Organic Photochemistry. IX. The Photocycloaddition of 2-Cyclopentenone to *cis*- and *trans*-Dichloroethylene. Evidence for Initial Attack at Carbon-3 and Rotational Equilibration of the Diradical Intermediates[1]

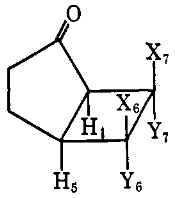
Sir:

We present evidence that in the two-step photocycloaddition of 2-cyclopentenone (**1**) to *cis*- (**2**) and *trans*-dichloroethylene (**3**)[2] the initial bond to the ketone **1** is formed at C-3, and the diradical intermediates are completely rotationally equilibrated before ring closure. It has been suggested that most of the products formed from the photoaddition of cyclic α,β-unsaturated ketones to unsymmetrical olefins[3] can be explained by a two-step reaction in which the first bond to the ketone is formed at C-2.[3c,4] If our results with the 1,2-dichloroethylenes can be extrapolated to other olefins, this explanation cannot be correct.

Irradiation of the ketone **1** in a *ca.* 20 molar excess of either the *cis* **2** or *trans* olefin **3** under nitrogen at 20 ± 1° through a Pyrex filter (λ >295 mμ) with a medium-pressure mercury arc lamp gave three cycloadducts **4–6** in *ca.* 80% isolated yields.[5,6] No evidence for the formation of the fourth isomer **7** was observed.[7]

The structures of the cycloadducts **4–6** were determined by comparison of their nmr spectra with those of the four trichloroethylene photoadducts **8–11** of the ketone **1** (Table I). The stereochemical assignments for the four trichloro isomers **8–11** were based on the spin-spin splitting patterns of H_1 and H_5 and the magnitude of the coupling constants $J_{1,7}$ and $J_{5,6}$. The relative chemical shifts are also consistent with these assignments. The shielding effect of vicinal *cis* carbon-carbon and carbon–chlorine single bonds is apparent. The similarity in chemical shifts of H_6 and H_7 of adduct **4** suggests *cis*-hydrogen atoms while the value of −4.51 implies that they are *cis* to the cyclopentane ring. The difference in chemical shifts between H_6 and H_7 for adducts **5** and **6** suggests a *trans* arrangement with the lowest field proton, −4.66, being due to H_6 which is *trans* to the cyclopentane ring. The relative magnitude of the coupling constants is also in agreement with the stereochemical assignments; J_{cis} = 7.3–10.7 cps, J_{trans} = 1.4–6.8 cps.[8]

The structure of the *trans*-dichloro adduct **6** was confirmed by X-ray diffraction. Single crystals of **6** belong to the space group $P2_1/c$, $a = 6.191 \pm 0.005$, $b = 11.172 \pm 0.008$, $c = 11.709 \pm 0.008$ Å, $\beta = 94.73 \pm 0.04°$, with $Z = 4$. Data were collected on a Picker automatic four-circle diffractometer using a 2θ scan and Mo Kα radiation. The structure was solved by reiterative application of Sayre's equation[9] on 209 *E*'s and refined by full-matrix least squares to an *R* factor of 5.6% for the 1236 reflections above background. The four-membered ring is puckered (dihedral angle 149.3°), and the five-membered ring has an envelope conformation with C-4 tilted out of the C-1, C-2, C-3, C-5, O plane (dihedral angle 153.3°).



4, $X_6 = X_7 = H$; $Y_6 = Y_7 = Cl$
5, $X_6 = Y_7 = H$; $X_7 = Y_6 = Cl$
6, $X_7 = Y_6 = H$; $X_6 = Y_7 = Cl$
8, $Y_7 = H$; $X_6 = X_7 = Y_6 = Cl$
9, $X_7 = H$; $X_6 = Y_6 = Y_7 = Cl$
10, $Y_6 = H$; $X_6 = X_7 = Y_7 = Cl$
11, $X_6 = H$; $X_7 = Y_6 = Y_7 = Cl$

Table I. Nuclear Magnetic Resonance Data for Di- and Trichlorobicyclo[3.2.0]heptan-2-ones

	δ^b				J^c			
Compd[a]	H_6	H_7	H_1	H_5	6–7	1–7	5–6	1–5
4	−4.51	−4.51	−2.97	−3.39	7.5	2.2	1.4	8.3
5	−4.20	−4.53	−3.11	−3.11	6.8	10.7	4.7	
6	−4.66	−4.17	−2.82	−3.34	6.5	6.2	8.2	7.3
8		−5.12	−3.25	−3.64		9.7		7.6
9		−4.66	−3.04	−3.68		6.7		8.1
10	−5.24		−3.6	−3.6			10.4	
11	−4.62		−3.4	−3.4			5.9	

[a] Spectra of **4–6** were obtained in CCl_4 solution, **8–11** in $CDCl_3$ solution, at both 60 and 100 Mcps. [b] In parts per million from tetramethylsilane used as an internal reference. [c] In cycles per second.

The product and olefin compositions for the additions of *cis*- (**2**) and *trans*-dichloroethylene (**3**) as a function of ketone **1** conversion are shown in Figures 1 and 2, respectively. The product distributions extrapolated to zero conversion by the least-squares method are shown in Table II. From these product distributions and the assumption that the first bond to the ketone **1** is formed at C-3, one calculates the relative amounts of the diradical[10] intermediates **12–15** and their partitioning to the products **4–7** as shown in Scheme I. This parti-

Table II. Product Distributions from Photoaddition of 2-Cyclopentenone and *cis*- and *trans*-Dichloroethylene Extrapolated to Zero Conversion

	Product distribution, %[a]		
Starting olefin	**4**[b]	**5**[c]	**6**[d]
cis-**2**	28.6 ± 1.3[e]	19.1 ± 1.6	52.4 ± 2.3
trans-**3**	47.8 ± 1.3	30.0 ± 1.5	22.2 ± 0.4

[a] Determined by gas chromatography of the crude reaction mixture with each component corrected for thermal conductivity variation in the detector. [b] Mp 52–52.5°. [c] Mp <25°. [d] Mp 83.5–84°. [e] Standard deviation.

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[1] Part VIII: W. L. Dilling and R. D. Kroening, *Tetrahedron Lett.*, in press.

[2] (a) P. de Mayo, J-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (b) R. Steinmetz, *Fortschr. Chem. Forsch.*, 7, 445 (1967).

[3] (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, 90, 1657 (1968); (c) T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969).

[4] (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 207; (b) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 118 (1968); (c) see also J. W. Hanifin and E. Cohen, *J. Amer. Chem. Soc.*, 91, 4494 (1969).

[5] de Mayo and coworkers[2a] also reported the formation of three products which were identified only as cycloadducts.

[6] Satisfactory infrared, nmr, ultraviolet, and mass spectra have been obtained for all new compounds reported in this paper.

[7] Spectroscopic examination of the crude reaction mixture after removal of the solvent at room temperature or below showed no evidence for significant amounts of another product.

[8] See *e.g.*, I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

[9] (a) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952); (b) R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis, University of California at Los Angeles, 1965.

[10] We assume that the intermediates are diradicals, but zwitterionic species cannot be ruled out.

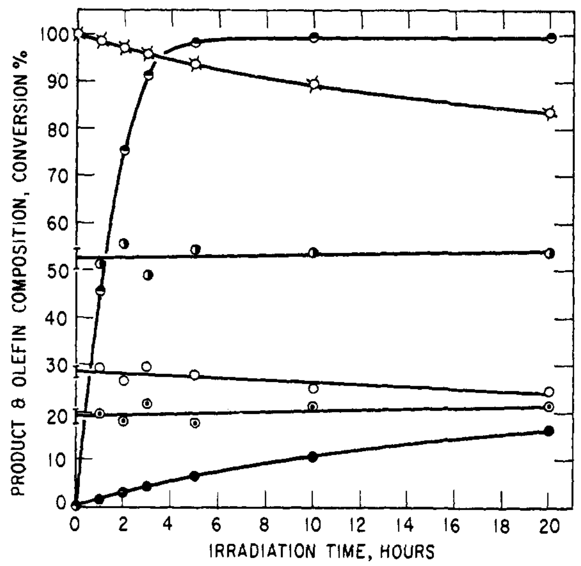
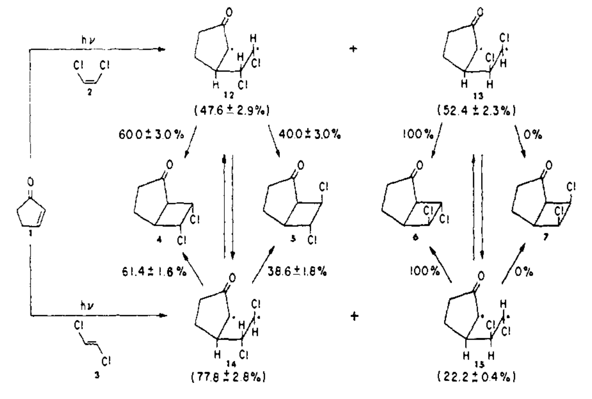


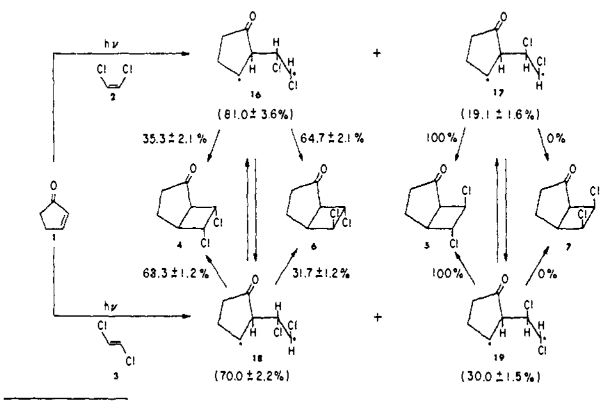
Figure 1. Product composition from photoaddition of 2-cyclopentenone (**1**) to *cis*-dichloroethylene (**2**): ○, % **4**; ⊙, % **5**; ◑, % **6**. Olefin composition: ✡, % **2**; ●, % **3**. Ketone **1** conversion (%), ◓.

tioning is consistent with a mechanism in which, within experimental error, the diradical intermediates (**12** and **14**, **13** and **15**) are completely rotationally equilibrated before ring closure.[11] The alternate analysis assuming initial bond formation at C-2 is shown in Scheme II.

Scheme I



Scheme II



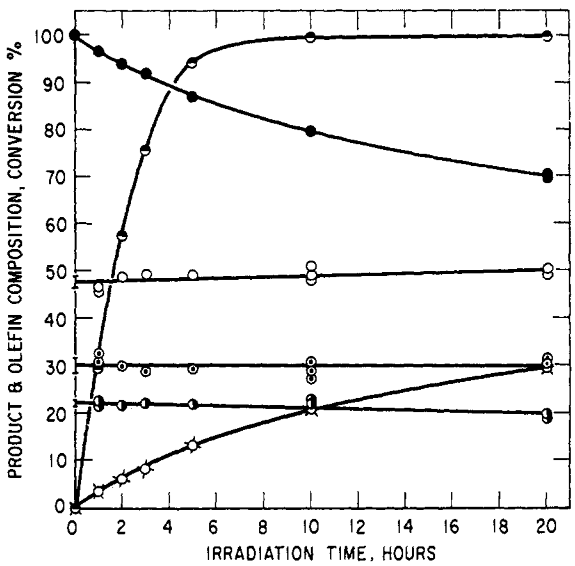


Figure 2. Product composition from photoaddition of 2-cyclopentenone (**1**) to *trans*-dichloroethylene (**3**): ○, % **4**; ⊙, % **5**; ◑, % **6**. Olefin composition: ●, % **3**; ✡, % **2**. Ketone **1** conversion (%), ◓.

The partitioning of the intermediates **16** and **18** seems inconsistent with any reasonable mechanism since more *trans* product **6** would be formed from the *cis* olefin **2** than would be formed from the *trans* olefin **3** and *vice versa*.

The products of the photoaddition of unsymmetrical olefins to cyclic α,β-unsaturated ketones may still be explained by the formation of a π complex.[3a] This complex could be formed in the rate-determining step following excitation, with the formation of one of the less stable diradical intermediates occurring at a later stage.

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[11] Contrary to the conclusion in ref 2a concerning the relative rates of ring closure and rotation, the only substrates from which identical product distributions can be expected in two-step cycloadditions of *cis* and *trans* olefins are those which have two like substituents on the sp^2 carbon atom to which the initial bond is formed. Since the ketone **1** does not possess this property the product distributions from the additions of the *cis* and *trans* olefins **2** and **3** are not expected to be the same even though the intermediates are rotationally equilibrated, *i.e.*, a slow second step. The results with 2-cyclohexenone and the isomeric 2-butenes[3a] have been interpreted as involving a common reaction intermediate.[12] This cannot be correct since more than two *cis*-bicyclo[4.2.0]-octane derivatives are formed. At least two enantiomeric intermediates must be involved. Bartlett and coworkers[13] have recently pointed out the cause of different product distributions from the cycloaddition of cyclopentadiene triplet to the olefins **2** and **3**. These arguments are analogous to ours above.

(12) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

(13) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968).

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Nucleosides. VI. The Synthesis and Circular Dichroism Spectra of 5′-(9-Adenyl)-2′,5′-dideoxy-β-D-ribofuranosylthymine and -adenine

Sir:

In our previous study of 5′-substituted nucleoside analogs as potential antiviral agents[1] it was noted that

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(1) (a) T. Neilson, W. V. Ruyle, R. L. Bugianesi, K. H. Boswell, and T. Y. Shen, Abstracts, 154th National Meeting of the American