Energy Transfer Processes Involving Ultraviolet Stabilizers. Quenching of Excited States of Ketones

J. P. Guillory* and C. F. Cook

Contribution from the Phillips Petroleum Company, Research and Development Division, Bartlesville, Oklahoma 74004. *Received March 20, 1973*

Abstract: The excited-singlet and triplet-state quenching properties of ultraviolet stabilizers have been investigated using the ketone photosensitized cis–trans isomerization of piperylene in solution as the energy transfer system. Both benzophenone and 4-methyl-2-pentanone were used as photosensitizers. Nickel chelate stabilizers, particularly nickel dibutyldithiocarbamate, were found to quench singlet and triplet states by a diffusional exchange energy transfer process. The excited carbonyl quenching rate constants of metal chelates can be roughly correlated with stabilization effectiveness in thin polypropylene and polyethylene films; however, evidence is presented which questions whether the principal action of the metal chelates in the polymer involves only excited carbonyl quenching. The possibility of quenching electronically excited singlet oxygen in the polymer by metal chelates is discussed. Three organic stabilizers, a hydroxybenzophenone and two hydroxyphenylbenzotriazoles, were also examined and found to be effective quenchers of the excited states of 4-methyl-2-pentanone. In order to correlate these results with the behavior in polyolefins, mechanisms involving steric hindrance to energy transfer in the polymer and generation of singlet oxygen by the stabilizers are proposed and discussed.

Ultraviolet stabilizers can protect polymers from photodegradation by ultraviolet light-screening and/or by energy-quenching mechanisms. The properties of absorbers which function primarily as light screeners have been discussed in detail.[1,2] Reactive stabilizers (usually nickel chelates) are believed to operate by quenching the excited states of polymer molecules[3–6] and/or by quenching electronically excited molecular oxygen (singlet oxygen) formed in the polymer.[7] It has been shown that nickel chelate stabilizers can function as quenchers of singlet oxygen by an energy transfer process.[7] The present work deals with the quenching of the excited states of ketones by stabilizers. The ketone photosensitized cis–trans isomerization of piperylene is used to measure the quenching behavior of ultraviolet stabilizers in solution. Our results indicate that some nickel chelates can quench both the excited singlet and triplet states of ketones and the quenching mechanism involves diffusional exchange energy transfer. Three organic stabilizers (a hydroxybenzophenone and two hydroxyphenylbenzotriazoles) were also found to quench the excited states of ketones. These quenching behaviors are discussed in terms of the effectiveness of stabilizers in protecting polyolefins from photodegradation.

Until recent quenching studies of singlet oxygen,[7] it has generally been believed that those ultraviolet stabilizers which are chelates of transition metals function by quenching electronically excited polymer molecules before photodegradation can occur. Mechanistically, the process is thought to involve energy transfer from carbonyl groups in the polymer (formed during polymer processing) to the stabilizer, thereby preventing Norrish type I and/or type II reactions in the polymer.[3–6,8,9] Briggs and McKellar[3] have shown a rough correlation between the triplet quenching action of nickel oxime chelates and their stabilization effectiveness in polypropylene. They used flash photolysis techniques with anthracene as the donor; however, as pointed out by Carlsson and Wiles,[5] anthracene is a poor model for the polypropylene system. Chien and Conner[10] have measured the quenching behaviors of a nickel chelate in the diethyl ketone sensitized photooxidation of cumene. Hammond and Foss[11] have used the photoreduction of benzophenone by benzhydrol to study the effects of metal complex quenchers. The system we have chosen to examine the quenching properties of ultraviolet stabilizers is the ketone photosensitized cis–trans isomerization of piperylene. Both benzophenone and 4-methyl-2-pentanone (MP) were used as photosensitizers. MP is energetically and structurally similar to the carbonyl segments shown to exist in melt-oxidized polypropylene films[12] and therefore is a good model for evaluating the quenching ability of stabilizers.

Kinetic Scheme

The mechanistic scheme for dissipation of the excitation energy of nonreactive ketone (K) in the presence of piperylene and a quenching-type stabilizer (Q) is shown in Scheme I, where cis and trans represent the ground state of *cis*- and *trans*-piperylene, the superscripts 0, 1, and 3 denote the ground state, excited singlet state, and excited triplet state, respectively, and ^3X is the common triplet intermediate for piperyl-

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[1] W. L. Hawkins and F. H. Winslow in "Crystalline Olefin Polymers," R. A. V. Raff and K. W. Doak, Ed., Interscience, New York, N. Y., 1964, Chapter 8; J. H. Claudet, G. C. Newland, H. W. Patton, and J. W. Tamblyn, *SPE (Soc. Plast. Eng.) Trans.*, **1**, 26 (1961); V. I. Goldenberg, V. Ya. Shlyapintokh, L. M. Postnikov, and G. A. Sukhanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. **10**, 2232 (1968).

[2] J. P. Guillory and C. F. Cook, *J. Polym. Sci., Part A-1*, **9**, 1529 (1971).

[3] P. J. Briggs and J. F. McKellar, *J. Appl. Polym. Sci.*, **12**, 1825 (1968).

[4] M. Heskins and J. E. Guillet, *Macromolecules*, **1**, 97 (1968).

[5] D. J. Carlsson, T. Suprunchuk, and D. M. Wiles, *J. Appl. Polym. Sci.*, **16**, 615 (1972).

[6] P. Hrdlovic, I. Lukac, and Z. Manasek, IUPAC Conference on Chemical Transformation of Polymers, Bratislava, Czech., June 1971, Preprint P-61.

[7] J. P. Guillory and C. F. Cook, *J. Polymer Sci., Part A-1*, submitted for publication.

[8] O. Cicchetti, *Advan. Polym. Sci.*, **7**, 70 (1970).

[9] M. Heskins and J. E. Guillet, *Macromolecules*, **3**, 224 (1970).

[10] J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, **90**, 1001 (1968).

[11] G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, **68**, 3739 (1964); R. P. Foss, D. O. Cowan, and G. S. Hammond, *ibid.*, **68**, 3747 (1964).

[12] D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 587 (1969); D. J. Carlsson and D. M. Wiles, *ibid.*, **2**, 597 (1969); D. J. Carlsson, Y. Kato, and D. M. Wiles, *ibid.*, **1**, 459 (1968).

Scheme I

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\begin{array}{lll}
{}^0\mathrm{K} \longrightarrow {}^1\mathrm{K} & I_a & (1)\\
{}^1\mathrm{K} \longrightarrow {}^0\mathrm{K} & k_2 & (2)\\
{}^1\mathrm{K} + {}^0\mathrm{Q} \longrightarrow {}^0\mathrm{K} + {}^1\mathrm{Q} & k_q{}^S & (3)\\
{}^1\mathrm{Q} \longrightarrow {}^0\mathrm{Q} & k_4 & (4)\\
{}^1\mathrm{K} \longrightarrow {}^3\mathrm{K} & k_{ISC} & (5)\\
{}^3\mathrm{K} \longrightarrow {}^0\mathrm{K} & k_6 & (6)\\
{}^3\mathrm{K} + {}^0\mathrm{Q} \longrightarrow {}^0\mathrm{K} + {}^3\mathrm{Q} & k_q{}^T & (7)\\
{}^3\mathrm{Q} \longrightarrow {}^0\mathrm{Q} & k_8 & (8)\\
{}^3\mathrm{K} + \mathrm{cis} \longrightarrow {}^0\mathrm{K} + {}^3\mathrm{X} & k_9 & (9)\\
{}^3\mathrm{K} + \mathrm{trans} \longrightarrow {}^0\mathrm{K} + {}^3\mathrm{X} & k_{10} & (10)\\
{}^3\mathrm{X} \longrightarrow \mathrm{cis} & k_{11} & (11)\\
{}^3\mathrm{X} \longrightarrow \mathrm{trans} & k_{12} & (12)
\end{array}
$$

ene.[13,14] The Stern–Volmer formulation for quenching of a nonreactive ketone like benzophenone gives

$$\phi^0{}_{c\rightarrow t}/\phi^q{}_{c\rightarrow t} = (1 + K_S[Q])(1 + K_T[Q]) \qquad (13)$$

where $\phi^0{}_{c\rightarrow t}$ is the initial quantum yield for cis–trans isomerization of piperylene in the absence of quencher, *i.e.*, ultraviolet stabilizer, $\phi^q{}_{c\rightarrow t}$ is the initial "quenched" quantum yield, K_S is $k_q{}^S/(k_2 + k_{ISC})$, K_T is $k_q{}^T/(k_6 + k_9[\mathrm{cis}])$, and [Q] is the molar concentration of stabilizer. Equation 13 is based on short irradiation time where $[\mathrm{trans}] \ll [\mathrm{cis}]$.

Hammond and Foss[11] have shown that many metal chelates are essentially only triplet-state quenchers of benzophenone. Under this assumption, eq 13 can be simplified to

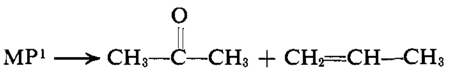
$$\phi^0{}_{c\rightarrow t}/\phi^q{}_{c\rightarrow t} = 1 + K_T[Q] \qquad (14)$$

It has been shown by Lamola and Hammond[14] that $k_9[\mathrm{cis}] \gg k_6$ for $[\mathrm{cis}] \geq 0.01\ M$. If the quenching rate of a stabilizer is equal to the diffusion-controlled rate for triplet state quenching by piperylene, then $k_q{}^T = k_9$ and eq 14 becomes

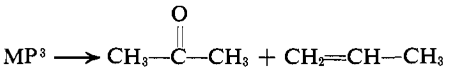
$$\phi^0{}_{c\rightarrow t}/\phi^q{}_{c\rightarrow t} = 1 + [Q]/[\mathrm{cis}] \qquad (15)$$

Equation 15 defines the upper limit of the quantum yield ratio for diffusion-controlled quenching of triplet states by ultraviolet stabilizers.

In the case of MP as the photosensitizer, two reactions must be added to the kinetics scheme for type II photoelimination, the dominant degradative process for MP[12,15]



$$\mathrm{MP}^1 \longrightarrow \mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3} + \mathrm{CH_2{=}CH{-}CH_3} \qquad k_r{}^S \quad (16)$$



$$\mathrm{MP}^3 \longrightarrow \mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3} + \mathrm{CH_2{=}CH{-}CH_3} \qquad k_r{}^T \quad (17)$$

where MP^1 and MP^3 are the excited singlet and triplet states of MP, respectively.

The form of eq 13 does not change with the addition of reactions 16 and 17; however, K_S and K_T are now

$$K_S' = k_q{}^S/(k_2 + k_r{}^S + k_{ISC}) \qquad (18)$$

$$K_T' = k_q{}^T/(k_6 + k_r{}^T + k_9[\mathrm{cis}]) \qquad (19)$$

Consequently

$$\phi^0{}_{c\rightarrow t}/\phi^q{}_{c\rightarrow t} = (1 + K_S'[Q])(1 + K_T'[Q]) \qquad (20)$$

for quenching by the stabilizer in the MP–piperylene system.

Another quantum yield ratio can be derived for the MP system based on the type II photoelimination of MP. In this system, piperylene is not used and the quantum yield ratio for propylene production is measured where

$$\phi_p{}^0/\phi_p{}^q = (1 + K_S'[Q])(1 + K_T{}^p[Q])/(1 + K^p[Q]) \qquad (21)$$

and $\phi_p{}^0$ is the initial quantum yield for propylene production in the absence of stabilizer quenching, $\phi_p{}^q$ is the initial "quenched" quantum yield, K_S' is defined in eq 18, $K_T{}^p$ is $k_q{}^T/(k_6 + k_r{}^T)$, and K^p is $k_r{}^Sk_q{}^T/(k_r{}^Sk_6 + k_r{}^Sk_r{}^T + k_r{}^Tk_{ISC})$. Equation 21 is in agreement with the kinetics analysis of Dalton and Turro[16] for photochemical reactions which involve quenching of both singlet and triplet states.

The rate constants K_S' and K_T' in eq 20 can be determined separately from a concentration study. $K_T'[Q]$ is negligible for $[\mathrm{cis}] \gg [Q]$ since piperylene is the dominant triplet-state quencher under such conditions. Consequently, K_S' alone can be determined directly from the quantum yield ratio. K_T' can then be calculated from quantum yield data in which [cis] and [Q] are of comparable values. This analysis assumes that $k_q{}^S$ and $k_q{}^T$ are independent of the concentration of stabilizers, *i.e.*, only diffusional exchange singlet and triplet state quenching takes place. In the case of long-range resonance quenching, the quenching rate constants have an r^{-6} dependence which is equivalent to a dependence on $[Q]^2$.[10,17] A study of the quantum yield ratio as a function of [Q] can be used to not only separate K_S' and K_T' but also to determine whether the quenching mechanism involves diffusional exchange or long range resonance processes.

Experimental Section

All experiments were conducted in benzene as the solvent. The solutions were degassed by argon saturation and sealed in quartz cells. The irradiation system consisted of a PEK 200-W short-arc mercury lamp mounted on an optical bench with quartz lens and a mirror to provide a collimated beam. A 3650-Å filter system was used for excitation of the benzophenone–piperylene solutions and consisted of Corning C.S. 7-37 and 0-52 glass filters. The MP–piperylene solutions were excited using a 3130-Å filter system which consisted of Corning C.S. 7-54 and 0-53 glass filters and a 2.0-cm cell of 0.0005 M K_2CrO_4. Baker *cis*-piperylene was purified by preparative vapor phase chromatography before use. Benzophenone (zone refined) and benzene (99.99%) were obtained commercially from James A. Hinton. 4-Methyl-2-pentanone (MP) was Matheson Coleman and Bell reagent grade. Ferric acetylacetonate $[\mathrm{Fe(AA)_3}]$ from J. T. Baker Chemical Co. was used without further purification. Commercially available ultraviolet stabilizers which were examined included nickel dibutyldithiocarbamate (BTN), zinc dibutyldithiocarbamate (BTZ), [2,2′-thiobis(4-*tert*-octylphenolato)]-*n*-butylaminenickel(II) (Ni-I), bis[2-(2-hydroxy-5-*tert*-octylthiophenol)-4-*tert*-octylphenolato]nickel(II) (Ni-II), nickel bis[*O*-butoxy(3,5-di-*tert*-butyl-4-hydroxybenzyl)]phosphonate (Ni-III), 2-hydroxy-4-*n*-octyloxybenzophenone (UV-I), 2-(3′,5′-di-*tert*-butyl-2′-hydroxyphenyl)-5-chlorobenzotriazole (UV-II), and 2-(2′-hydroxy-5′-methylphenyl)benzotriazole (UV-P). A Cary Model 14 spectrophotometer was used for all ultraviolet and visible absorption measurements. Magnetic susceptibilities of the ultra-

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(13) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(14) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(15) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165 (1968).

(16) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970).

(17) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, Chapter 5.

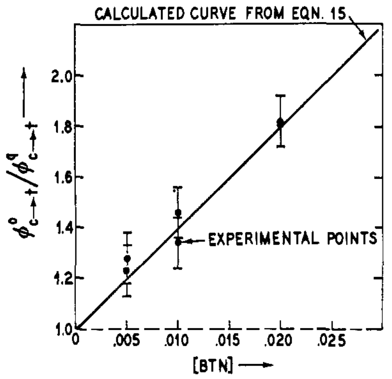

Figure 1. Stern–Volmer plot for quenching of benzophenone photosensitized isomerization of piperylene by BTN in benzene at 25°.

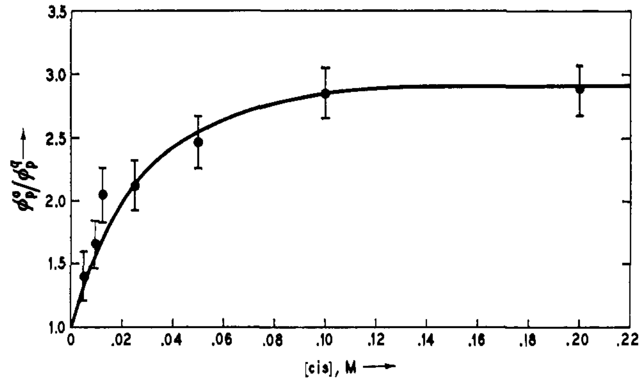

Figure 2. Stern–Volmer plot for quenching of Norrish type II photoelimination of 4-methyl-2-pentanone by *cis*-piperylene in benzene at 25°.

violet stabilizers as solids were measured at room temperature with a Gouy balance. Fluorescence spectra of MP were obtained using a Perkin-Elmer 12-C monochromator with an EMI 9634 QR photomultiplier and a Hanovia 10-W low-pressure mercury lamp for excitation. Phosphorescence spectra of MP were measured in the laboratory of Professor R. S. Becker at the University of Houston using the apparatus described by Becker, *et al.*[18]

Sample analyses for cis–trans conversion of piperylene and for propylene production were made with a Perkin-Elmer F11 gas chromatograph equipped with a flame ionization detector. The vpc column was 15 ft × 1/8 in. packed with 15% dimethylsulfolane on Chromosorb P (80–100 mesh).

The quantum yield ratios (eq 13, 20, and 21) were experimentally determined by the simultaneous irradiation of two sample cells (rectangular, quartz cells with 10-mm light path). The first cell contained only the ketone photosensitizer and *cis*-piperylene (standard solution), whereas the other contained ketone, *cis*-piperylene, and the stabilizer (*i.e.*, quencher) in question. Typical concentrations used in the MP–piperylene solutions were 2.66 M 4-methyl-2-pentanone (1:3 v/v), 0.025 M *cis*-piperylene, and 0.02 M stabilizer. The MP is replaced by 0.05 M benzophenone for the benzophenone–piperylene system. The ratio of per cent cis–trans conversion (or amount of propylene production) in the standard solution to that in the solution containing stabilizer gives the quantum yield ratio after correcting for light screening by the ultraviolet stabilizer. A screening correction value for each system can be easily calculated from the absorbances of the ketone and ultraviolet stabilizer in question once the relative light intensity distribution of the mercury lamp–filter system is known. Intensity distributions for the 200-W mercury lamp with the 3650- and 3130-Å filter systems were measured using a Perkin-Elmer 12-C monochromator system modified for the ultraviolet–visible range with an EMI 9634 QR photomultiplier. Screening correction values, C_{SC}, were calculated using

$$C_{SC} = \sum_{\lambda_1}^{\lambda_2} I(\lambda)\left(\frac{A_K(\lambda)}{A_K(\lambda) + A_S(\lambda)}\right)\Bigg/\sum_{\lambda_1}^{\lambda_2} I(\lambda) \qquad (22)$$

where $I(\lambda)$ is the experimental light intensity distribution of the mercury lamp–filter system as a function of wavelength, λ, $A_K(\lambda)$ is the absorbance of the ketone photosensitizer (benzophenone or MP), and $A_S(\lambda)$ is the absorbance of the ultraviolet stabilizer. According to eq 22, C_{SC} is the fraction of filtered light absorbed by the ketone photosensitizer in the presence of stabilizer. In calculating the quantum yield ratio, the rate of cis–trans conversion of piperylene (or propylene production) in the standard ketone–piperylene solution is multiplied by C_{SC} to correct it for the light screening that occurs in the ketone–piperylene–stabilizer solution. Values for C_{SC} range from 0.032 for BTN to 0.575 for Ni-III with the 3130-Å filter system, 2.66 M MP, and 0.02 M stabilizer. The screening correction calculation was tested experimentally by comparing the rate of cis–trans conversion in a solution of 0.05 M benzophenone and 0.025 M *cis*-piperylene screened by a separate solution of 3×10^{-4} M BTN in benzene with that of an identical benzophenone–piperylene solution which was not screened. After correcting for BTN screening by C_{SC}, the rates of conversion in the two solutions were within 10% agreement with each other. However, because of the large screening corrections which are sometimes necessary, this experiment showed that the uncertainty in the quantum yield ratio could be as large as 10–20%.

Diffusional Exchange Quenching

Fe(AA)$_3$ has been shown in the literature to be a good triplet-state quencher.[11] Its deactivation and quenching rate constants (k_6 and k_q^T, respectively) have been determined[19] and, consequently, Fe(AA)$_3$ should be a good check of our ketone–piperylene technique. The quantum yield ratio, $\phi^0_{c\to t}/\phi^q_{c\to t}$, was measured with the benzophenone–piperylene technique and found to be 1.37 ± 0.1 for 0.02 M Fe(AA)$_3$, 0.025 M *cis*-piperylene, and 0.05 M benzophenone. Assuming triplet-state quenching only and using eq 14, this ratio corresponds to a K_T of 19 ± 4 M^{-1}. A value of 22 M^{-1} is calculated using the measured rate constants of Bell and Linschitz[19] of $k_q^T = 2.7 \times 10^9$ M^{-1} sec^{-1} and $k_6 = 10^5$ sec^{-1} with $k_9 = k$(diffusion) $= 5 \times 10^9$ M^{-1} sec^{-1} in benzene at 25°[20] and [cis] = 0.025 M. This good agreement shows that the benzophenone–piperylene technique can be used to quantitatively measure the triplet quenching behavior of molecules.

The triplet quenching properties of BTN were investigated using the benzophenone–piperylene technique. This ultraviolet stabilizer was selected because it has been found to be one of the best nickel chelate stabilizers for thin polypropylene and polyethylene films.[7,21] The quantum yield ratio, $\phi^0_{c\to t}/\phi^q_{c\to t}$, for [BTN] = 0.02 M and [cis] = 0.025 M, was found to be 1.80 ± 0.05. According to eq 15, this is the upper limit for $\phi^0_{c\to t}/\phi^q_{c\to t}$ and indicates that the triplet quenching effectiveness of BTN is equal to that of piperylene. The latter has been shown to quench triplet states at a diffusion-controlled rate.[13,14] A concentration study of BTN in the benzophenone–piperylene system verified the diffusion-controlled nature of the energy transfer process. The results are shown in Figure 1 and are predictable from eq 15.

Just as in the benzophenone–piperylene case, a maximum value for K_T' can be estimated for the MP–piperylene system. It is first necessary to determine the

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(18) R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969).

(19) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

(20) P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968); P. J. Wagner, *ibid.*, **89**, 5898 (1967); W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

(21) G. C. Newland and J. W. Tamblyn, *J. Appl. Polym. Sci.*, **9**, 1947 (1965).

value of $k_6 + k_r^T$ in eq 19. These rate constants can be determined from a Stern–Volmer plot of the triplet-state quenching of Norrish type II reaction of MP by *cis*-piperylene. Such a plot is shown in Figure 2 (based on the formation of propylene). The curve levels off at the point where all excited triplet states of MP are quenched by piperylene, and the type II reaction occurs only from the singlet state. This indicates that 65% of the type II reaction originates from the triplet state in agreement with reported results for similar alkyl ketones.[22–24] Figure 2 can be corrected for singlet-state reaction using the 65:35, triplet:singlet ratio for type II reaction and

$$\phi_P = \phi_P(S) + \phi_P(T) \tag{23}$$

where $\phi_P(S)$ and $\phi_P(T)$ refer to the quantum yields of propylene production from the singlet and triplet states of MP, respectively.[24] The corrected data can now be fitted with a linear Stern–Volmer formulation for triplet-state quenching. The slope of eq 24 can be

$$\frac{\phi_P{}^0(T)}{\phi_P{}^q(T)} = 1 + \frac{k_q{}^T}{k_6 + k_r{}^T}[\mathrm{cis}] \tag{24}$$

used to calculate $k_6 + k_r^T$ and gives $(k_6 + k_r^T) = 3 \pm 2 \times 10^7$ sec^{-1} assuming $k_q{}^T = k(\text{diffusion}) = 5 \times 10^9$ sec^{-1} M^{-1} for benzene at 25°. This value agrees well with the reported results of Bibart, *et al.*,[23] for the photolysis of 2-pentanone. All the foregoing considerations provide values for the rate constants required to estimate the upper limit of K_T'. If the quenching ability of the stabilizer is equal to that of *cis*-piperylene in benzene, *i.e.*, diffusion controlled, then $k_q{}^T = k_9 = 5 \times 10^9$ sec^{-1} M^{-1}. Using the above value for $(k_6 + k_r^T)$, this gives a maximum value of K_T' of 32 M^{-1} for [cis] = 0.025 M. As will be shown later, this upper limit becomes useful in evaluating the behavior of BTN as a quencher of excited MP.

We have already shown in the benzophenone–piperylene system that BTN quenches the triplet state of benzophenone at a diffusion-controlled rate. BTN was also examined as a quencher in the MP–piperylene system. The results are shown in Table I. The singlet state quenching properties of BTN were examined by using high concentrations of *cis*-piperylene (0.2 M) with 0.01 M BTN so that the triplet states of MP are quenched primarily by the *cis*-piperylene. Under these conditions, K_T' which is a function of [cis] is small and K_S' can be calculated using eq 20. For a quantum yield ratio of 1.2 ± 0.1 (from Table I), a K_S' of 20 ± 10 M^{-1} was calculated. This value is in agreement with the collisional quenching constants reported for biacetyl quenching of the singlet state of diethyl ketone ($K_q = 28 \pm 2$ M^{-1}), methyl ethyl ketone ($K_q = 47 \pm 3$ M^{-1}), and cyclopentanone ($K_q = 25 \pm 1$ M^{-1}).[25] Using $K_S' = 20$ M^{-1} and the quantum yield ratios in Table I for low *cis*-piperylene concentrations, *i.e.*, 0.025 M, a K_T' value of 42 ± 12 M^{-1} is obtained with eq 20. This is in reasonable agreement with the theoretical maximum value of K_T' of 32 M^{-1} which assumes diffusional-controlled quenching. These results indicate that BTN quenches MP by a diffusional exchange energy transfer mechanism.

Table I. Quenching of MP by BTN[a]

[BTN], M	[cis], M	$\phi^0{}_{c\to t}/\phi^q{}_{c\to t}$
0.02	0.025	2.3 ± 0.2
0.02	0.025	2.4 ± 0.2[b]
0.01	0.025	1.9 ± 0.3
0.01	0.2	1.2 ± 0.1

[a] [MP] = 2.66 M. [b] [MP] = 1.33 M.

In almost all the quenching experiments, an MP concentration of 2.66 M was used to ensure adequate light absorption by MP in the presence of stabilizer. The possibility of energy migration from MP-to-MP exists, however, because of this high concentration. Such a process was not considered in the kinetics analysis. Consequently, experiments with BTN were run at MP concentrations of 1.33 M. As shown in Table I, this result was identical with that at higher concentrations of MP indicating the absence of energy migration.

Our kinetic analyses assume that the ultraviolet stabilizers after direct excitation do not photosensitize the cis–trans isomerization of piperylene. This is probably a valid assumption for the nickel chelates since they all have weak absorption bands in the 600–700-nm region; their low-lying energy levels should therefore be below the lowest triplet state of piperylene. This assumption was checked with BTN and Ni-II by direct excitation of these stabilizers in the presence of *cis*-piperylene. No cis–trans conversion was observed. Nevertheless, photosensitization of piperylene by stabilizers in the ketone–piperylene system would be reflected by a quantum yield ratio of <1.

Quenching by Metal Chelate Stabilizers

The quenching behaviors of other metal chelate stabilizers were investigated in the MP–piperylene system. Results are reported in Table II. Ni-I and Ni-III have been found to exist as a tetramer and a trimer, respectively, in benzene.[7] The molar concentrations shown in Table II have been adjusted accordingly.

Table II. Quenching of MP by Metal Chelate Stabilizers

Stabilizer	[cis], M	$\phi^0{}_{c\to t}/\phi^q{}_{c\to t}{}^a$	K_T', M^{-1}	K_S', M^{-1}
0.025 M Ni-I[b]	0.025	1.4	11	
0.025 M Ni-I	0.2	1.1		4
0.1 M Ni-II	0.025	1.1	1	0
0.02 M BTZ	0.025	1.1	5	0 (assumed)
0.033 M Ni-III	0.025	0.8	?	?

[a] Standard deviation (1σ) = 10%. [b] No quenching was observed for 0.005 or 0.01 M Ni-I.

A further study of Ni-III was conducted since a quantum yield ratio of <1 was observed. It was found that Ni-III can transfer triplet energy to piperylene both after direct excitation and after indirect excitation from quenching excited MP. The quantum yield ratio for propylene production, $\phi_P{}^0/\phi_P{}^q$, in eq 21 was conse-

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(22) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970).

(23) C. H. Bibart, M. G. Rockley, and F. S. Wettack, *ibid.*, **91**, 2802 (1969).

(24) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(25) J. T. Dubois and M. Cos, *J. Chem. Phys.*, **38**, 2536 (1963).

quently measured for Ni-III and BTN (for comparison purposes) in the absence of piperylene. A value of 1.8 ± 0.4 was found for 0.033 M Ni-III compared with 2.2 ± 0.4 for 0.01 M BTN. From Figure 2 it can be seen that 0.033 M *cis*-piperylene gives a quantum yield ratio of 2.3 for triplet-state quenching of MP. Quenching rate constants cannot be determined from ϕ_p^0/ϕ_p^q because of the complexity of eq 21; however, the results do indicate that Ni-III is an effective quencher of the excited states (singlet and/or triplet states) of MP.

On the basis of the excited carbonyl quenching results above, the commercial metal chelate stabilizers can be ordered BTN > Ni-I > BTZ > Ni-II. In the case of Ni-III we can only conclude that it is not as good as BTN but is a better quencher than Ni-II (a poor quencher). Despite this, the above ordering is in approximate agreement with the stabilization effectiveness of these stabilizers in thin polypropylene and polyethylene films.[7]

Magnetic susceptibility measurements of the metal chelate stabilizers as solids indicate that BTN and BTZ are diamagnetic whereas Ni-I, Ni-II, and Ni-III are paramagnetic. The observed quenching effects cannot therefore be related directly to the magnetic properties of the metal chelates.

The fluorescence and phosphorescence spectra of MP are shown in Figure 3. The spectra are in agreement with those of similar aliphatic ketones reported by O'Sullivan and Testa.[26] Only the absorption spectra of BTN and Ni-I showed any appreciable overlap with the emission spectra of MP. The quenching of singlet states by long-range resonance transfer requires overlap of the fluorescence spectrum of the donor and the absorption spectrum of the acceptor.[17,27] The overlap shown in Figure 3 is indeed proper to explain the singlet quenching results we have observed. However, singlet quenching rate constants, k_q^S, for the resonance mechanism are usually 10^{10}–10^{11} M^{-1} sec^{-1} [17,27] which would have led to a value of Ks' for BTN an order of magnitude larger than the 20 M^{-1} we observed. Nevertheless, we cannot at this time completely rule out the possibility of singlet resonance energy transfer from MP to BTN and Ni-I. The effects of long-range resonance transfer in systems involving molecular diffusion are not easily evaluated.[27,28]

Quenching by Organic Stabilizers

The MP system can be used to study the quenching properties of organic stabilizers. This is accomplished by monitoring the type II photoelimination of MP in the absence of piperylene. Piperylene was omitted from these quenching measurements because of the possibility of triplet transfer from stabilizer to piperylene after quenching of MP's triplet state has occurred. The results are given in Table III. BTN and *cis*-piperylene have been included as quenchers for comparison purposes.

The results above show that UV-I, UV-II, and UV-P are as effective as BTN in quenching the excited states of MP. A comparison with *cis*-piperylene shows that stabilizers are quenching both singlet and triplet states. The quenching process is probably the diffusional exchange mechanism as evidenced by the slow increase in quantum yield ratio with increasing quencher concentration. Diffusional exchange quenching by hydroxybenzophenones and hydroxyphenylbenzotriazoles has also been observed by Hrdlovic, *et al.*,[6] in the photolysis of polyvinyl phenyl ketone and by Goldenberg, *et al.*,[29] in the benzophenone photosensitized oxidation of diphenylmethane and ethylbenzene. Our quenching results would suggest that UV-I and UV-II are equally effective in polyolefins and should behave as quenchers as well as screeners. However, previous studies show that while UV-I behaves as both screener and quencher in stabilizing thin polypropylene films, UV-II acts only as a screener.[2,5] Photostabilities after direct excitation cannot explain these differences since UV-II is actually much more photostable than UV-I.[2] In addition, singlet oxygen quenching by these stabilizers has already been shown to be negligible.[7] This leaves two arguments which may explain the above effects: (a) steric hindrance to energy transfer in the polymer medium; and (b) the generation of singlet oxygen by the stabilizers after quenching excited carbonyls in the polymer.

Steric hindrance to energy transfer may result from the *tert*-butyl groups in UV-II. This effect could be one of unfavorable spatial orientation for effective energy transfer in the polymer[30] or may be associated

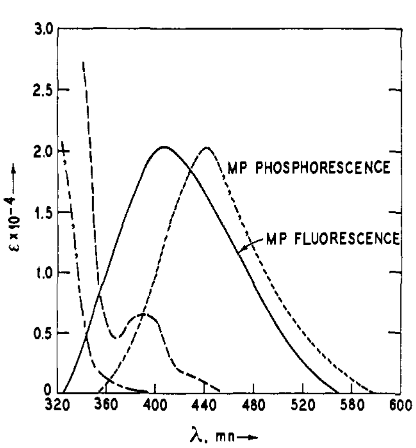

Figure 3. Fluorescence (—) spectrum in arbitrary units of MP in 3-methylpentane at 25° (λ_{exc} 254 nm); phosphorescence (···) spectrum in arbitrary units of MP in 3-methylpentane at 77°K (λ_{exc} 275 nm); absorption spectra of Ni-I (–·–) and BTN (– –) in benzene at 25°.

Table III. Quenching of MP by Stabilizers

Quencher	[Q], M	ϕ_p^0/ϕ_p^q
UV-I	0.0025	1.3 ± 0.2
	0.0034	1.6 ± 0.3
	0.01	2.1 ± 0.4
UV-II	0.0025	1.3 ± 0.2
	0.01	1.9 ± 0.3
UV-P	0.01	2.0 ± 0.4
BTN	0.01	2.2 ± 0.4
cis-Piperylene	0.01	1.6[a]

[a] From Figure 2.

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(26) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 258 (1970); M. O'Sullivan and A. C. Testa, *ibid.*, **92**, 5842 (1970).

(27) A. A. Lamola in "Technique of Organic Chemistry, Energy Transfer and Organic Photochemistry," Vol. XIV, P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, Chapter 2.

(28) M. Tomura, E. Ishiguro, and N. Mataga, *J. Phys. Soc. Jap.*, **25**, 1439 (1968).

(29) V. I. Goldenberg, V. Y. Shlyapintokh, and L. M. Postnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 7, 1483 (1968).

(30) W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4777 (1966).

with the absence of intermolecular hydrogen bonding to the detrimental carbonyl groups in the polymer chain. The latter is supported by our studies of the phosphorescence of UV-I, UV-II, and UV-P in hydrocarbon and polar solvents. Both UV-I and UV-P show a weak phosphorescence at 77°K in 3-methylpentane and a strong phosphorescence in EPA (ethyl ether–isopentane–ethyl alcohol, 5:5:2). The phosphorescence spectrum of UV-I and the dependence of intensity on the nature of the solvent have also been observed by Lamola and Sharp for *o*-hydroxybenzophenones.[31] Our emission spectrum of UV-P agrees with that reported for amidophenylbenzotriazoles.[32] UV-II, on the other hand, shows no phosphorescence in either 3-methylpentane or EPA. The phosphorescence of UV-I and UV-P can be explained in terms of intermolecular hydrogen bonding between stabilizer and the hydrogen-bonding solvent, EPA.[31] Intramolecular hydrogen bonding in UV-I and UV-P is broken by interaction with EPA and strong phosphorescence is observed. The *tert*-butyl groups in UV-II prevent this latter interaction and the existence of very fast radiationless decay (probably from the singlet state) would prevent the observation of any emission. In terms of polymer stabilization, this means that intermolecular hydrogen bonding between stabilizer and the detrimental carbonyl segments in the polymer is possible in the case of UV-I but not for UV-II. This interaction could serve as the mechanism for concentrating UV-I near the carbonyl segments in the polymer and for allowing effective quenching of the excited carbonyls by UV-I. Nurmukhametov, Shigorin, and Mileshina have proposed a similar mechanism for hydroxybenzophenones.[33]

o-Hydroxybenzophenones have been shown to have triplet-state lifetimes of about 10^{-8} sec in ethanol at room temperature,[31] whereas intramolecularly hydrogen bonded *o*-acetamidophenylbenzotriazole has a triplet-state lifetime of approximately 0.5 sec in a terpolymer at room temperature.[32] If indeed both UV-I and UV-II behave as carbonyl quenchers in the polymer, UV-II with its long triplet-state lifetime could generate singlet oxygen by energy transfer after quenching the excited carbonyls. This could cancel any beneficial effects resulting from carbonyl quenching. On the other hand, UV-I with its short triplet-state lifetime would generate relatively little singlet oxygen and, consequently, would behave as both screener and quencher in the polymer. More study is obviously necessary to determine the relative importance of this singlet oxygen generation argument as compared to the intermolecular hydrogen-bonding mechanism.

Discussion and Conclusions

It has long been assumed that excited-state quenching is an important property of ultraviolet stabilizers. Some attempts have recently been made to measure the quenching action of stabilizers;[2,3,5,10] however, a detailed understanding of the quenching mechanism was not possible in some of these studies or they were restricted by the choice of energy donor. The MP–piperylene technique is not limited in this sense. Based on the studies of Carlsson and Wiles on the initiation of photodegradation in polypropylene,[12,34] 4-methyl-2-pentanone is a good model for the harmful species in polyolefins. All types of quenching processes can be measured either separately or collectively (*i.e.*, singlet- and/or triplet-state quenching) in the MP–piperylene system. The effects of collisional exchange or long-range resonance quenching can be examined by concentration studies. Studies of the quenching of excited states of MP by ultraviolet stabilizer should give important clues as to the quenching processes which may occur in the polymer.[35]

Our studies of the quenching action of metal chelate stabilizers indicate that there may be a correlation between carbonyl quenching efficiency and stabilization effectiveness in polyolefins. BTN, for example, is a good ultraviolet stabilizer of thin polyolefin samples[2,7] and a good quencher of excited singlet and triplet states of 4-methyl-2-pentanone. Although the possibility of long-range resonance quenching of singlet state by BTN cannot be completely ruled out, our results indicate that collisional exchange energy transfer dominates in solution. Our studies and those of Hrdlovic, *et al.*,[6] show that most of the metal chelate stabilizers (with the exception of BTN) are much less effective quenchers of excited states than the organic stabilizers like UV-I and UV-II. However, in polymer stability tests the metal chelates and organic stabilizers like UV-I are of comparable efficiency.[2,5,6] All these observations raise serious question as to whether excited carbonyl quenching by stabilizers in the polymer is the most important mechanism for polymer stabilization. In view of our recent correlation of the quenching of singlet oxygen by metal chelate stabilizers with stabilization effectiveness in thin polyolefin films,[7] it is tempting to propose that singlet oxygen quenching in the polymer is an important mode of ultraviolet stabilization in polyolefins.[35,36] An investigation of excited carbonyl and singlet oxygen quenching by metal chelate stabilizers in the polymer matrix is necessary to determine the relative importance of these two quenching processes. We are presently engaged in such studies and the results will be reported elsewhere.

Our investigations of the quenching action of hydroxybenzophenones and hydroxyphenylbenzotriazoles demonstrate the difficulties involved in extrapolating liquid-phase quenching results to quenching processes occurring in a polymer matrix. Both UV-I and UV-II are effective quenchers of excited MP, but only UV-I functions as a quencher in the polymer.[2,5] Whether intermolecular hydrogen bonding between UV-I and carbonyls in the polymer or the generation of singlet oxygen by UV-II is important in explaining these results has yet to be determined.

The key to the development of improved ultraviolet stabilization systems lies in understanding the quenching mechanism by which stabilizers operate. Our studies with the MP–piperylene system have given insight into the energetic and structural requirements for

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(31) A. A. Lamola and L. J. Sharp, *J. Phys. Chem.*, 70, 2634 (1966).

(32) J. R. Merrill and R. G. Bennett, *J. Chem. Phys.*, **43**, 1410 (1965).

(33) R. N. Nurmukhametov, D. N. Shigorin, and L. A. Mileshina, *Vysokomol. Soedin., Ser. B*, 9, 26 (1967).

(34) D. J. Carlsson and D. M. Wiles, *J. Polym. Sci., Part B*, **8**, 419 (1970).

(35) D. J. Carlsson, D. E. Sproule, and D. M. Wiles, *Macromolecules*, **5**, 659 (1972).

(36) D. J. Carlsson, T. Suprunchuk, and D. M. Wiles, *J. Polym. Sci., Part B*, **11**, 61 (1973).

effective stabilization. Measurements in the polymer which consider both excited carbonyl and singlet oxygen quenching are now needed to completely characterize the behavior of stabilizers.

Acknowledgment. We wish to thank R. P. Hendrix for performing many of the quenching experiments and Professor R. S. Becker of the University of Houston for many helpful suggestions.

2,4,6-Trisubstituted Pyridines. Synthesis, Fluorescence, and Scintillator Properties[1a]

Maria del Carmen G. Barrio, Jorge R. Barrio, Graham Walker, Armando Novelli,[1b] and Nelson J. Leonard*

Contribution from the Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina, and the Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received December 9, 1972*

Abstract: The synthesis of 2,4,6-trisubstituted pyridines from chalcones and formamide, under the conditions of the Leuckart reaction, is described. In contrast to 2,4,6-triphenylpyridine, which yields 2,4,6-tricyclohexylpiperidine on catalytic hydrogenation with platinum in acetic acid, 2,6-diphenyl-4-(*p*-methoxyphenyl)pyridine and 2,6-di(*p*-methoxyphenyl)-4-phenylpyridine yield 2,6-dicyclohexyl-4-(*p*-methoxyphenyl)pyridine and 4-cyclohexyl-2,6-di(*p*-methoxyphenyl)pyridine, respectively. Physical and chemical evidence firmly established the proposed structures. The ultraviolet absorption and fluorescence excitation and emission spectra of the substituted pyridines synthesized showed structure and pH dependence. Most of the compounds showed extremely high fluorescence intensity, being readily visible at concentrations even below 1×10^{-9} *M*. Initial studies have demonstrated that certain 2,4,6-triaryl substituted pyridines show promising potential as scintillators that will allow liquid scintillation counting to be carried out at high efficiency in strongly acidic solution.

A convenient and relatively simple procedure for the preparation of 2,4,6-triarylpyridines has been developed during the course of attempts to synthesize 1,3-diarylallylamines. The starting materials for this synthesis are the commercially available or easily accessible chalcones (**1**). The reaction of chalcones (**1**) with formamide under conditions of the Leuckart reaction[2] (Scheme I) yielded 2,4,6-triarylpyridines (**2**) as the major products. The overall yields, in the range of 30–33%, were good compared with those obtained by other routes. The spectroscopic properties of certain of the 2,4,6-trisubstituted pyridines are of interest, particularly the high degree of fluorescence and the efficiency of liquid scintillation counting in strongly acidic solution.

Previously, 2,4,6-triarylpyridines have been prepared by the condensation of 1,5-diketones with formamide–formic acid[3] and by other synthetic procedures including the Chichibabin method.[4-7] Following this procedure, the yields of single products are low because of the formation of mixtures of pyridines and various by-products.[7] Formamide has proved to be a versatile agent in heterocyclic syntheses,[8-10] in the Leuckart reaction with aldehydes and ketones,[11-17] and in addition reactions to olefins in the presence of ultraviolet light[18-24] or peroxides.[25,26] The course of the reaction of the chalcones (**1**) with the product mixture resulting from heating ammonium carbonate and formic acid in *ca.* 1:2 molar proportion, or with excess formamide–ammonium formate, is complicated because of the combined functionality in **1**. Formamide alone during 6 hr at 180–190° did not produce appreciable triarylpyridine from chalcone **1c**. The structures of the products formed in the general condensation reaction, **1** → **2** (Scheme I), were established by elemental analysis, nmr spectra, and positive compari-

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(1) (a) The synthetic methodology described in this article was initiated at the University of Buenos Aires under the guidance of Professor Armando Novelli. (b) Deceased.

(2) M. L. Moore, *Org. React.*, **5**, 301 (1949).

(3) F. Chubb, A. S. Hay, and R. B. Sandin, *J. Amer. Chem. Soc.*, **75**, 6042 (1953).

(4) W. Dilthey, *J. Prakt. Chem.*, **102**, 209 (1921).

(5) R. Lombard and J. P. Stephan, *Bull. Soc. Chim. Fr.*, 1458 (1958).

(6) W. Zecher and F. Kröhnke, *Chem. Ber.*, **94**, 690 (1961).

(7) R. L. Frank and R. P. Seven, *J. Amer. Chem. Soc.*, **71**, 2629 (1949), and references therein.

(8) H. Bredereck, R. Gompper, H. G. v. Schuh, and G. Theilig, *Angew. Chem.*, **71**, 753 (1959).

(9) H. Bredereck, R. Gompper, H. G. v. Schuh, and G. Theilig, *Newer Methods Prep. Org. Chem.*, **3**, 241 (1964).

(10) H. W. Gibson, *Chem. Rev.*, **69**, 673 (1969).

(11) P. A. S. Smith and A. J. Macdonald, *J. Amer. Chem. Soc.*, **72**, 1037 (1950).

(12) W. H. Davies and M. A. T. Rogers, *J. Chem. Soc.*, 126 (1944).

(13) M. Mousseron, R. Jacquier, and R. Zagdoun, *Bull. Soc. Chim. Fr.*, 197 (1952).

(14) V. Komarov, E. A. Chernikova, and G. V. Komarov, *Zh. Fiz. Khim.*, **36**, 540 (1962); *Chem. Abstr.*, **57**, 1605 (1962).

(15) A. N. Kost and I. I. Grandberg, *Zh. Obshch. Khim.*, **25**, 1432 (1955); *Chem. Abstr.*, **50**, 4800 (1956).

(16) D. S. Noyce and F. W. Bachelor, *J. Amer. Chem. Soc.*, **74**, 4577 (1952).

(17) A. Chatterjee and R. Raychaudhuri, *J. Org. Chem.*, **33**, 2546 (1968).

(18) D. Elad, *Proc. Chem. Soc., London*, 225 (1962).

(19) D. Elad, *Chem. Ind.* (*London*), 362 (1962).

(20) D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964).

(21) D. Elad and J. Rokach, *ibid.*, **30**, 3361 (1965).

(22) D. Elad and J. Rokach, *J. Chem. Soc.*, 800 (1965).

(23) D. Elad, *Angew. Chem., Int. Ed. Engl.*, **5**, 255 (1966).

(24) M. Fish and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1325 (1966).

(25) A. Rieche, E. Schmitz, and E. Gruendemann, *Z. Chem.*, **4**, 177 (1964).

(26) A. Rieche, E. Schmitz, and E. Gruendemann, *Angew. Chem.*, **73**, 621 (1961).

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