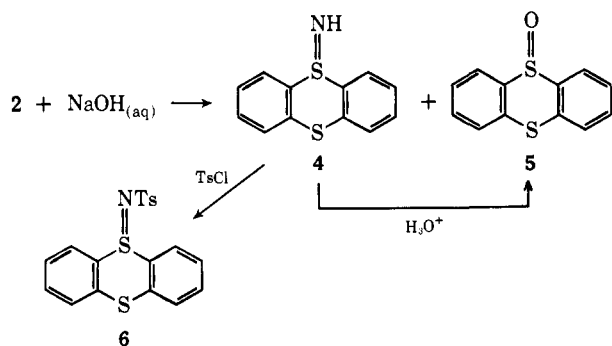


Scheme I



ucts were extracted into benzene from the aqueous methanol solution, and separated on a column of silica gel, giving 51.3 mg (0.221 mmol, 99%) of **5** and 30 mg (0.129 mmol, 53%) of **4** (5,5-dihydro-5-iminothianthrene<sup>9</sup>), mp 130–143° dec. A sample of **4** was taken up in methanol and hydrolyzed by stirring with 30% hydrochloric acid for 2 hr. Tlc showed the presence of **5** only. Extraction of **5** into benzene and assay (ultraviolet spectrum) gave 90% of the anticipated **5**. The acidic methanol solution was made alkaline with sodium hydroxide and heated. Ammonia was evolved (silver nitrate–manganese nitrate paper test).

The tosylate **6** of **4** was obtained without isolating **4** because **4** was found to be unstable to too much handling in the light. A sample (52 mg, 0.095 mmol) of **2** was hydrolyzed by base as described. The products were extracted into benzene, the benzene was evaporated, and the residue was dissolved in dry ether. To the ether solution was added the calculated amounts of pyridine (0.1 ml, 0.12 mmol), and, dropwise, *p*-toluenesulfonyl chloride (18 mg, 0.1 mmol). The solid residue from the evaporated ether solution was washed with water and was shown to contain only two compounds by tlc: **5**,  $R_f$  (benzene) = 0.30, and the tosylate **6**,  $R_f$  (benzene) = 0.11. The two compounds were separated on a column of silica gel. Elution with benzene–ether (10:1) gave 21 mg (0.090 mmol, 95%) of **5**, while elution with ether gave 11 mg (0.026 mmol, 27%) of 5,5-dihydro-5-(*N-p*-toluenesulfonyl)iminothianthrene (**6**), mp 172–173° (methanol); lit. mp 168–169° (reaction of thianthrene with chloramine-T).<sup>12</sup>

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{15}\text{S}_3\text{NO}_2$ : C, 59.2; H, 3.89; S, 24.9; N, 3.63. Found:<sup>11</sup> C, 59.3; H, 3.88; S, 24.8; N, 3.75.

The mass spectrum<sup>13</sup> of **6** showed the parent peak, mass 385. The ratio of the intensities of peaks 387/385 (16.3%) was consistent with the formula for **6**.<sup>14</sup>

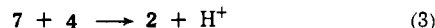
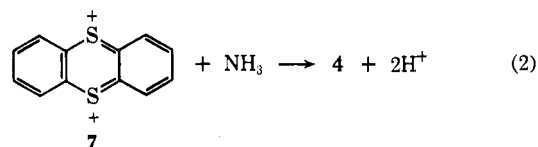
Reaction of **1** with water leads to **3** and **5**, and the reaction has been interpreted from kinetic data as going through the thianthrene dication **7**.<sup>8</sup> Reaction of **1** with ammonia can be interpreted similarly, in which case compound **4**, formed in the reaction of **7** with ammonia (eq 2), would have to react rapidly with another molecule of **7** to give **2** (eq 3). Kinetic data are needed to settle this point.

Compound **2** is a member of an only recently discovered class of compounds containing the group

(12) D. Hellwinkel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, **715**, 68 (1969).

(13) Morgan-Schaffer Laboratories, Montreal, Canada.

(14) J. H. Beynon, "Mass Spectrometry and Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, p 301.



$\text{R}_2\text{S}^+\text{N}=\text{SR}_2$ , analogous in form to the allyl cation. The first known example ( $\text{R} = \text{Me}$ ; anion  $\text{Cl}^-$ ) was made by the reaction of DMSO with trithiazyl chloride,<sup>15</sup> while an aromatic analog ( $\text{R} = \text{phenyl}$ ; anion  $\text{Cl}_3^-$ ) was made by reaction of phenyl sulfide with nitrogen trichloride.<sup>16</sup> The present reaction (leading to **2**) may be general for organosulfur cation radicals. This and the reaction of organosulfur cation radicals with alkylamines are being explored.

(15) M. Becke-Goehring and H. P. Latscha, *Angew. Chem.*, **74**, 695 (1962).

(16) G. Appel and G. Buchler, *Justus Liebigs Ann. Chem.*, **684**, 112 (1965).

(17) Predoctoral student.

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### Cycloaddition of *tert*-Butylcyanoketene to 1,2-Cyclononadiene and *cis*- and *trans*-Cyclooctene

Sir:

Reported here is the first stereochemical investigation of the cycloaddition of a ketene to an allene, specifically *tert*-butylcyanoketene<sup>1</sup> (**1**) to racemic and optically active 1,2-cyclononadiene (**2**). These cumulenes react to give a mixture of the diastereomeric cyclobutanones **5** and **6** in a ratio of 3:2. When partially resolved 1,2-cyclononadiene is used both epimers show appreciable optical activity. It is also established that *tert*-butylcyanoketene behaves as a "normal" ketene in its cycloadditions to simple alkenes, *i.e.*, it reacts stereospecifically with *cis*- and *trans*-cyclooctene to give, respectively, the cyclobutanones **7** and **8**.<sup>2</sup>

The cycloaddition of *tert*-butylcyanoketene (**1**) to 1,2-cyclononadiene (**2**) was accomplished by adding the allene to a benzene solution of the ketene. The reaction was complete within a few minutes at room temperature to give a mixture of the cyclobutanones **5** and **6** in a ratio of 3:2 as evidenced by gas chromatography and nmr analysis of the crude reaction mixture. Compounds **5** and **6** were separated by preparative gas chromatography.<sup>3</sup> The nmr spectra of **5** and **6** are consistent with their proposed formulations, *i.e.*, the *tert*-butyl is *cis* to the adjacent  $\text{CH}_2$  group in the major isomer **5** and *trans* to it in **6**. The pertinent

(1) H. W. Moore and W. Weyler, Jr., *J. Amer. Chem. Soc.*, **92**, 4132 (1970); H. W. Moore and W. Weyler, Jr., *ibid.*, **93**, 2812 (1971).

(2) The cycloadditions of ketenes to alkenes have received marked attention. These highly regio- and stereoselective reactions are best interpreted as concerted [ $\pi 2_s + \pi 2_s$ ] cycloadditions in which the ketene functions as the antarafacial component: (a) T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970); (b) W. T. Brady, E. F. Hoff, R. Row, Jr., and F. H. Parry, *ibid.*, **91**, 5679 (1969); (c) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970); (d) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970); (e) R. Montaigne and L. Ghosey, *Angew. Chem., Int. Ed. Engl.*, **80**, 194 (1968); (f) R. Huisgen, L. A. Feiler, and P. Oho, *Tetrahedron Lett.*, 4485 (1968); (g) N. S. Isaacs and P. F. Stanbury, *Chem. Commun.*, 1061 (1970).

(3) 10 ft  $\times$  1/4 in. 15% SE-30 Chromosorb W 60–80 acid-washed dimethylchlorosilane-treated columns, 85°.

point in making this assignment is the chemical shifts of the bridgehead CH groups at 2.93 ppm in **6** and 3.49 ppm in **5**. That is, in **5** this proton is strongly deshielded relative to that in **6**. Such deshielding would be expected for the *cis* isomer, since the proton appears (models) to lie in the deshielding region of the cyano group. Other critical structural data for these compounds follow. **5** showed: mp 78–79°; ir (Nujol) 2235 (CN), 1770 ( $>C=O$ ), 1660  $cm^{-1}$  ( $=C<$ );<sup>4</sup> nmr ( $CCl_4$ )  $\delta$  6.45 (1) triplet of doublets ( $J = 7.5$  Hz) into triplet ( $J = 3.1$  Hz) into doublets ( $>C=CH-$ ), 2.93 (1) broad (CH), 1.25–2.65 (12) multiplet ( $CH_2$ ), 1.16 (9) singlet ( $C(CH_3)_3$ );  $M^+$ , 245. Anal. Found: C, 78.25; H, 9.44. Compound **6** showed: mp 113–114°; ir (Nujol) 2235 (CN), 1770 ( $>C=O$ ), 1660  $cm^{-1}$  ( $>C=C<$ ); nmr ( $CCl_4$ )  $\delta$  6.60 (1) triplet of doublets ( $J = 8.0$  Hz) into triplets ( $J = 3.0$  Hz) into doublets ( $>C=CH-$ ), 3.49 (1) broad (CH), 1.32–2.15 (12) multiplet ( $CH_2$ ), 1.33 (9) singlet ( $C(CH_3)_3$ );  $M^+$ , 245. The ultraviolet spectra of these epimers are characteristic of an  $\alpha,\beta$ -unsaturated carbonyl chromophore. Compound **5**, for example, shows absorptions at 355 (114) and 249 nm (14,000) which are in strict agreement with other ketene–allene adducts.<sup>5</sup>

When the above cycloaddition was carried out with partially resolved<sup>6</sup> 1,2-cyclononadiene [ $[\alpha]^{25D} + 20.43^\circ$  (neat)]<sup>7</sup> both isomers **5** and **6** showed appreciable optical activity, *i.e.*, **5**,  $[\alpha]^{25D} + 29.68 \pm 0.03^\circ$  ( $c$  4.85 g/100 ml,  $CCl_4$ ); **6**,  $[\alpha]^{25D} - 21.41 \pm 0.02^\circ$  ( $c$  4.95 g/100 ml,  $CCl_4$ ). This fact along with the observation that the major product **5** from the reaction is believed to be the isomer in which the bulky *tert*-butyl group is *cis* to the adjacent  $CH_2$  argues in favor of a concerted mechanism for the cycloaddition.<sup>8</sup> The major product **5** is envisaged as arising from transition state **3** and the minor product from **4**.

The observed ratio of the major product **5** to the minor product **6** (3:2) is small in comparison to epimeric ratios obtained for the concerted reactions of a variety of other ketenes with alkenes.<sup>2a–d</sup> This may reflect a lower steric requirement for the orthogonal approach of a ketene to a cumulene double bond as opposed to an alkene functionality. In order to probe this possibility the reactions of *tert*-butylcyanoketene (**1**) with *cis*- and *trans*-cyclooctene were studied. These alkenes react with the ketene in a remarkably stereospecific [ $\pi 2_s + \pi 2_a$ ] concerted cycloaddition, giving respectively, the cyclobutanones **7** and **8**. In both cyclobutanones the geometrical configuration of the parent alkene is maintained and the bulky *tert*-butyl group is *cis* to the adjacent  $CH_2$ . Such results are in complete accord with predictions of the Woodward–Hoffmann orbital symmetry conservation rule<sup>9</sup> as well

(4) These data are consistent with those reported by D. C. England and C. G. Krespan (*J. Org. Chem.*, **35**, 3322 (1970)) for the cyclobutanones obtained from the cycloaddition of bis(trifluoromethyl)ketene to 1,3-dimethylallene.

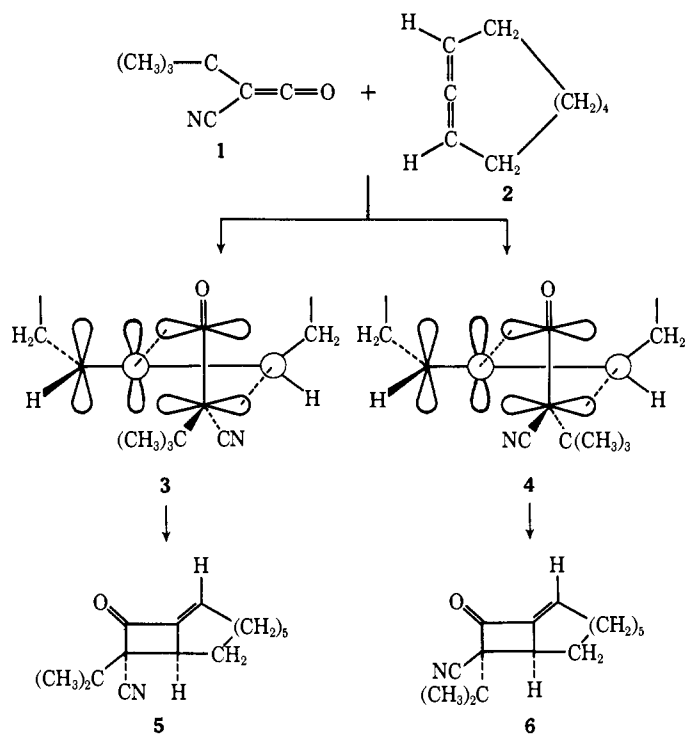
(5) J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *ibid.*, **30**, 4175 (1965).

(6) Resolution of **2** was accomplished according to the method previously reported by W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6714 (1968).

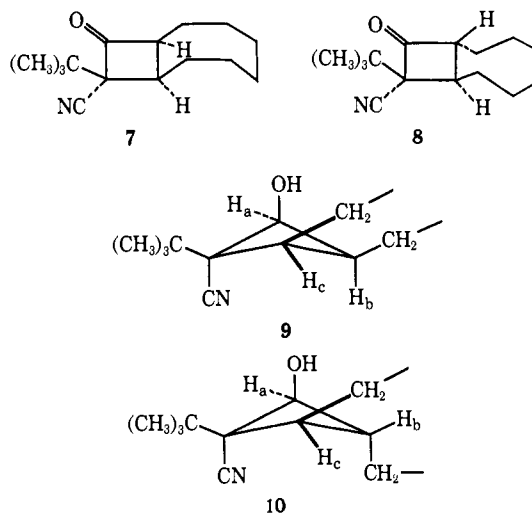
(7) Optically pure 1,2-cyclononadiene is believed to have a specific rotation of 170–175°: W. R. Moore, R. D. Bach, and T. M. Ozretich, *ibid.*, **91**, 5918 (1969).

(8) The induction of optical activity in **5** and **6** does not in itself demand a concerted reaction. This could be more firmly established from the optical purities of **5** and **6** which have not yet been determined.

(9) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).



as with the observed cycloadditions of ethoxyketene to alkenes,<sup>2a</sup> dichloroketene to *cis*- and *trans*-cyclooctene,<sup>2c</sup> and a variety of ketenes to cyclopentadiene.<sup>2b,d</sup> The stereochemistry of the bridgehead positions in **7** and **8** was readily assigned from nmr decoupling experiments which showed the coupling constants for the vicinal methine protons in **7** and **8** to be 10 and 6 Hz, respectively.<sup>2a,10</sup> The *cis* relationship between the *tert*-butyl groups and the adjacent  $CH_2$  substituents was established from the nmr spectra of the alcohols **9** and **10** which were obtained by sodium borohydride reduction of the respective ketones **7** and **8**. The nmr spectra of these alcohols showed  $H_a$  and  $H_b$  to be in an axial–equatorial relationship ( $J = 9.7$  Hz) in **9** and an equatorial–equatorial relationship ( $J = 5.0$  Hz) in **10**.<sup>2c,11</sup> Since the relative configurations at the bridge-



(10) The coupling constants for vicinal ring protons in cyclobutanones have been shown to be larger for the *cis* configuration  $J_{cis} \approx 9-10$  Hz *vs.*  $J_{trans} \approx 5$  Hz: L. H. Sutcliffe and S. M. Walker, *J. Phys. Chem.*, **71**, 555 (1967).

(11) These assignments are based upon the report of K. B. Wiberg and D. E. Barth (*J. Amer. Chem. Soc.*, **91**, 5124 (1969)) who have shown

head positions ( $H_b$ ,  $H_c$ ) were established from the decoupling experiments on the cyclobutanones, the stereochemical relationships between  $H_a$  and  $H_b$  in the alcohols allowed the assignment of the relative configurations at all four asymmetric carbon atoms. It is of course necessary to assume that the reduction of the carbonyls took place from the least-hindered side of the molecules, *i.e.*, the side opposite the bulky *tert*-butyl group. As a result, the *tert*-butyl substituent is *trans* to  $H_a$  and *cis* to the adjacent methylene in both alcohols **9** and **10**. Therefore, *tert*-butylcyanoketene reacts with alkenes in complete analogy to other ketene cycloadditions.

The results reported above for the reaction of **1** with **2** are of particular interest in view of the current investigations into the mechanism of cumulene cycloadditions. Allene dimerizations, for example, have been studied in some detail.<sup>12-17</sup> The high stereoselectivity of these dimerizations is consistent with a concerted [ $\pi 2_s + \pi 2_a$ ] cycloaddition in which the allene functions as both the suprafacial and antarafacial components. However, a recent kinetic secondary deuterium isotope effect study on the dimerization of allene itself shows this to be a two-step process.<sup>17</sup> Ketenes on the other hand react with alkenes in a concerted manner, and, as shown above, *tert*-butylcyanoketene (**1**) is no exception. An important unresolved question existing prior to the results reported here concerned the concertedness of the ketene plus allene cycloadditions. A sweeping generalization to the above question cannot yet be made. However, the observed optical activity in both cyclobutanones **5** and **6** from the reaction involving optically active allene **2**, the fact that the major product **5** has a *cis* relationship between the *tert*-butyl and the adjacent  $CH_2$ , and the propensity of *tert*-butylcyanoketene to react with C=C double bonds in a concerted fashion all suggest that the cycloaddition of cyanoketene **1** to the cyclic allene **2** is a one-step synchronous reaction.

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$J_{ae}$  coupling to be appreciably larger than  $J_{ee}$  coupling in nonplanar cyclobutanols.

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(14) J. J. Gajewski and W. A. Black, *Tetrahedron Lett.*, 899 (1970).

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(16) E. F. Kiefer and M. Y. Okamura, *ibid.*, **90**, 4187 (1968).

(17) W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **92**, 1775 (1970).

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### Remarkable Solvent Effects on the Lifetime of $^1\Delta_g$ Oxygen<sup>1</sup>

Sir:

Knowledge of the lifetime of singlet oxygen in solution plays an important role in interpreting many of the

(1) This work was supported by a grant (CA 11459) from the U. S. Public Health Service.

photooxidation studies now being carried out. There now appears to be a widespread belief that the lifetime of singlet oxygen ( $^1\Delta_g$ ) is approximately solvent independent.<sup>2-7</sup> This is based on experimental observations that the " $\beta$ " value for a given oxygen acceptor, the ratio of the rate of the decay of singlet oxygen to the rate of reaction with the acceptor, does not depend strongly on the nature of the solvent. In most of the recent collections of data we find that  $\beta$  values for some of the common acceptors vary by at most a factor of 4 in different solvents.<sup>2,3,5</sup> In contrast to these more recent findings, Bowen<sup>7</sup> and Livingston and Owens<sup>8</sup> found relatively large solvent effects on the *rate* of photooxidation of anthracene (and hence presumably on its  $\beta$  value), but the significance of these observations was questioned because of the possible solvent effects on the fluorescence of anthracene.<sup>2</sup>

Recently we developed a spectroscopic method which has permitted us to directly measure the lifetime of singlet oxygen in solution.<sup>9</sup> We have used this method to measure the lifetime of singlet oxygen in some of the solvents which are commonly used in photooxidation studies. Contrary to previous conclusions, we find that the lifetime of singlet oxygen is remarkably sensitive to the nature of the solvent.

In our experiments singlet molecular oxygen ( $\sim 5 \times 10^{-5} M$ ) was generated in  $\sim 10^{-7}$  sec by energy transfer from methylene blue triplets which were excited by a 20-nsec ruby laser pulse.<sup>9</sup> Singlet oxygen was then monitored spectroscopically by following its reaction with the colored acceptor, 1,3-diphenylisobenzofuran, to form a colorless product.

The results of these experiments, which are presented in Table I, demonstrate that the lifetime of  $^1\Delta_g$  varies by

Table I. Solvent Effects on the Lifetime of  $^1\Delta_g$

Solvent	Viscosity, cP <sup>a</sup>	Dielectric constant <sup>a</sup>	$\tau^1\Delta_g$ , $\mu$ sec
H <sub>2</sub> O	0.80 <sup>b</sup>	80	2
CH <sub>3</sub> OH	0.51	33	7
C <sub>6</sub> H <sub>6</sub>	0.56	2.2	24
CH <sub>3</sub> C(=O)CH <sub>3</sub>	0.29	~20	26
CS <sub>2</sub>	0.35	2.6	200

<sup>a</sup> "Handbook of Chemistry and Physics," 35th ed, Chemical Rubber Publishing Co., Cleveland, Ohio. <sup>b</sup> Extrapolation based on data using 1:1 H<sub>2</sub>O-CH<sub>3</sub>OH.

a factor of 100 in going from water to CS<sub>2</sub>. It is not surprising that there are large solvent effects on the  $^1\Delta_g$  lifetime since it represents a good example of what Robinson<sup>10</sup> and others,<sup>11-13</sup> would classify as a small

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