chlorosulfonic acid in 15 ml of carbon tetrachloride[12]) in 80 ml of dimethyl sulfoxide containing 34 ml of triethylamine, according to the general procedure of Parikh and Doering.[3] The crude product (1.50 g) was recrystallized from pentane at Dry Ice–acetone temperature and gave 1.35 g (45%) of norbornadien-7-one-iron tricarbonyl, mp 93.5–95.5° (sealed, partially evacuated capillary tube); resolidified material melted at 93–95° and evolved some gas. The major impurities were dimethyl sulfoxide decomposition products which gave the solid a pungent odor; several recrystallizations from pentane reduced the odor and gave orange needles. *Anal.* Calcd for $C_7H_6OFe(CO)_3$: C, 48.82; H, 2.46. Found: C, 48.89; H, 2.51. A stable orange 2,4-dinitrophenylhydrazone, mp 164° dec, was obtained.

Future communications will deal with the chemical reactivity, including photochemistry, of this novel system.

Acknowledgment. We thank Miss V. Parmakovich, Columbia University, for determining the mass spectra. We gratefully acknowledge financial support by a Petroleum Research Fund grant from the American Chemical Society and by a Frederick Gardner Cottrell grant from the Research Corporation.

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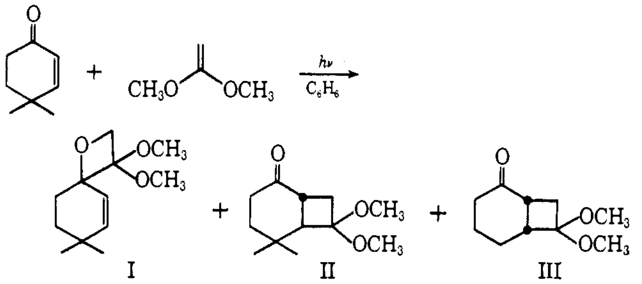
Two Triplet Mechanisms in Photochemical Addition of 2-Cyclohexenones to 1,1-Dimethoxyethylene[1]

Sir:

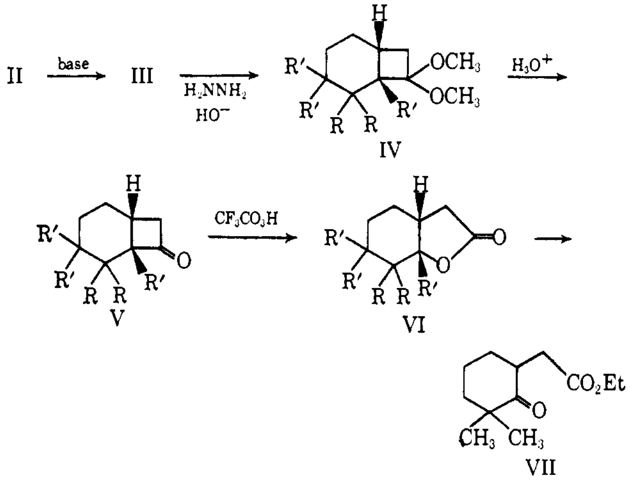
Photocycloaddition of 2-cyclohexenone[2] and 2-cyclopentenone[3] to olefins gives bicyclo[4.2.0]octan-2-ones and bicyclo[3.2.0]heptan-2-ones. In the case of cyclohexenone both *cis* and *trans* isomers of the bicyclic system are formed.[2] Cyclopentenone gives only the *cis* isomer.[3]

In our investigation of the photodimerization of isophorone we were led to postulate that two excited triplets react with ground-state isophorone.[4] Earlier, Yang had considered the possibility that two triplets were involved in the photochemical addition of 9-anthraldehyde to trimethylethylene[5] and in the photochemistry of 9-nitroanthracene[5,6] and has shown that two reactive excited states are involved in the former reaction.[7] Yang has also detected phosphorescence from 1-indanone which involves two triplet states of differing lifetimes.[8] Recently, de Mayo has suggested that an upper triplet of 2-cyclopentenone is involved in its photochemical addition to cyclohexene.[9] We now wish to describe the addition of 4,4-dimethyl-2-cyclohexenone to 1,1-dimethoxyethylene and the addition of isophorone to 1,1-dimethoxyethylene. In each case two triplets are involved which lead to different products.

Irradiation of 4,4-dimethyl-2-cyclohexenone (0.2 *M*) and 1,1-dimethoxyethylene (0.1 *M*) in benzene gave an oxetane (I), a *trans* adduct (II), and a *cis* adduct (III). The structure of the oxetane is based on the empirical



formula ($C_{12}H_{20}O_3$), the nmr spectrum, the absence of carbonyl absorption in the infrared spectrum, and the loss of CH_2O on electron-impact ionization. The *trans* isomer was isomerized to the *cis* isomer by base.



a, R = CH_3; R′ = H
b, R = H; R′ = CH_3

Reduction, hydrolysis, and oxidation gave γ-lactone VIa. The γ-lactone was reduced to a diol which on oxidation and esterification gave keto ester VII identical with an authentic sample.

Irradiation of isophorone and 1,1-dimethoxyethylene in benzene gave a mixture of products from which the *cis* and *trans* adducts VIII and IX were isolated and characterized. The *trans* adduct isomerized to the *cis* adduct which was converted to lactone VIb by the same series of transformations used above. Lactone VIb was synthesized from 2,4,4-trimethyl-2-cyclohexenone by catalytic reduction, a Reformatsky reaction using ethyl

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[1] Photochemical Transformations. XXV. Portions of this work were described at the 20th National Organic Chemistry Symposium of the American Chemical Society, June 18–22, 1967, Burlington, Vt., Abstracts, pp 127–139.

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[3] P. Eaton, *ibid.*, **84**, 2454 (1962); *Tetrahedron Letters*, 3695 (1964).

[4] O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Record Chem. Progr.*, **28**, 167 (1967).

[5] N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

[6] O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. W. Reasoner, *ibid.*, **9**, 585 (1964); O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Am. Chem. Soc.*, **88**, 5550 (1966).

[7] N. C. Yang, R. Loeschen, and D. Mitchell, *ibid.*, **89**, 5465 (1967).

[8] N. C. Yang and S. Murov, *J. Chem. Phys.*, **45**, 4358 (1966).

[9] P. de Mayo, J.-P. Pete, and M. Tchir, *J. Am. Chem. Soc.*, **89**, 5712 (1967).

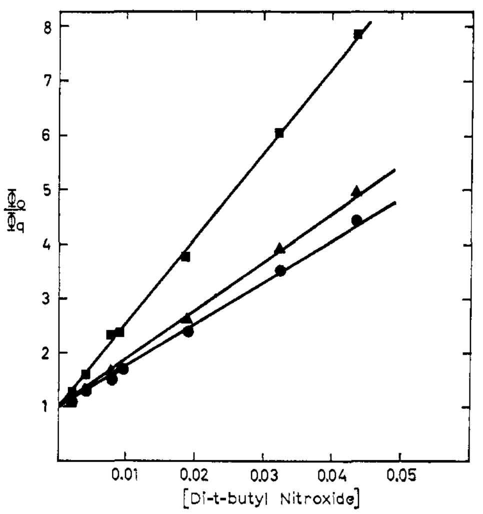


Figure 1. Stern–Volmer plot of quenching of photoaddition of 4,4-dimethyl-2-cyclohexenone (0.20 *M*) to 1,1-dimethoxyethylene (0.10 *M*) by di-*t*-butyl nitroxide in hexane at 43°. Quencher concentration is expressed in moles per liter. Points were obtained in two separate experiments: ●, oxetane (I); ▲, *trans* adduct (II); ■, *cis* adduct (III).

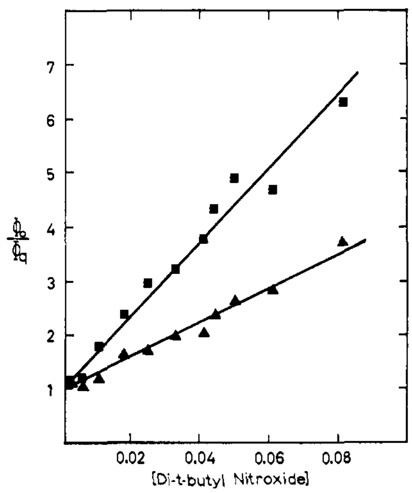
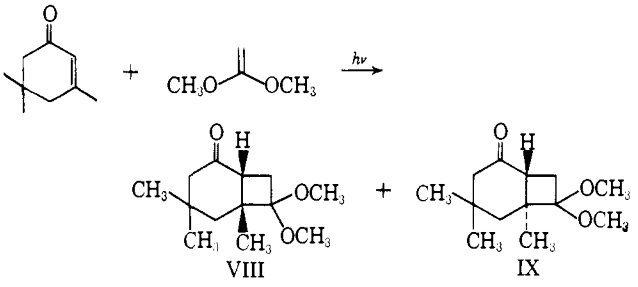


Figure 2. Stern–Volmer plot of quenching of photoaddition of isophorone (0.15 *M*) to 1,1-dimethoxyethylene (0.15 *M*) by di-*t*-butyl nitroxide in benzene at 43°. Quencher concentration is expressed in moles per liter. Points were obtained in three separate experiments: ■, *cis* adduct (VIII); ▲, *trans* adduct (IX).

bromoacetate, dehydration, iodolactonization, and catalytic reduction.



The photoaddition is sensitive to solvent. In *t*-butyl alcohol rearrangement[10] is observed in competition with the formation of *cis* and *trans* adducts, and oxetane formation is not observed. In benzene oxetane (13%) is observed, and in *n*-hexane it is the major product (42%). In both the 4,4-dimethyl-2-cyclohexenone and isophorone additions the ratio of *cis*-to-*trans* adducts varies significantly with solvent. Plots of 1/[olefin] *vs.* $1/\Phi_{\text{addition}}$ are linear in benzene.

The formation of oxetane and *cis* and *trans* adducts can be sensitized. Using 4,4-dimethyl-2-cyclohexenone (0.100 *M*) and triphenylamine (0.100 *M*), under conditions such that the triphenylamine absorbed about 80% of the light (350 mμ) the ratio of the quantum yield for the sensitized to the unsensitized reaction ($\phi_{\text{sens}}/\phi_0$) was 1.00 in benzene. A similar experiment with isophorone and triphenylamine in which the sensitizer absorbed 79% of the light gave $\phi_{\text{sens}}/\phi_0 = 0.88$.[11]

Quenching studies leave no doubt that the photocycloaddition processes responsible for the formation of oxetane and *cis* and *trans* adducts involve triplet excited states. More important, Stern–Volmer plots (Figures 1 and 2) using di-*t*-butyl nitroxide lead to the dramatic conclusion that *cis* and *trans* adducts are derived from different triplet excited states.[12] Formation of *cis* adduct is quenched substantially faster than formation of *trans* adduct. Formation of oxetane is quenched with about the same efficiency as the *trans* adduct from 4,4-dimethyl-2-cyclohexenone. Oxetane may be derived from the same triplet that directly or indirectly gives *trans* adduct, since the quenching lines (Figure 1) are within experimental error. The nature of the two chemically distinct triplets which lead respectively to *cis* and *trans* adducts cannot be inferred from the available data. They may differ in electronic configuration, geometry, structure, or some combination of these features. The nature of the observed quenching suggests the two triplets have a common excited-state precursor and are not formed sequentially.

The preferential quenching of the triplet which gives rise to *cis* adduct and the solvent effect can be put to use in synthesis. High quencher concentrations in benzene lead to a high yield of *trans* adduct. In hexane solution oxetane becomes the major product. Equilibration of mixtures of *cis* and *trans* adducts gives only *cis* adduct. Any one of the three photoadducts can be thus obtained.

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[10] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).

[11] Triphenylene gave similar results. Thioxanthone sensitized the reaction but to a lesser extent than triphenylene and triphenylamine.

[12] The *cis* and *trans* adducts formed by photoaddition of 2-cyclohexenone to 1,1-dimethoxyethylene[2] show similar differential quenching.

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