Organic Photochemistry. XIII. Photocycloaddition of Aliphatic Ketones to α,β-Unsaturated Nitriles[1]

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Abstract: Ultraviolet irradiation of dialkyl or alicylic ketones in the presence of acrylonitrile (**1**) or methacrylonitrile (**2**) has been observed to lead to two classes of product: oxetanes (**4–5**) from photocycloaddition of the ketone to the α,β-unsaturated nitrile, and dimers (**8–11**) from photosensitized dimerization of **1** and **2**. Irradiation of acetone in the presence of crotononitrile (**3**) led to cis–trans isomerization of **3** and the production of the *cis*- and *trans*-oxetanes, **6** and **7**. The latter were formed stereospecifically, in that each arose exclusively from *cis*-**3** or *trans*-**3**, respectively. In the acetone–methacrylonitrile system, oxetane formation was not quenched by piperylene, whereas the formation of the dimers of **2** was so quenched. Furthermore, a study of the quantum yield of photocycloaddition to give the oxetane **5** as a function of the concentration of methacrylonitrile suggested that reaction must involve a singlet complex of excited ketone with ground-state α,β-unsaturated nitrile. This exciplex decays to ground-state reactants, or reacts to produce oxetane. The fluorescence of the ketones studied was partially quenched in the presence of α,β-unsaturated nitriles, and the extent of fluorescence quenching and relative quantum yields of photocycloaddition were measured for several pairs of reactants. Thus the rate constants for complexation, and the partition of the complex between deactivation and oxetane formation, were estimated. Simple perturbation MO theory is used to examine the structure of the exciplex.

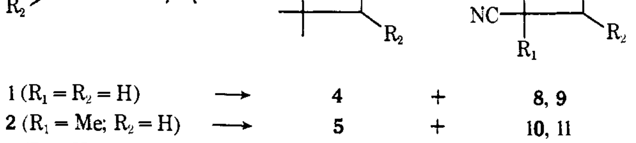
Recently there has been considerable interest in the photocycloaddition reaction of carbonyl compounds to olefins, to yield oxetanes.[2,3] Reaction is generally initiated by attack of the electron-deficient oxygen atom of the $^3(n,\pi^*)$ state of the carbonyl compound.[2a,b,d] Evidence has been advanced for a biradical intermediate, which can subsequently ring close to form an oxetane; the major oxetane isomer is usually that which would be expected from formation of the most stable biradical intermediate.[3b,3d] The biradical may also play a part in photosensitized olefin isomerization (a Schenck-type mechanism[4]) without necessarily involving the triplet state of the olefin.[5,6]

Attack of the $^3(n,\pi^*)$ carbonyl compound on ground-state olefin is not the only allowed mechanism for oxetane formation. Aliphatic ketones can attack electron-deficient olefins by a mechanism involving the singlet excited state of the ketone.[7,8] Alternatively, photocycloaddition may occur by both singlet and triplet mechanisms concurrently, as in the addition of acetone to 1-methoxy-1-butene,[9] or the addition of fluorenone to a ketenimine.[10] Two unusual possible mechanisms for oxetane formation deserve mention. The photocycloaddition of benzophenone to 2,3-dimethyl-1,3-butadiene has been postulated to involve attack of a triplet diene molecule on a ground-state ketone.[11,12] Secondly, the photocycloaddition of acetone to dimethyl maleate or fumarate has been suggested to involve attack of excited unsaturated ester on ground-state acetone.[13] The proposal that a molecular triplet oxetane intermediate is involved in the irradiation of acetone–tetramethylethylene mixtures has important implications, if such a process can occur in other systems.[14]

We wish to report results on the photocycloaddition of aliphatic ketones to α,β-unsaturated nitriles, and our studies concerning the mechanism of these additions.[15]

Results and Discussion

Reaction Products. Ultraviolet irradiation of solutions of α,β-unsaturated nitriles (**1–3**) in acetone with



1 ($R_1 = R_2 = H$) ⟶ **4** + **8, 9**
2 (R_1 = Me; R_2 = H) ⟶ **5** + **10, 11**
3 (R_1 = H; R_2 = Me) ⟶ *cis*-**6**, *trans*-**7**

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[1] Part XII: J. A. Barltrop and J. D. Coyle, *J. Chem. Soc.*, in press.

[2] (a) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964); (b) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964); (c) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964); (d) J. S. Bradshaw, *J. Org. Chem.*, 31, 237 (1966); (e) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, **89**, 598 (1967); (f) S. Toki and H. Sakurai, *Bull. Chem. Soc. Jap.*, 40, 2885 (1967); (g) N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, **89**, 5465 (1967); (h) N. C. Yang and R. Loeschen, *Tetrahedron Lett.*, 2571 (1968); (i) H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, **33**, 2774 (1968); (j) S. H. Schroeter and C. M. Orlando, *ibid.*, **34**, 1181 (1969).

[3] (a) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909); (b) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954); reviews: (c) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience, New York, N. Y., 1967, p 111; (d) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

[4] G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.*, 71, 781 (1962).

[5] N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968); see, however, R. A. Caldwell and G. W. Sovocool, *ibid.*, **90**, 7138 (1968).

[6] J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

[7] (a) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967); (b) N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968); (c) J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, 1318 (1970); (d) N. J. Turro and P. A. Wriede, *J. Org. Chem.*, 34, 3562 (1969).

[8] J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968).

[9] N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 90, 6863 (1968).

[10] L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969).

[11] J. Saltiel, R. M. Coates, and W. G. Dauben, *ibid.*, **88**, 2745 (1966).

[12] We have evidence to suggest that this mechanism is incorrect: J. A. Barltrop and H. A. J. Carless, *ibid.*, **93**, 4794 (1971).

[13] E. S. Albone, *ibid.*, 90, 4663 (1968).

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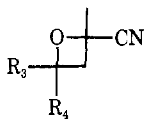
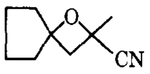
[15] For a preliminary report, see ref 8.

a medium-pressure mercury arc, in Pyrex or quartz apparatus, generally led to two kinds of photoproduct: oxetanes, **4–7**, and dimers of the α,β-unsaturated nitrile, **8–11**.

The cycloadditions were a general property of aliphatic ketones, in that oxetanes **12–15** were obtained from 2-butanone, 3-pentanone, cyclopentanone, and cyclohexanone when irradiated in the presence of methacrylonitrile (**2**). Irradiation of 3-pentanone in the presence of acrylonitrile (**1**) gave an analogous oxetane, **16**.



12, $R_3 = Me$; $R_4 = Et$
13, $R_3 = R_4 = Et$



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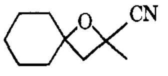

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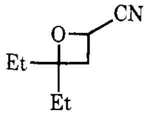
The isolated products were the only ones apparent by vpc. Yields of oxetane were 26–55% based on converted α,β-unsaturated nitrile; irradiations involving **1** and **2** produced some polymer.

The products assigned the oxetane structures were 1:1 adducts of ketones with unsaturated nitrile, and the ir spectra showed the absence of any carbonyl or hydroxyl groupings. Instead, each compound showed one or more strong bands in the region 1000–900 cm^{-1}, which is the reported absorption region of the oxetane ring.[16]

The nmr spectra of the oxetanes confirmed structures **4–7**, rather than those, **17**, from the alternative orientation of cycloaddition. Arnold[2a] has suggested that hydrogen on the carbon atom α to the oxygen of an oxetane ring has a chemical shift τ 5–6, whereas hydrogen on the β carbon atom has a shift of τ 6.4–7.4. In the ten oxetanes we have studied, the oxetane absorptions fell in two distinct ranges, τ 4.9–5.5 and 7.0–7.7, in broad agreement with the above description.



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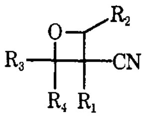

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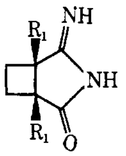

18, $R_1 = H$
19, $R_1 = Me$

The magnitude of the geminal coupling (~11.5 Hz) of the oxetane ring protons provides further evidence for the oxetane structures as **4–7** and **12–16**. Lustig, Ragelis, and Duy[17] have analyzed the nmr spectrum of 2,2-dideuteriooxetane and obtained a value for the geminal coupling constant of the oxetane ring C_3 protons ($J_{3,3}$) of 11.15 Hz, compared to the geminal coupling $J_{4,4}$ of 6.02 Hz. This, together with other examples of oxetane ring coupling constants taken from the literature,[18] shows that $J_{3,3}$ is of the order of 11–12 Hz, whereas $J_{4,4}$ is 5–7 Hz.

Mass spectra of the oxetanes generally showed weak molecular ions, and mainly fragments arising from fission across the oxetane ring. Such ring fission is a known process;[2d,19] thus, the parent oxetane gives predominantly ring cleavage to ethylene.[20] Again, the possible structures **17** were eliminated from consideration by the lack of a large peak at *m/e* corresponding to the loss of R_2CHO from the molecular ion.

Irradiation of acetone and crotononitrile (**3**) slowly led to the formation of two oxetanes, the *cis*-**6** and *trans*-**7** isomers. The assignment of these isomers was based on the magnitude of the nmr coupling constants (see Table I)[21] and the appearance of **6** or **7** from irradiation of acetone and *cis*-**3**- or *trans*-**3**, respectively (*vide infra*).

Table I. Oxetane Ring Proton Coupling Constants (Hertz)

	$J_{3,4}$[a]			
	J_{cis}	J_{trans}	$J_{3,3}$[b]	Ref
cis- or *trans*-di-COOMe[c]	9.0	6.9		e
cis- or *trans*-di-CN[d]	8.5	6.5		f
6	8.5			
7		6.5		
4	8.3	6.3	11.5	
16	8.9	6.7	11.6	
5, 12–15			11.5	

[a] $J_{3,4}$ is the vicinal coupling constant between the C_3 and C_4 protons. [b] $J_{3,3}$ is the geminal coupling between the C_3 protons. [c] 3,4-Dicarbomethoxy-2,2-dimethyloxetane. [d] 3,4-Dicyano-2,2-dimethyloxetane. [e] Reference 13. [f] Reference 19.

Irradiation of acetone and β,β-dimethylacrylonitrile led to little apparent reaction, and no oxetane could be isolated.

In those irradiations involving acrylonitrile (**1**), two dimeric products, **8** (mp 67°) and **9** (mp 31°), were formed in the ratio 5:4. The products were isolated and assigned the structures *cis*- and *trans*-1,2-dicyanocyclobutane, respectively.[22,23] Reports of the photodimerization of **1** have recently appeared, and the cis/trans ratio is in good agreement with the present work.[24] Acidic hydrolysis of **8** or **9** gave the *cis*- or *trans*-cyclobutane-1,2-dicarboxylic acids, respectively. Hydrolysis of **9** with cold, alkaline hydrogen peroxide gave a diamide; **8**, however, gave a bicyclic derivative **18**. A similar bicyclic derivative **19** was obtained by hydrolysis of **10**. The formation of these bicyclic derivatives has an aromatic analogy in the thermal cyclization of *o*-cyanobenzamide to iminophthalimidine.[25]

In all the irradiations involving methacrylonitrile (**2**), three other products were apparent: these were the dimers of **2**, *cis*- and *trans*-1,2-dicyano-1,2-dimethyl-

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(16) G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).

(17) E. Lustig, E. Ragelis, and N. Duy, *Spectrochim. Acta, Part A*, **23**, 133 (1967).

(18) (a) P. Yates and A. G. Szabo, *Tetrahedron Lett.*, 485 (1965); (b) M. J. Jorgenson, *ibid.*, 5811 (1966); (c) H. Hogeveen and P. J. Smit, *Recl. Trav. Chim. Pays-Bas*, **85**, 1188 (1966); (d) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **89**, 184 (1967); (e) N. J. Turro and J. R. Williams, *Tetrahedron Lett.*, 321 (1969).

(19) J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.*, **30**, 1231 (1965).

(20) E. J. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **66**, 136 (1962).

(21) Models of the oxetane ring suggest that the vicinal coupling constant should be greater for the cis isomers than for the trans isomers, by consideration of the dihedral angles of the C–H bonds (~0 and ~125° respectively). See, *e.g.*, S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

(22) The lower boiling compound had previously been reported to be the cis isomer (E. C. Coyner and W. S. Hillman, *J. Amer. Chem. Soc.*, 71, 324 (1949)) but our present evidence suggests this to be the trans isomer.

(23) J. Runge and R. Kache, *Z. Chem.*, **8**, 382 (1968).

(24) (a) S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968); (b) R. S. H. Liu and D. M. Gale, *J. Amer. Chem. Soc.*, **90**, 1897 (1968); (c) U. S. Patent 3,265,723 (1966); *Chem. Abstr.*, **66**, 2236j (1967); (d) British Patent 1,068,230 (1967); *Chem. Abstr.*, **67**, 73215s (1967).

(25) A. Braun and J. Tcherniac, *Ber.*, **40**, 2709 (1907).

cyclobutane (**10** and **11**), and 2,5-dicyano-1-hexene, formed in the ratios 1:4:0.07. Evidence for these structures has been presented,[26] and our nmr and mass spectra support those assignments. The compounds **10** and **11** were hydrolyzed to the known dicarboxylic acids.[26,27] Hammond and Herberhold[28] have studied the photosensitized dimerization of **2**, and although they did not report the use of an aliphatic ketone as a photosensitizer, the ratios of dimers we have found are in reasonable agreement with their results.

On irradiation of acetone and crotononitrile (**3**) or β,β-dimethylacrylonitrile, no dimers of the unsaturated nitrile could be isolated. The photodimerization of these latter two unsaturated nitriles appears to be much less efficient, in terms of quantum yield.

Reaction Mechanisms. There are two types of photoproduct to be accounted for in the reaction of aliphatic ketones with α,β-unsaturated nitriles: oxetanes and dimers of the olefinic derivatives. Using quartz apparatus, the incident light is mainly absorbed by the aliphatic ketones ($\lambda_{\max} \sim 280$ nm, log $\epsilon \sim 1$) to give the $^1(n,\pi^*)$ excited state of the ketone. Some tail absorption by the α,β-unsaturated nitrile ($\lambda_{\max} < 220$ nm) also occurs. To eliminate the possibility that the light absorbed by the nitrile is responsible for reaction an irradiation of acetone and **2** was conducted in Pyrex apparatus. Vpc showed exactly the same products as in quartz apparatus, despite the fact that **2** does not absorb light under these conditions. Uv spectra showed no evidence for a ground-state complex of the α,β-unsaturated nitriles with acetone.

Intersystem crossing occurs rapidly for aliphatic ketones (*e.g.*, at a rate of $\sim 5 \times 10^8$ sec^{-1} for acetone[7c,29]) to give the $^3(n,\pi^*)$ state. The energy of this state is about 74–80 kcal/mol.[29,30] Although α,β-unsaturated nitriles have never been observed to phosphoresce, their triplet energies are estimated from sensitization data to be 60–70 kcal/mol.[24a,28] Efficient, exothermic triplet–triplet energy transfer from excited acetone to the nitrile can therefore occur, and the triplet state of the nitrile is thereby introduced into the system. Attack of the triplet α,β-unsaturated nitrile on another ground-state nitrile molecule would then give the observed dimers.

The oxetanes could thus arise from the singlet or triplet (n,π^*) state of the ketone, or the triplet (π,π^*) state of the α,β-unsaturated nitrile. It was possible selectively to excite the triplet state of the nitrile by the use of a suitable sensitizer. Benzophenone (triplet energy, $E_T = 69$ kcal/mol[31]) should not transfer triplet energy to acetone ($E_T \sim 80$ kcal/mol[32]) at all efficiently, whereas the energy transfer to methacrylonitrile (**2**) should occur. Therefore, a solution of acetone and **2** containing benzophenone was irradiated under conditions such that virtually all the light was absorbed by the benzophenone sensitizer: only the methacrylonitrile dimers **10** and **11** were formed, and no oxetane (**5**) could be detected. Formation of an oxetane from benzophenone and **2** was not observed. This experiment provided evidence that the triplet state of **2** was formed by sensitization, but that it did not attack acetone to give an oxetane. Instead, oxetane formation must involve photoexcited acetone.

Quenching Experiments. A commonly used method for determining whether a photochemical reaction proceeds *via* a singlet or triplet state is the introduction of a triplet quencher into the system. However, piperylene (1,3-pentadiene), an effective quencher of ketone triplet states, failed to inhibit oxetane formation from acetone and methacrylonitrile even at a concentration of 6 *M*.[33] However, the formation of dimers **10** and **11** was quenched, to give an approximately linear Stern–Volmer plot (slope ~ 5)[34] (see Table IV).

The absence of quenching of oxetane formation by piperylene is significant. If the triplet state of acetone were involved, some quenching would be expected. A Stern–Volmer slope ≥ 0.2 would have been detected, and this leads to a value for $k_r{}^3$, the rate of triplet cycloaddition, of $\geq 4 \times 10^{10}$ M^{-1} sec^{-1}.[35] This is an impossibly high rate constant for a bimolecular reaction in this solvent, being considerably greater than the diffusion-controlled limit. Thus, it seems unlikely that the cycloaddition could be proceeding *via* a very short-lived, reactive triplet state.

Stereochemistry of Addition. If the reaction is a singlet one, then it may (but need not) be concerted. This is in contrast to the triplet additions, where spin inversion of a biradical intermediate must be involved at some stage, in order to give ground-state products. It was of interest to see whether reaction of an α,β-unsaturated nitrile with acetone was stereospecific, or involved a biradical intermediate where there might be time for bond rotation to occur before ring closure, thus leading to two geometric isomers of the oxetane from one isomer of the olefin.

Irradiation of a solution of *cis*-crotononitrile (*cis*-**3**) in acetone led to cis → trans isomerization of **3**, and *cis*-oxetane (**6**) formation. Cis → trans isomerization was much more efficient than oxetane formation (by a factor of several hundred) and so the reaction was examined at very small conversion to products, to obtain meaningful results. It was found that initially *cis*-**3** gave stereospecifically (greater than 98%) *cis*-oxetane (**6**); *trans*-oxetane (**7**) appeared in significant amounts only when an appreciable quantity of *trans*-**3** had been formed. An irradiation of *trans*-**3** and acetone showed that this led in the early stages to reaction, before appreciable isomerization of **3**, to greater than 98% stereospecific formation of the *trans*-oxetane (**7**).

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(26) C. J. Albisetti, D. C. England, M. J. Hogsed, and R. M. Joyce, *J. Amer. Chem. Soc.*, **78**, 472 (1956).

(27) C. G. Overberger, G. Kesslin, and N. R. Byrd, *J. Org. Chem.*, **27**, 1568 (1962).

(28) M. Herberhold and G. S. Hammond, *Ber. Bunsenges. Phys. Chem.*, **72**, 309 (1968).

(29) J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, **21**, 499 (1970).

(30) E. K. C. Lee, M. W. Schmidt, R. G. Shortridge, Jr., and G. A. Haninger, Jr., *J. Phys. Chem.*, **73**, 1805 (1969).

(31) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(32) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

(33) The quenching of acetone fluorescence by piperylene has a rate constant of 9×10^7 sec^{-1} (H. A. J. Carless, D. Phil. Thesis, Oxford, 1969; F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970)). We would thus expect to observe some quenching of oxetane formation by *singlet* quenching at high piperylene concentrations. At present, we have no explanation for this interesting discrepancy.

(34) The kinetic situation is complex, because piperylene is capable of quenching both triplet **2** and its precursor (triplet acetone), so that the slope is *not* simply $k_q\tau$, where τ would normally be the lifetime of the triplet **2**, and k_q its rate of quenching by piperylene.

(35) Assuming the rate of quenching of triplet acetone by piperylene in acetonitrile is 1×10^{10} M^{-1} sec^{-1}. This value has been assumed for hexane, whose viscosity is similar; see P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

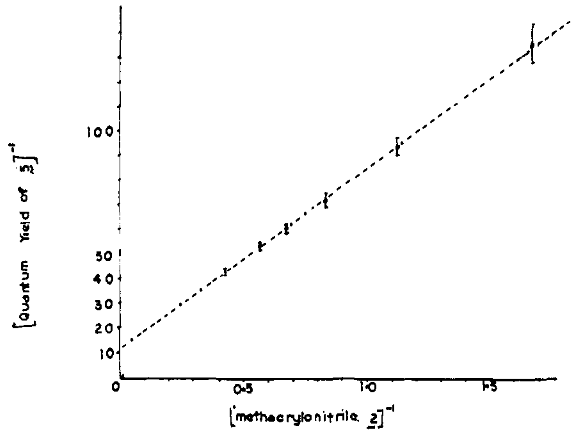

Figure 1. Plot of reciprocal of quantum yield of oxetane (**5**) *vs.* reciprocal of concentration of methacrylonitrile (**2**).

The stereospecificity of the crotononitrile addition, if it applied to the other α,β-unsaturated nitriles, suggests that reaction involves either a very short-lived biradical intermediate (with insufficient time for bond rotations) or else some mechanism involving formation of both new bonds to some extent in the transition state. It seems relevant that the singlet part of the photocycloaddition of acetone to 1-methoxy-1-butene gave only 80% retention of stereochemistry;[9] the higher stereospecificity observed in the crotononitrile addition argues against a short-lived biradical. More evidence against a singlet biradical comes from the orientation of the product; the only detected oxetane product is not that expected on the basis of biradical stability. Attack of the oxygen atom of excited acetone on the double bond would be expected to give the more stable biradical, which would ring close to a 3-cyanooxetane (**17**).[36]

Quantum Yields. Experiments were performed to determine the quantum yield of the acetone–methacrylonitrile (**2**) cycloaddition with variation of concentration of **2**. Tubes containing acetone and various concentrations of **2** in hexane were simultaneously irradiated in a photochemical roundabout; the concentrations of oxetane photoproduct (**5**) were determined by vpc. Quantum yields were obtained by reference to simultaneous 2-hexanone actinometry.[37] Figure 1 is a plot of (quantum yield of oxetane (**5**))$^{-1}$ against (concentration of methacrylonitrile)$^{-1}$. The error in the relative quantum yields is shown; when the actual quantum yields are determined, further errors are introduced, and the absolute value of the intercept may be in error by ±25%. A least-squares analysis of the points gave an intercept of 11 and a slope of 74.

Consider the kinetic scheme (eq 1–4) for the fate of singlet excited acetone (A_1). The scheme postulates the reaction of A_1 with methacrylonitrile (M) to give oxetane in competition with intersystem crossing and deactivation and leads to an expression for the reciprocal of the quantum yield of oxetane (Φ^{-1}) with variation of methacrylonitrile concentration: $\Phi^{-1} = 1 + (k_2 + k_3)/k_4\,[\mathrm{M}]$. A plot of Φ^{-1} against $[\mathrm{M}]^{-1}$ would have an intercept of 1, and this is in disagreement with the observed value.

$$A \xrightarrow{I} A_1 \qquad (1)$$

$$A_1 \xrightarrow{k_2} A_3 \qquad (2)$$

$$A_1 \xrightarrow{k_3} A \qquad (3)$$

$$A_1 + M \xrightarrow{k_4} \text{oxetane} \qquad (4)$$

A scheme which can explain the observed data is shown below (Scheme I). It involves reaction of excited acetone with methacrylonitrile to give a complex which partitions predominantly to ground-state reactants and partly to oxetane.[38] The scheme leads to an expression given by eq 8. The intercept of Figure 1

Scheme I

$$A \xrightarrow{I} A_1 \qquad (1)$$

$$A_1 \xrightarrow{k_2} A_3 \qquad (2)$$

$$A_1 \xrightarrow{k_3} A \qquad (3)$$

$$A_1 + M \xrightarrow{k_5} [\text{complex}] \qquad (5)$$

$$[\text{complex}] \xrightarrow{k_6} A + M \qquad (6)$$

$$[\text{complex}] \xrightarrow{k_7} \text{oxetane} \qquad (7)$$

$$\Phi^{-1} = \frac{k_6 + k_7}{k_7} + \frac{(k_6 + k_7)(k_2 + k_3)}{k_5 k_7[\mathrm{M}]} \qquad (8)$$

(11) is now associated with $(k_6 + k_7)/k_7$, and using this value in conjunction with the slope (74), $(k_2 + k_3)/k_5 = 74/11 = 6.7(\pm 2.8)$. Now, k_3 is thought small in comparison with k_2, because the triplet quantum yield of acetone is near 1.0,[32] so $k_2/k_5 = 6.7\ (\pm 2.8)$.

Fluorescence Studies. Another approach to a value of k_2/k_5 is from fluorescence quenching experiments.[7c] Acetone and other aliphatic ketones fluoresce weakly in solution[39,40] and this fluorescence was found to be quenched by the addition of α,β-unsaturated nitriles. The quenching obeyed Stern–Volmer kinetics up to at least 3 *M* α,β-unsaturated nitrile. The relative intensity of fluorescence is given by $F_0/F = 1 + k_9[\mathrm{N}]/(k_2 + k_3)$, where F_0 and F are the intensities of fluorescence in the absence and presence of a concentration of α,β-unsaturated nitrile, [N], and k_9 is the rate constant for fluorescence quenching of the ketone by the nitrile. If we associate k_9 with k_5, the rate of complexation (because both processes lead to deactivation of the singlet excited acetone), then we can estimate k_2/k_5 independently of the previously discussed quantum yield measurements. Values of the Stern–Volmer slopes $(k_9/(k_2 + k_3))$ for the fluorescence quenching of acetone or cyclopentanone by **1**, **2**, and **3** are shown in Table II. For the acetone–**2** system, $(k_2 + k_3)/k_9 \simeq k_2/k_5 = 3.7\ (\pm 0.5)$, since k_3 is small in comparison with k_2. This value is in fair agreement with that obtained from quantum yield measurements (6.7 ± 2.8).

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[36] The cyano group would be expected to stabilize the free-radical center. The "most stable biradical" hypothesis frequently explains the major oxetane product, although there are limitations (see ref 3d).

[37] D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

[38] Turro and coworkers have proposed a similar scheme for photocycloaddition of acetone to *trans*-1,2-dicyanoethylene.[7b]

[39] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

[40] (a) S. R. La Paglia and B. C. Roquitte, *J. Phys. Chem.*, **66**, 1739 (1962); (b) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 5842 (1970).

Table II. Slopes of Stern–Volmer Plots for Fluorescence Quenching of Acetone and Cyclopentanone by α,β-Unsaturated Nitriles[a]

	1	**2**	**3**
Acetone	0.25	0.27	0.03
Cyclopentanone	0.26 (±0.03)	0.25 (±0.03)	0.03 (±0.01)

[a] The slope is $k_9/(k_2 + k_3)$, M^{-1}.

Mechanistic Discussion. The intersystem crossing rate of acetone (k_2) is thought to be $\sim 5 \times 10^8$ sec^{-1};[7c,29] this would give a value for the rate of complexation of 7.5×10^7 M^{-1} sec^{-1}, using $k_2/k_5 = 6.7$. It was found that $k_6/k_7 = 10$, so that the complex decays at a rate ten times greater than the rate of cycloaddition to give oxetane.

For acetone, it is interesting to compare the relative quantum yields for cycloaddition to the α,β-unsaturated nitriles (measured by the amount of oxetane formed: **1**, 19.9; **2**, 9.7; **3**, 1.0) with the fluorescence quenching reactivities (0.25, 0.26, and 0.03, respectively). These figures suggest that there are not large differences in the partition of the complex once formed, but that its rate of formation depends very much on the particular α,β-unsaturated nitrile. From eq 8, it is possible to calculate a value for $(k_6 + k_7)/k_7$, the partition of the complex, using the values of k_2/k_5 estimated from fluorescence quenching, and the relative quantum yields of oxetane formation. The values of $(k_6 + k_7)/k_7$ are shown in Table III,[41] together with the rate constants for exciplex formation with acetone (k_5). It is interesting that our mechanistic conclusions are very similar to those recently published by Turro[7c] on the acetone–1,2-dicyanoethylene system. Similar factors appear to control the stereospecificity and mechanism of the photoreaction of acetone with these unsaturated nitriles, although our experiments reveal an additional regiospecific requirement.

$$\begin{tikzcd}
\text{acetone}^1 + \alpha,\beta\text{-unsaturated nitrile} \arrow[r, "k_5"] & \text{complex} \arrow[r, "k_6"] \arrow[dr, "k_7"'] & \text{reactants} \\
& & \text{oxetane}
\end{tikzcd}$$

Table III. Complex Formation and Complex Partition for Acetone with α,β-Unsaturated Nitriles

	k_5[b]	$(k_6 + k_7)/k_7$[c]
t-DCE[a]	3×10^9	10, 13[d]
1	1.5×10^8	5
2	1.5×10^8	11
3	1.5×10^7	20

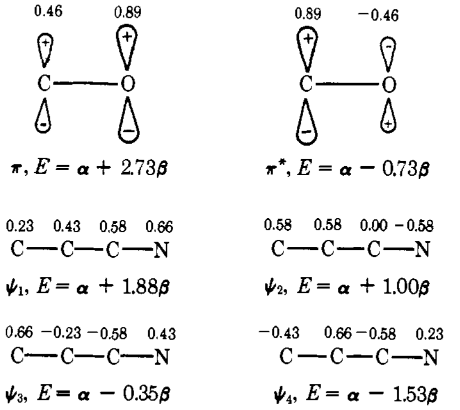
[a] *trans*-1,2-Dicyanoethylene. [b] Rate constant for complexation (M^{-1} sec^{-1}) assuming an intersystem crossing rate (k_2) of 5×10^8 sec^{-1}. [c] Ratio representing partition of the complex between deactivation (k_6) and oxetane formation (k_7). [d] Reference 7b.

It remains to consider the nature of the proposed complex. The simplest hypothesis is that a π complex is formed between the electron-rich π,π^* orbital of the $^1(n,\pi^*)$ ketone with the electron-deficient double bond of the unsaturated nitrile. Such a complex would be stabilized by electron-attracting substituents on the olefinic double bond and destabilized by electron-donating substituents. Furthermore, since in a π complex the olefinic double bond is largely present intact, one might expect oxetane formation from such a complex to proceed stereospecifically and with retention of the configuration of the original olefin.

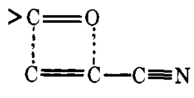
It is possible that an electron is actually transferred from the (n,π^*) state of acetone to the α,β-unsaturated nitrile, to form the complex. Such electron-transfer mechanisms are known to quench fluorescence.[42] It is difficult to obtain evidence for such electron transfer since the charge-transfer complex, if formed, does not give rise to any new fluorescence emission band.

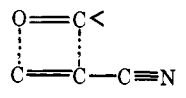
A steric factor might also be involved; thus substitutents on the β position of the unsaturated nitrile, $CH_2(\beta)\!=\!CH(\alpha)CN$, will interact strongly with the acetone methyl groups and make a close enough approach for complexation less likely; they therefore reduce the quantum yield of photocycloaddition. This point is especially important, since crotononitrile (**3**) gave a low rate of complexation, and no oxetane at all could be made from β,β-dimethylacrylonitrile.

Calculations. Some insight into the nature of the exciplex may be gained by applying perturbational MO theory (in the HMO approximation) to the electronic energy of interaction of $^1(n,\pi^*)$ acetone with acrylonitrile. With the following values for Coulomb and resonance integrals, $\alpha_C = \alpha$, $\alpha_N = \alpha + \beta$, $\alpha_O = \alpha + 2\beta$, $\beta_{CC} = \beta$, $\beta_{CN} = \beta$, $\beta_{CO} = \beta\sqrt{2}$, the coefficient and energies of the Hückel MO's are as follows.



Let us now calculate the energy of interaction of $^1(n,\pi^*)$ acetone with S_0 acrylonitrile in the two orientations A and B. If we further assume for simplicity that


A


B

the resonance integrals of the new partial bonds are identical and equal to β_1, the approach of the two molecules perturbs the energies of the MO's as shown diagrammatically (Chart I; perturbations given in units of β_1^2/β. If one assumes that $\beta_1 = 0.5\beta$ the units would be 0.25β).[43]

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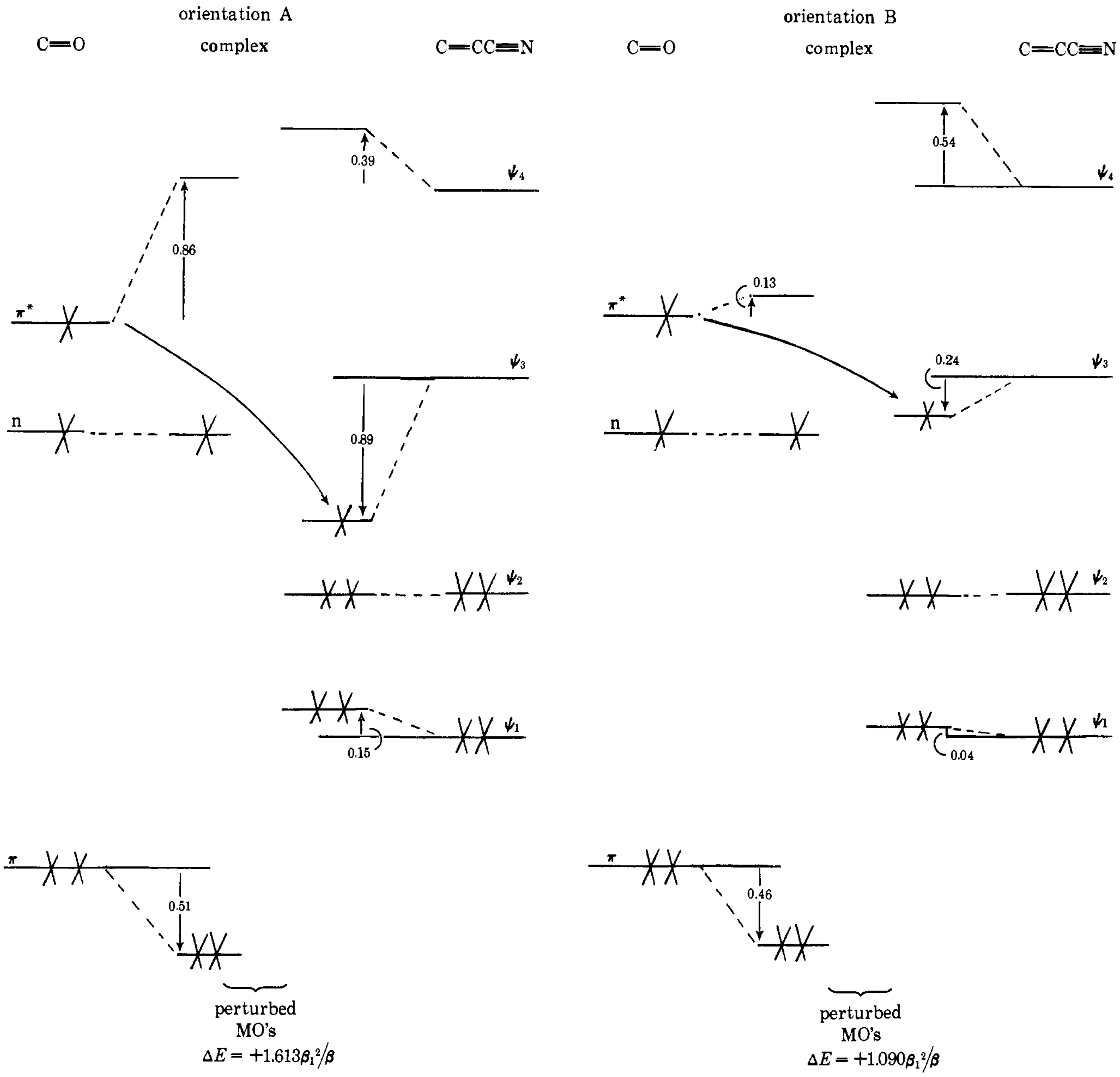
[41] Values are based on the assumption that $(k_6 + k_7)/k_7 = 11$ for acetone–**2**. The values for *trans*-1,2-dicyanoethylene are also included, as reaction seems to follow a similar path.[7b]

[42] A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

[43] Method: M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341 (1952); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 206.

Chart I



From this the following points emerge.[44] (1) It is energetically preferable for $^1(n,\pi^*)$ ketone and acrylonitrile to approach each other as depicted in orientation A. Hence this is probably the preferred orientation of the exciplex. (2) In the perturbed system, the π^* electron of the excited carbonyl group is transferred to ψ_3 of the acrylonitrile. This corresponds to the previously described charge-transfer complex. (3) The energetic preference of orientation A with respect to B largely derives from the splitting produced by the interaction of the levels π^* and ψ_3. This is to be expected since filled shell interactions are usually small and because π^* and ψ_3 are of similar energies.

Experimental Section

Acetone (Analar, Hopkin, and Williams) was used without further purification. 2-Butanone, 3-pentanone, cyclopentanone, and cyclohexanone (BDH) were distilled before use. Acrylonitrile (BDH), methacrylonitrile (Eastman-Kodak), and crotononitrile (**3**) (Koch-Light) were stored over quinol, and distilled immediately before use. β,β-Dimethylacrylonitrile was prepared by the reaction of cyanoacetic acid with acetone in pyridine.[45] Separate samples of *cis*- and *trans*-**3** were isolated by preparative vpc (F and M 770 machine) using an 8 ft × 1 in. 15% didecyl phthalate column at 105°; each contained less than 0.15% of the other isomer.

Nmr spectra were recorded on Perkin-Elmer 60- and 100-MHz machines. Nmr coupling constants are given in hertz, and tetramethylsilane was used as the internal standard; the other abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were obtained on an AEI MS-9 spectrometer, and fluorescence spectra on an Aminco-Bowman spectrophotofluorometer.

Vpc employed the following columns: 5- or 12-ft 15% fluorosilicone oil, FS 1265 (Perkin-Elmer) on Anakrom (QF 1); three commercially available columns (Perkin-Elmer), 6 ft × $^1/_8$ in. o.d. for an F 11 chromatogram; 10 and 20% polyethylene glycol succinate (PEGS) on Chromosorb P, and 20% diisodecyl phthalate (DDP) on Chromosorb P.

General Irradiation Procedure. Preparative irradiations were carried out under nitrogen in either a water-cooled quartz reactor having 75- and 20-ml compartments, or in a cylindrical reactor

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[44] Similar results are obtained for a range of values of the parameters.

[45] S. M. Mukherjee, *J. Ind. Chem. Soc.*, **25**, 163 (1948).

(200 ml) having an inner annular space for a filter solution and equipped with a water-cooled quartz or Pyrex probe. The light source in each case was a centrally positioned Hanovia 450-W medium-pressure mercury arc. Comparative photolyses were carried out in one of two photochemical roundabouts. The first has been described,[46] and the second was a Rayonet (RPR-100) photochemical reactor equipped with a merry-go-round unit holding eight Pyrex tubes; the light for the RPR-100 was provided by a set of 16 phosphor-coated RPR 3000-Å lamps, having mainly a broad emission at 280–320 nm.

Irradiation of Acetone and 2. A mixture of **2** (30 ml) and acetone (45 ml) was irradiated in a quartz reactor for 63 hr. Vpc (QF 1, 125°) showed three main products, and one minor one. A portion of the product (25 ml) was fractionated to remove reactants, leaving a viscous residue (5.96 g). This residue (4.45 g) was chromatographed on silica gel (100 g), eluting with 25-ml portions of 25% v/v diethyl ether–petroleum ether (bp 40–60°). Fractions were analyzed by vpc and tlc. Fractions 6–12 contained a colorless liquid, 2-cyano-2,4,4-trimethyloxetane (**5**) (1.3 g): ir (film) 2250 (w), 1380 (s), 982 (s), 915 (s), 845 (s) cm^{-1}; nmr (CCl_4) τ 7.19 and 7.55 (each d, J = 11.5, 1 H), 8.31 (s, 3 H, C(CN)CH_3), 8.42 and 8.61 (each s, 3 H, *gem*-dimethyl); mass spectrum, *m/e* (rel intensity) 125 (1), 110 (19), 98 (5), 67 (4), 58 (14), 56 (15), 43 (100).

Anal. Calcd for $C_7H_{11}NO$: C, 67.2; H, 8.9; N, 11.2. Found: C, 67.4; H, 9.0; N, 11.3.

Fractions 17–30 contained one component, *trans*-1,2-dicyano-1,2-dimethylcyclobutane (**11**) (0.74 g): ir (CS_2) 2250 (s), 1100 (s), 940 (w) cm^{-1}; nmr (CCl_4) τ 7.3–8.1 (24 lines, 4 H), 8.30 (s, 6 H); mass spectrum, *m/e* (rel intensity) 133 (0.5), 119 (2), 106 (9), 68 (100), 67 (40).

Anal. Calcd for $C_8H_{10}N_2$: C, 71.6; H, 7.5; N, 20.9. Found: C, 71.4; H, 7.6; N, 20.8.

Fractions 32–36 contained the minor photoproduct (0.02 g), which was rechromatographed on silica gel (5 g) and shown to have identical properties with a larger sample of 2,5-dicyano-1-hexene. The latter was prepared by the photosensitized dimerization of **2** (32 g) using benzophenone (0.91 g) as a sensitizer in a quartz reactor for 125 hr followed by distillation of the product. The fraction bp 160–170° (20 mm) was chromatographed on silica gel, as for the acetone-**2** product.

Fractions 38–59 contained mainly one compound, and were rechromatographed on silica gel (25 g) to give *cis*-1,2-dicyano-1,2-dimethylcyclobutane (**10**) (0.18 g): ir (CS_2) 2250 (s), 1100 (s), 1022 (m) cm^{-1}; nmr (CCl_4) τ 7.0–8.0 (16 lines, 4 H), 8.50 (s, 6 H); mass spectrum, *m/e* (rel intensity) 133 (0.5), 119 (1.5), 106 (7), 68 (100), 67 (43).

Anal. Calcd for $C_8H_{10}N_2$: C, 71.6; H, 7.5; N, 20.9. Found: C, 71.6; H, 7.5; N, 20.6.

Quantitative vpc of the photolysis product with *n*-decane as internal standard showed yields of 42% of the oxetane (**5**), 17% of **11**, and 4% of **10**, all based on converted **2**. The products **5**, **10**, and **11** were also isolated by preparative vpc (QF 1, 160°). An irradiation of acetone and **2** under similar conditions, except that a Pyrex probe was substituted for the quartz probe, showed the same products on vpc, but formed at a slower rate.

Similar irradiations were carried out on: 2-butanone (40 ml) and **2** (35 ml) (41 hr); 3-pentanone (50 ml) and **2** (25 ml) (50 hr); cyclopentanone (25 ml), **2** (25 ml), and acetonitrile (30 ml) (40 hr); cyclohexanone (60 ml) and **2** (20 ml) (60 hr). The products were shown by vpc to contain the dimers of **2** (**10** and **11**). An additional product was present in each case. It was isolated by fractionating off the reactants from the photoproduct and column chromatography of the residue on silica gel. In this manner, the following oxetanes were prepared.

2-Butanone and 2 gave 2-cyano-4-ethyl-2,4-dimethyloxetane (35%) (**12**) as a 1:1 mixture of the two stereoisomers (by nmr): ir (film) 2245 (w), 1382 (s), 915 (s), 865 (s) cm^{-1}; nmr (CCl_4) τ 7.14, 7.52 and 7.29, 7.63 (two sets of AB doublets, J = 11.5, 2 H, oxetane ring CH_2CO), 8.15, 8.37 (two quartets, J = 7.5, 2 H, CH_2-CH_3), 8.28, 8.33 (two singlets, 3 H, C(CN)CH_3), 8.45, 8.65 (two singlets, 3 H, C(Et)CH_3), 9.02, 9.11 (two triplets, J = 7.5, 3 H, CH_2CH_3); mass spectrum, *m/e* (rel intensity) 139 (1), 124 (1), 110 (45), 72 (4), 70 (9), 57 (22), 43 (100).

Anal. Calcd for $C_8H_{13}NO$: C, 69.0; H, 9.4; N, 10.1. Found: C, 69.3; H, 9.7; N, 10.4.

3-Pentanone and 2 gave 2-cyano-4,4-diethyl-2-methyloxetane (**13**) (in 26% yield by quantitative vpc): ir (film) 2245 (w), 1380 (s), 928 (s) cm^{-1}; nmr (CCl_4) τ 7.29 and 7.63 (each d, J = 11.5, 1 H), 8.14 and 8.36 (each q, J = 7, 2 H), 8.31 (s, 3 H), 9.05 and 9.15 (each t, J = 7, 3 H); mass spectrum, *m/e* (rel intensity) 126 (10), 124 (26), 84 (10), 67 (4), 57 (100).

Anal. Calcd for $C_9H_{15}NO$: C, 70.5; H, 9.9; N, 9.2. Found: C, 70.5; H, 10.0; N, 9.4.

Cyclopentanone and 2 gave 2-cyano-2-methyl-1-oxaspiro[4,3]-octane (**14**) (34%): ir (film) 2245 (w), 1380 (m), 965 (s) cm^{-1}; nmr (CCl_4) τ 7.04 and 7.36 (each d, J = 11.5, 1 H), 7.5–8.5 (complex with singlet at 8.31, 11 H); mass spectrum, *m/e* (rel intensity) 151 (3), 124 (26), 84 (28), 67 (34), 43 (100).

Anal. Calcd for $C_9H_{13}NO$: C, 71.5; H, 8.7; N, 9.3. Found: C, 71.6; H, 8.6; N, 9.3.

Cyclohexanone and 2 gave 2-cyano-2-methyl-1-oxaspiro[5,3]-nonane (**15**) (55%): ir (film) 2245 (w), 1380 (m), 940 (s), 925 (s) cm^{-1}; nmr (CCl_4) τ 7.27 and 7.66 (each d, J = 11.5, 1 H), 8.0–8.8 (complex with singlet at 8.30, 13 H); mass spectrum, *m/e* (rel intensity) 165 (8), 138 (3), 98 (100), 96 (11), 67 (21).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.7; H, 9.17; N, 8.5. Found: C, 72.8; H, 8.9; N, 8.4.

Irradiation of Acetone and 1. Using a similar irradiation and work-up procedure to that described above, acetone (100 ml) and **1** (100 ml) were irradiated for 22 hr in a quartz reactor. Vpc showed the formation of three products in the proportions 8:4:5; yields were not determined because of the formation of polymer from **1** (~10 g). Column chromatography of the photoproduct on silica gel showed the products to be **4**, **9**, and **8**, in order of elution by diethyl ether–petroleum ether (bp 40–60°) mixtures.

4-Cyano-2,2-dimethyloxetane (**4**) (0.32 g), also isolated by preparative vpc (QF 1, 140°) of the photoproduct, showed the following: ir (film) 2245 (w), 1385 (m), 1378 (m), 984 (s), 970 (s), 840 (s) cm^{-1}; nmr (CCl_4) τ 5.04 (dd, J = 6.3 and 8.3, 1 H), 7.18 (dd, J = 8.3 and 11.5, 1 H), 7.35 (dd, J = 6.3 and 11.5, 1 H), 8.42 and 8.57 (each s, 3 H); mass spectrum, *m/e* (rel intensity) 111 (0.5), 96 (24), 58 (22), 56 (20), 54 (15), 43 (100).

Anal. Calcd for C_6H_9NO: C, 64.8; H, 8.2; N, 12.6. Found: C, 65.0; H, 8.3; N, 12.4.

trans-1,2-Dicyanocyclobutane (**9**) (mp 30.5–31.5°, bp 160° (15 mm)) showed the following characteristics: ir (Nujol) 2250 (s), 1245 (m), 1210 (m), 1070 (m), 930 (s) cm^{-1}; nmr (CCl_4) τ 6.4–6.65 (m, 2 H), 7.4–7.65 (m, 4 H); mass spectrum, *m/e* (rel intensity) 106 (2), 105 (3), 79 (30), 66 (30), 54 (100), 53 (70), 52 (22).

Anal. Calcd for $C_6H_6N_2$: C, 67.9; H, 5.7; N, 26.4. Found: C, 67.8; H, 6.0; N, 25.9.

cis-1,2-Dicyanocyclobutane (**8**) (mp 67–67.5°, bp 190° (15 mm)) showed the following characteristics: ir (Nujol) 2250 (s), 1245 (s), 1205 (s), 1055 (m), 945 (m), 895 (m) cm^{-1}; nmr (CCl_4) τ 6.25–6.7 (m, 2 H), 7.3–7.65 (m, 4 H); mass spectrum, *m/e* (rel intensity) 106 (5), 79 (50), 66 (67), 54 (100), 53 (80), 52 (27).

Anal. Calcd for $C_6H_6N_2$: C, 67.9; H, 5.7; N, 26.4. Found: C, 67.7; H, 5.8; N, 26.2.

3-Pentanone (75 ml) and 1 (125 ml), when similarly irradiated for 5 hr, gave **8** and **9** (and polymer) together with 4-cyano-2,2-diethyloxetane (**16**) (15%): ir (film) 2245 (w), 1024 (s), 990 (s), 965 (s), 915–895 (s) cm^{-1}; nmr (CCl_4) τ 5.05 (dd, X of ABX spectrum, 1 H), 7.15–7.25 (m, AB of ABX spectrum, 2 H), 8.20 and 8.33 (each q, J = 7.2, 2 H), 9.00 and 9.06 (each t, J = 7.2, 3 H); nmr (C_6H_6) the ABX spectrum appeared as τ 5.70 (dd, J = 6.7 and 8.9), 7.92 (dd, J = 6.7 and 11.6), 8.14 (dd, J = 8.9 and 11.6); mass spectrum, *m/e* (rel intensity) 139 (1), 124 (1), 112 (12), 110 (100), 84 (10), 57 (70), 55 (42).

Anal. Calcd for $C_8H_{13}NO$: C, 69.0; H, 9.4; N, 10.1. Found: C, 68.8; H, 9.2; N, 10.2.

Irradiation of Acetone and 3. (1) A mixture of acetone (35 ml) and **3** (40 ml, cis–trans mixture) was irradiated in a quartz reactor for 72 hr, to give a photoproduct containing mainly unreacted starting materials plus two main components on vpc (QF 1, 75°, retention times 14 and 16 min, area 1:1). These were isolated as a mixture (0.1 g) by column chromatography on silica gel or preparative vpc (QF 1, 160°) and identified as *cis*- and *trans*-4-cyano-2,2,3-trimethyloxetane (**6** and **7**, respectively): ir (film) 2250 (w), 1388 (s), 1382 (s), 1016 (s), 980 (s), 838 (s) cm^{-1}; mass spectrum, *m/e* (rel intensity) 110 (17), 98 (1), 70 (22), 68 (9), 67 (11), 58 (25), 43 (100). The nmr spectrum of a sample which had been rechromatographed on silica gel (and which was found by vpc to contain peaks of retention times 14 and 16 min in the ratio 1:2) allowed the assignment of the spectral peaks due to each isomer, without completely separating the mixture. The peaks due to the more abundant isomer, where resolvable, are given in italics: nmr (CCl_4) τ 4.94 (d, J = 8.5) and *5.50* (d, J = 6.5) (together 1 H), 6.99 (q,

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(46) J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, 90, 6584 (1968).

J = 7, further split by J = 8.5) and *7.03* (quintet, $J \simeq 7$) (together 1 H), 8.47 and 8.60 (each s, together 6 H), *8.74* and 8.77 (each d, J = 7, together 3 H).

Anal. Calcd for $C_7H_{11}NO$: C, 67.2; H, 8.9; N, 11.2. Found: C, 67.4; H, 9.1; N, 11.5.

(2) An irradiation of acetone and **3** in Pyrex apparatus gave similar products.

(3) A mixture of *cis*-**3** (1 ml, containing less than 0.05% of *trans*-**3**) and acetone was irradiated in a thick-walled Pyrex tube clamped next to the quartz reactor. Samples (2 μl) were taken at intervals up to 8 hr, and analyzed by vpc (20% PEGS, 150°) to follow the isomerization of *cis*-**3** to *trans*-**3** and the formation of the *cis*- and *trans*-oxetanes, **6** and **7** (retention times 4.5, 6, 20.4, and 18.7 min, respectively). The total concentration of *cis*- and *trans*-**3** was used as an internal standard. The concentrations of both *trans*-**3** and **6** were directly proportional to the time of irradiation. The *cis*-**3** isomerized to *trans*-**3** at the rate of 0.7%/hr, and 0.003%/hr of **6** was produced. No *trans*-oxetane (**7**) could be detected in the early stages of irradiation. The limits of detection showed that initially less than 2% of the total oxetane produced was the trans isomer.

A similar irradiation using acetone and *trans*-**3** (containing less than 0.15% of *cis*-**3**) showed isomerization to *cis*-**3**, and in the early stages of the irradiation, **7** as the only detectable oxetane product. From the measured vpc areas, reaction was greater than 98% stereospecific, *trans*-**3** giving **7**.

Irradiation of Acetone and β,β-Dimethylacrylonitrile. Acetone (18 ml) and β,β-dimethylacrylonitrile (1.5 ml) were irradiated in a quartz reactor for 20 hr. Vpc (QF 1, 100°) showed largely unreacted starting materials, plus two very minor photoproducts: the area of these peaks suggested that the total amount of volatile photoproducts in solution was less than 2 mg. No attempt was made to isolate them.

Acidic Hydrolysis of 8–11. Dimer **8** (400 mg) was refluxed with 2 *M* aqueous hydrochloric acid (25 ml) for 24 hr. Ether extraction and work-up gave a white solid (346 mg, 64%) recrystallized from benzene, then water, to yield colorless crystals of *cis*-1,2-cyclobutanedicarboxylic acid: mp 136–137° (lit.[47] mp 139–140°); ir (Nujol) 2640 (w), 1700 (s), 948 (s) cm^{-1}.

Anal. Calcd for $C_6H_8O_4$: C, 50.0; H, 5.6. Found: C, 50.4; H, 5.9.

Similar hydrolysis of 9 (500 mg) gave the *trans*-1,2-cyclobutanedicarboxylic acid (530 mg, 78%), recrystallized from benzene–dioxane (5:1, v/v): mp 127.5–128° (lit.[22] mp 129–130°); ir (Nujol) 2640 (w), 1695 (s), 940 (s), 920 (s) cm^{-1}.

Anal. Calcd for $C_6H_8O_4$: C, 50.0; H, 5.6. Found: C, 49.8; H, 5.4.

Dimer **10** (400 mg) was hydrolyzed by refluxing with 50% aqueous sulfuric acid (10 ml) for 1.5 hr. Work-up gave *cis*-1,2-dimethylcyclobutane-1,2-dicarboxylic acid (290 mg, 57%), mp 133–134° (lit.[26] mp 134–135°).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.8; H, 7.0. Found: C, 55.9; H, 7.0.

Dimer **11** (970 mg) was treated similarly with 50% aqueous sulfuric acid (20 ml) to give *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylic acid (1.04 g, 84%), mp 233.5–235° (lit.[26] mp 237–238°).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.8; H, 7.0. Found: C, 55.6; H, 6.9.

Alkaline Peroxide Hydrolysis of 8–11. Dimer **8** (500 mg) was hydrolyzed by dissolving it in a mixture of 10% hydrogen peroxide (5 ml), acetone (5 ml), and 10% aqueous sodium hydroxide (1 ml), and allowing the solution to stand for 3 days at −8°. Colorless crystals (127 mg, 19%) were formed and identified as *cis*-cyclobutane-1,2-dicarboxamide: ir (Nujol) 3350 (s), 3160 (s), 1660 (s), 1630 (s) cm^{-1}; nmr (DMSO) τ 3.2 (broad, $CONH_2$); mass spectrum, *m/e* (rel intensity) 142 (0.5), 99 (80), 98 (100).

Anal. Calcd for $C_6H_{10}N_2O_2$: C, 50.7; H, 7.1; N, 19.7. Found: C, 50.9; H, 7.0; N, 19.9.

The solution was evaporated to half its bulk, filtered, and allowed to stand for 3 weeks at −8°. Colorless crystals were formed (69 mg, 12%) and assigned the structure 4-imino-3-azabicyclo[3.2.0]-heptan-2-one (mp 226–228°) (**18**): ir (Nujol) 3275 (s), 1695 (s), 1520 (s), 1292 (s) cm^{-1}; nmr (DMSO-d_6) τ 1.65 and 1.95 (each broad, 1 H), 7.0–8.4 (m, ~6 H); mass spectrum, *m/e* (rel intensity) 125 (10), 124 (100), 97 (6), 96 (11), 95 (13), 82 (29), 54 (60).

Anal. Calcd for $C_6H_8N_2O$: C, 58.0; H, 6.5; N, 22.6. Found: C, 57.9; H, 6.2; N, 22.6.

Dimer **9** (500 mg) was hydrolyzed as described above, to give colorless crystals of *trans*-cyclobutane-1,2-dicarboxamide (394 mg, 60%): mp 227–228°; ir (Nujol) 3380 (s), 3200 (s), 1660 (s), 1630 (s) cm^{-1}; mass spectrum, *m/e* (rel intensity) 142 (12), 125 (100), 99 (95), 98 (75), 97 (60).

Anal. Calcd for $C_6H_{10}N_2O_2$: C, 50.7; H, 7.1; N, 19.7. Found: C, 50.9; H, 7.0; N, 20.1.

Dimer **10** (400 mg) was likewise hydrolyzed to give colorless crystals (320 mg, 70%), mp 305–308° dec, assigned the structure 4-imino-1,5-dimethyl-3-azabicyclo[3.2.0]heptan-2-one (**19**): ir (Nujol) 3295 (s), 1690 (s), 1540 (s), 1385 (m) cm^{-1}; nmr (DMSO-d_6) τ 1.60 and 2.05 (each broad, 1 H), 7.85–8.3 (m, 4 H), 8.81 and 8.98 (each s, 3 H); mass spectrum, *m/e* (rel intensity) 152 (53), 151 (17), 137 (19), 124 (100), 82 (40), 67 (55).

Anal. Calcd for $C_8H_{12}N_2O$: C, 63.1; H, 7.95; N, 18.4. Found: C, 62.9; H, 8.0; N, 18.2.

Dimer **11** (500 mg) was hydrolyzed to give colorless crystals (520 mg, 82%) of *trans*-1,2-dimethylcyclobutane-1,2-dicarboxamide: mp 264.5–266° (lit.[27] mp 262–265.5°); ir (Nujol) 3350 (s), 3175 (s), 1660 (s), 1625 (s), 1380 (m) cm^{-1}; mass spectrum, *m/e* (rel intensity) 170 (3), 153 (40), 127 (22), 126 (16), 125 (35), 86 (100).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.5; H, 8.3; N, 16.5. Found: C, 56.5; H, 8.2; N, 16.8.

Benzophenone Sensitization of Acetone–2 Reactions. A solution of **2** (14 ml) and benzophenone (1.82 g) in acetone (100 ml) was deoxygenated by nitrogen bubbling, sealed, and irradiated for 18 hr using a Pyrex probe. A filter solution (520 g/l. of sodium nitrate in water) ensured that acetone did not absorb an appreciable quantity of light. Vpc (QF 1, 100°) of the product showed starting materials plus peaks with retention times of **11** and **10** (areas 1.0: 0.22). No trace of **5** was evident, though a relative area of 0.005 would have been detected. A comparison irradiation omitting the benzophenone sensitizer and filter solution gave **5**, **11**, and **10** in the vpc ratios 4.8:1.0:0.28.

Attempted Quenching of Acetone–2 Photoreactions. Seven Pyrex tubes, each containing acetone (2.5 ml, 2 *M*) and **2** (1.5 ml, 1.05 *M*) with various concentrations of piperylene (cis–trans mixture, 0.0, 0.0, 0.05, 0.1, 0.5, 2, and 10 ml, respectively), were each made up to 17 ml with dry acetonitrile. The tubes were irradiated in the laboratory-built roundabout for 26 hr, using a quartz probe. An internal standard (durene) was added to each tube, the contents analyzed by vpc (10% PEGS, 125°), and the area ratio (*R*) of the **5** peak to internal standard peak was measured, the average of two determinations being taken. A correction was applied for the differences in absorption between Pyrex tubes. The corrected value of *R* was then directly proportional to the quantum yield (Φ) of **5**; hence values of Φ_0/Φ were calculated, where Φ_0 is the quantum yield of formation of **5** in the absence of piperylene quencher. The results are given in Table IV.

Table IV. Quenching of Acetone–**2** Photoreactions[a]

Tube	Piperylene, *M*	Φ_0/Φ (**5**)	Φ_0/Φ (**11**)
1	0.0	1.00	1.00
2	0.0		
3	0.029	0.93	1.12
4	0.059	0.89	1.28
5	0.29	0.88	2.45
6	1.18	0.92	7.27
7	5.85	1.04	27

[a] Errors in measurement of Φ_0/Φ, ±20%.

Samples from the same tubes were analyzed by vpc (10% PEGS, 150°) to determine the ratio (R_1) of peak areas of **11** to internal standard, measured in duplicate. The average of these two determinations was corrected for differing light absorption of the tubes. Values of Φ_0/Φ for formation of **11** *vs.* molarity of piperylene gave a line of slope 5.3 (by least-squares analysis) for tubes 1–6. The results for tube 7 were excluded from this slope determination, since Φ_0/Φ was too large to be measured accurately. Vpc (QF 1, 150°) showed the ratio (1.00:0.28) of **11** to **10** was similar in tubes 1, 4, and 6. The results are also given in Table IV.

Quantum Yields of Acetone–2 Photocycloaddition. Pyrex tubes containing acetone (0.8 ml) and various known volumes of **2** were

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(47) E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, *J. Amer. Chem. Soc.*, **64**, 2696 (1942).

each made up to 20 ml with hexane. They were deoxygenated, sealed, and irradiated for 3 hr in the Rayonet merry-go-round, in parallel with an actinometer solution of 2-hexanone. After irradiation, tetradecane (4 mg) in hexane was added to each tube as internal standard. Samples from each tube were analyzed by vpc (QF 1, 85°) to determine the ratio (R_2) of the peak area of **5** to that of tetradecane: calibration experiments allowed this ratio to be converted to the weight of **5** produced in each tube, $0.0031R_2$ mol/l.

The actinometer solution was 2-hexanone (0.829 g) and chlorobenzene (internal standard, 1.134 g) in pentane (to 20 ml), similar to that described by Coulson and Yang.[37] The concentrations of 2-hexanone before and after irradiation were measured by vpc (DDP, 120°) relative to the internal standard; peak areas were measured using a Kent Chromalog 2 digital integrator, and were reproducible to better than 0.3%. Precision in this measurement was important, because only 5.6% (0.0232 mol/l.) of the 2-hexanone reacted in 3 hr of irradiation. Assuming a quantum yield of disappearance of 2-hexanone of 0.327,[37] values for the quantum yield of photocycloaddition can be found, $(0.327 \times 0.0031R_2)/0.0232 = 0.0437R_2$. The results, in the form of a plot of (quantum yield of **5**)$^{-1}$ *vs.* (**2**-molarity)$^{-1}$, are shown in Figure 1. Control uv spectra showed that none of the other components used (**2**, chlorobenzene, hexane, or pentane) would absorb an appreciable amount of light under the conditions used. The relative errors of the quantum yield values were estimated from the accuracy with which the vpc peak areas could be measured, and included a term due to nonuniformity of the Pyrex tubes; volumetric errors were comparably small. The absolute errors in quantum yield (±25% additionally) included the differing absorptions of 2-hexanone and acetone, inaccuracy of measurement of the conversion of 2-hexanone, and light absorption by the actinometer photoproduct (acetone). A least-squares analysis of the points in Figure 1, using a Hewlett-Packard 9100A programmable calculator, gave an intercept of 11.1 and a slope of 74.

Competition Experiments. A solution of **1** and **2** (2 ml each) in acetone (5 ml) was deoxygenated and sealed in a Pyrex tube, and irradiated for 12 hr next to the quartz reactor. Vpc (10% PEGS, 80°) showed less than 2% conversion to product, and an essentially unchanged ratio of reactants. The relative areas of the oxetane (**4** and **5**) peaks were determined. Calibration experiments, injecting known weights of oxetanes, allowed this area ratio to be converted to a molar ratio. A similar irradiation of **2** and **3** in acetone was conducted. Hence, the relative reactivities per mole of α,β-unsaturated nitrile were calculated: **1**, 19.9; **2**, 9.7; **3**, 1.0.

Fluorescence Quenching. Solutions of acetone (0.14 *M*) or cyclopentanone (0.02–0.10 *M*) with various concentrations of quencher (**1**, **2**, or **3**) were made up in Spectrosol cyclohexane; both cyclohexane and the quenchers showed negligible fluorescence. Solutions were placed in a 1-cm^2 Suprasil cell and deoxygenated by nitrogen bubbling for 30 sec, and the fluorescence spectra were recorded. The excitation wavelength was 310 nm; the intensity of emission (F) at the maximum (~410 nm for acetone, 405 nm for cyclopentanone) was compared to the intensity (F_0) in the absence of quencher. A Stern–Volmer plot was drawn of F_0/F *vs.* molarity of quencher, and the slope measured on at least four points over the lower linear portion of the curve; the results are given in Table II. For the acetone–*trans*-1,2-dicyanoethylene system in diethyl ether as solvent, the slope of the plot was 5.7 (±0.6) M^{-1}.

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Substituent Effects on Aromatic Proton Chemical Shifts. VIII. Conformational Effects of the Carbonyl Group in Benzenes and Naphthalenes

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Abstract: The nmr parameters for a series of 2-substituted benzaldehydes and acetophenones as well as a number of 1,4-disubstituted naphthalenes are presented. The chemical shifts of the protons adjacent to the varying substituents follow the parameter Q as previously observed in other series. In the benzene series, the behavior of the H-6 protons is revealing about the steric requirements of the formyl and acetyl groups. Extension of the conclusions of this study to the chemical shifts of a series of 1-X-4-methoxynaphthalenes leads to the conclusion that when X is formyl there is a definite hydrogen-bond-like interaction between the oxygen and the peri hydrogen, H-8.

In preceding papers in this series[1] it has been shown that the proton chemical shifts at C-3 in a series of 1-X-2-Y-benzenes (X is constant and Y varied) follow the previously defined, semiempirical parameter Q.[2] An experimental method of determining Q has been described,[1c] and a table of Q values presented.[1g,3]

For groups which are not cylindrically symmetrical about the axis of the bond to the benzene ring, two values of Q are required. For such instances where the group Y is flanked only by hydrogens, the $Q(1)$ value obtains. When some large bulky group or a group which holds Y in some specific orientation as by a hydrogen bond is adjacent, then the H-3 chemical shift requires the $Q(2)$ value of Y. The necessity of two Q values was first made clear for the nitro group. Subsequently, the hydroxyl and amino groups were shown to require specific Q values when hydrogen bonded to an ortho substituent.[1g]

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(3) During the course of the present study, we found that the predictive utility of the Q value for fluorine could be improved with a value of 1.50. Whether this represents a flaw in the data used to calculate Q_F[2a] or a change in the basis of the original Q correlation is a moot point. Similarly, we have found that the Q values for methoxyl are dependent on the size of the adjacent substituent increasing with the size of Y over the range 0.4–0.8.