Quenching experiments were carried out in a Rayonet Srinivasan-Griffin photochemical reactor, Model RPR 100, equipped with 16 RPR lamps and a merry-go-round, Model MGR-100. For the determination of the quantum yields, a Bausch & Lomb monochromator with a super-high-pressure mercury light source (Osram-200 HB) was used. The nmr spectra were recorded on a Varian XL 100 FT 15.

**Preparation of *N,N'*-Nonamethylenebis(dimethylmaleimide) and *N,N'*-Undecamethylenebis(dimethylmaleimide).** The bis(dimethylmaleimides) **1a** and **1b** and *N*-butyldimethylmaleimide (**1c**) can be synthesized by the method of Martin, Dickinson, and Rolands.<sup>10,11</sup> **1a** and **1b** were purified by column chromatography on Florisil with  $CH_2Cl_2$  as eluent, while **1c** was distilled under reduced pressure (bp 79° (0.6 mm)). Correct elementary analyses were obtained for the two substituted bismaleimides. *Anal.* Calcd for **1a**: C, 67.38; H, 8.02; N, 7.49; O, 17.11. Found: C, 67.20; H, 8.10; N, 7.35. Calcd for **1b**: C, 68.70; H, 8.46; N, 6.96; O, 15.88. Found: C, 68.70; H, 8.60; N, 6.95; O, 15.75. Calcd for **1c**: 66.27; H, 8.34; O, 17.66; N, 7.73. Found: C, 66.40; H, 8.30; N, 7.70.

**Preparation of 3,3,4,4-Tetramethyl-1,2-diazetidine 1,2-Dioxide.** 3,3,4,4-Tetramethyl-1,2-diazetidine 1,2-dioxide was prepared according to the method of Ullman and Singh,<sup>11-13</sup> starting from 2-nitropropane.

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

(11) R. Sayre, *J. Amer. Chem. Soc.*, **77**, 6689 (1955).

(12) M. Lamchen and T. W. Mittag, *J. Chem. Soc. C*, 2300 (1966).

(13) E. F. Ullman and P. Singh, *J. Amer. Chem. Soc.*, **94**, 5077 (1972).

**Kinetics of the Photopolymerization.** Pyrex tubes, each containing an equal amount of a 0.10 M solution of **1a** or **1b** in dichloromethane, were degassed in four successive freeze-thaw cycles and irradiated in a "merry-go-round" apparatus with lamps with  $\lambda_{\max}$  350 nm for **1a** or  $\lambda_{\max}$  310 nm for **1b**. All the incident light was absorbed by the system up to about 70–90% conversion. The solutions remained colorless during irradiation, and no precipitate was formed. The absorbance of the solution and the molecular weights of the formed polymers were measured as a function of the irradiation time. The intrinsic viscosities of the polymers were measured as a function of the degree of conversion.

**Quenching of the Photopolymerizations.** Different samples (5 ml) with a given concentration of *N,N'*-undecamethylenebis(dimethylmaleimide) or *N,N'*-nonamethylenebis(dimethylmaleimide), but with various concentrations of quencher (ferrocene or 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide) in dichloromethane or acetonitrile, were degassed in four freeze-thaw cycles and irradiated in parallel in a "merry-go-round" apparatus, equipped with lamps that have a maximum intensity at 352 nm (band width 40 nm). The conversion in each sample was determined by means of the optical density. The change in optical density in each sample was compared with that in the reference samples containing no quencher and was, when ferrocene was used as the quencher, eventually corrected for partial light absorption by the quencher. Such a quenching was carried out for different dimethylmaleimide chromophore

concentrations. The maximum conversion in the reference sample never exceeded 10%.

**Quantum Yields.** A solution (3 ml) with a given dimethylmaleimide chromophore concentration in dichloromethane or acetonitrile was degassed in four freeze-thaw cycles. 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, and irradiated. All the incident light was absorbed. During irradiation the solution was stirred with a magnetic stirrer. The degree of conversion was determined directly by measuring the optical density of the undiluted solution. The maximum conversion was about 8%. The amount of light absorbed was calculated from the optical density differences. The incident light intensity was measured by actinometry with *N,N'*-hexamethylenebismaleimide in dichloromethane.<sup>3</sup>

**Acknowledgment.** The authors are indebted to the Nationaal Fonds voor Wetenschappelijk Onderzoek and to the Fonds voor Wetenschapsbeleid for financial support. One of us (N. B.) is indebted to the Nationaal Fonds voor Wetenschappelijk Onderzoek (Belgium) for a fellowship. Dr. S. Toppet is thanked for taking the nmr spectra.

## Chemical Transformations with Regenerable, Polymer-Supported Trisubstituted Phosphine Dichlorides. The Efficacious Incorporation of Phosphorus Reagents on Polymer Supports

Howard M. Relles\* and Robert W. Schluez

*Contribution from General Electric Research & Development Center, Schenectady, New York 12301. Received October 25, 1973*

**Abstract:** Trisubstituted phosphine dichloride reagents have been prepared chemically bound to cross-linked polystyrene beads. The reaction of phosgene with the corresponding phosphine oxide reagents was the final step in the three synthetic approaches used. The reagents were employed successfully for the preparation of acid chlorides from acids, an imidoyl chloride from an anilide, a nitrile from a primary amide, an alkyl chloride from an alcohol, and a chloroolefin from a ketone. Each reaction simultaneously regenerated the resin-bound phosphine oxide reagent, which was readily recovered and rephosgenated for subsequent use.

A limited number of publications dealing with polymer-supported organophosphorus reagents have appeared in the past few years. Three groups<sup>1</sup> have prepared polymeric Wittig reagents by treating cross-linked polymeric triarylphosphines (**5**) with alkyl halides and then strong base. The reactions of ketones or aldehydes with these reagents then led to various olefins which were separated from the resulting cross-linked polymeric triarylphosphine oxide (**7**) by filtration. Several other reports<sup>2</sup> have indicated that metal com-

plexes of **4**, **5**, or similar polymeric trisubstituted phosphines could be prepared and used for a variety of transition-metal-catalyzed reactions, such as olefin hydrogenation, hydroformylation, and arylacetylene cyclo-trimerization.

In this paper we report the synthesis and synthetic utility of cross-linked, polymeric trisubstituted phosphine dichlorides. Not only can these materials be used for carrying out a wide variety of organic chemical transformations<sup>3</sup> and separating the reaction products conveniently by simple filtration,<sup>1,2</sup> but the nature of

(1) (a) W. Heitz and R. Michels, *Angew. Chem., Int. Ed. Engl.*, **11**, 298 (1972); (b) S. V. McKinley and J. W. Rakshys, Jr., *J. Chem. Soc., Chem. Commun.*, 134 (1972); (c) F. Camps, J. Castells, J. Font, and F. Vela, *Tetrahedron Lett.*, 1715 (1971).

(2) (a) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Amer. Chem. Soc.*, **94**, 1789 (1972); (b) R. H. Grubbs, L. C. Kroll, and E. M. Sweet, Abstracts of Papers, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, No. POLY-46; (c) R. H. Grubbs and L. C. Kroll, *J. Amer. Chem. Soc.*, **93**, 3062 (1971); (d) M. Capka, P. Svoboda, M. Cerny, and J. Hetflejš, *Tetrahedron Lett.*, 4787 (1971); (e) P. L. Ragg, British Patent 1,249,033 (1971); (f) J. Manassen, *Isr. J. Chem. Suppl. Proc. Isr. Chem. Soc.*, **8**, 5 (1970); (g) K. G. Allum, R. D. Hancock,

and P. J. Robinson, German Patent 1,948,987 (1970); U. S. Patent 3,652,778 (1972); (h) K. G. Allum and R. D. Hancock, German Patent 1,948,988 (1970); U. S. Patent 3,658,884 (1972).

(3) These transformations proceed analogously to similar reactions using triphenylphosphine dichloride. In effect, the latter reagent and the polymeric phosphine dichlorides behave like mild forms of  $\text{PCl}_5$ . See, for example, (a) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964); (b) L. Horner, H. Oediger, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **626**, 26 (1959); (c) H. M. Relles, U. S. Patent 3,715,407 (1973); (d) H. M. Relles, unpublished results.