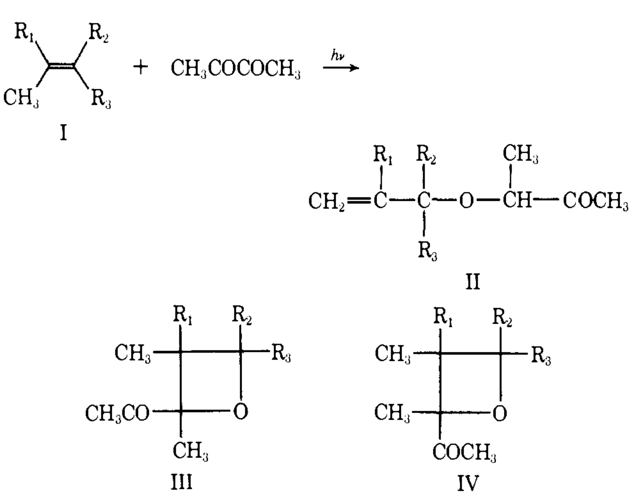
A Novel Photochemical Reaction of Biacetyl with Methyl-Substituted Olefins *via* the Biradical Intermediate

Sir:

In a previous communication[1] we have reported that the photoreaction of biacetyl with 2-methyl-2-butene (Ic) affords 1-acetoethyl 1,2-dimethylallyl ether (IIc), whose formation has never been reported for the photoreaction of monoketones or *o*-quinones with olefins. This novel reaction encouraged us to study the photoaddition of biacetyl to various methyl-substituted olefins such as α-methylstyrene (Ia), 2-ethoxypropene (Ib), and tetramethylethylene (Id).

Irradiations filtered through an *n*-hexane solution of naphthalene were carried out in benzene with a 350-W high-pressure mercury lamp under nitrogen atmosphere at room temperature. Major products were 1:1 adducts for these olefins. The various products were isolated by distillation and preparative vapor phase chromatography and their structures were determined by ir, nmr, and mass spectra, and elemental analysis.



a, $R_1 = C_6H_5$; $R_2 = R_3 = H$
b, $R_1 = OC_2H_5$; $R_2 = R_3 = H$
c, $R_1 = R_2 = CH_3$; $R_3 = H$
d, $R_1 = R_2 = R_3 = CH_3$

The reaction with Ia or Ib gave both allylic ethers and oxetanes, whereas no detectable amount of oxetanes was obtained for Id. The yields of the products are shown in Table I.

Table I. Product Yields in the Photoreaction of Biacetyl with Methyl-Substituted Olefins

Olefin	Product yield, %[a] II	III	IV	Ratio (III + IV)/II
Ia	27	41	7	1.8
Ib	27	36	21	2.1
Ic	54	21[b]		0.4
Id	70			0

[a] Based on biacetyl consumed. [b] An isomer of oxetanes alone has been observed.

The formation of II is very interesting in comparison with the results of monoketones or *o*-quinones, for which no compounds of this type have ever been reported. Photostability studies[2] and constant product ratios during the photolysis[3] have shown that the adducts are the primary photochemical products.

It is well known that α-diketones undergo primary photochemical addition to olefins to form 1,4 cycloadducts[4] in competition with hydrogen abstraction,[5] α cleavage,[6] and enol formation.[7] This information suggests that II is obtained through either path A—an attack of the excited carbonyl oxygen of biacetyl on the olefins to form the biradical intermediate, followed by an intramolecular disproportionation—or path B—an initial hydrogen abstraction from the olefins by the excited carbonyl oxygen of biacetyl, followed by the combination of the two radicals formed.[8] Though the small yields of pinacol[9] (<3%) produced in our case suggest that II is probably obtained through path A rather than path B, there is no direct evidence for our assumption. A similar mechanism is discussed for the photoreaction of 2-cyclohexenone with isobutene[10] and that of chromone with tetramethylethylene,[11] but again exact mechanisms for these reactions have not been determined.

In order to determine the mechanism for the formation of II, the photoreaction of biacetyl with α-methylstyrene-d_3 (Ia′) has been investigated. Ia′ was prepared by Wittig reaction of trideuteriomethyl phenyl ketone with methyltriphenylphosphonium bromide.[12] Irradiation and isolation of products have been done by the same procedure as for Ia. No deuterium was introduced into position C_α of the allyl moiety in IIa′.[13]

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[1] H-S. Ryang, K. Shima, and H. Sakurai, *Tetrahedron Lett.*, 1091 1970).

[2] Adducts IIa, IIIa, and IVa were individually irradiated under the reaction conditions. Each adduct was recovered unchanged.

[3] The yields of IIa, IIIa, and IVa were proportional to the irradiation time with the same ratio as in Table I.

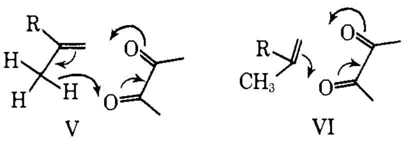
[4] G. P. Fundt and G. O. Schenck in "1,4-Cycloadditions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 345.

[5] (a) W. H. Urry, D. J. Trecker, and D. Winey, *Tetrahedron Lett.*, 609 (1962); (b) W. H. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, **84**, 118 (1962); (c) W. H. Bentrude and D. R. Darnall, *Chem. Commun.*, 810 (1968); (d) P. W. Jolly and P. De Mayo, *Can. J. Chem.*, **42**, 170 (1964); (e) N. J. Turro and T-J. Lee, *J. Amer. Chem. Soc.*, **91**, 5651 (1969); (f) N. J. Turro and R. Engel, *Mol. Photochem.*, **1**, 143 (1969); (g) T. L. Burkoth and E. F. Ullman, *Tetrahedron Lett.*, 145 (1969); (h) S. P. Pappas, J. F. Alexander, and R. D. Zehr, Jr., *J. Amer. Chem. Soc.*, **92**, 6927 (1970).

[6] (a) H. A. Staab and J. Ipaktchi, *Angew. Chem.*, **78**, 308 (1966); (b) H. A. Staab and J. Ipaktchi, *Chem. Ber.*, **101**, 1457 (1968).

[7] (a) J. Lemaire, *J. Phys. Chem.*, 71, 2653 (1967); (b) J. Lemaire, M. Niclause, X. Deglise, J. C. Andre, G. Penson, and M. Bouchy, *C. R. Acad. Sci., Ser. C*, **267**, 33 (1968); (c) R. J. Zepp and P. J. Wagner, *J. Amer. Chem. Soc.*, **92**, 7466 (1970); (d) N. J. Turro and T-J. Lee, *ibid.*, **92**, 7467 (1970). Enol formation of biacetyl at 4358 Å is essentially zero.[6a]

[8] A concerted mechanism *via* eight-membered transition state V also might be considered. But this mechanism would be unfavorable for the following reasons. (a) Biacetyl has its carbonyl groups in the trans configuration in its ground and probably excited states.[5b,6a] (b) In our case no detectable amount of 1,4 cycloadducts was obtained. If such a concerted mechanism is favorable, 1,4 cycloadducts would be given *via* six-membered transition state VI in preference to the formation of II.



V VI

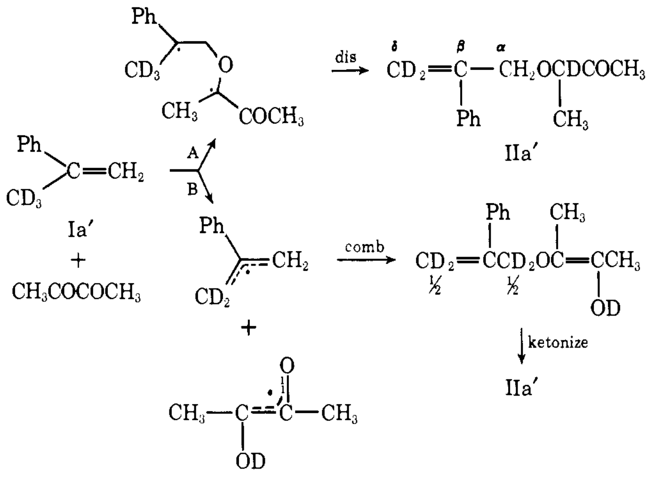
[9] Jolly and De Mayo have reported that the photoreduction of biacetyl in cyclohexene affords the corresponding pinacol as main products.[5d]

[10] E. J. Corey, J. D. Bass, R. LeMahiew, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

[11] J. W. Hanifin and E. Cohen, *ibid.*, **91**, 4494 (1969).

[12] H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **86**, 677 (1967).

[13] Deuterium contents were determined by nmr. The oxetanes

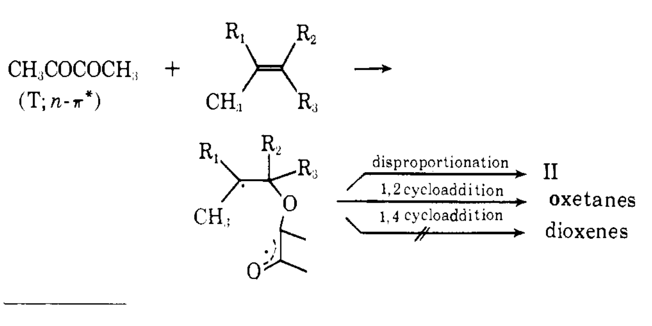


This result demonstrates that II is produced through path **A**, since path **B** would introduce deuterium equally into positions C_α and C_δ. With regard to the photoreactions of carbonyl compounds with olefins, this is conclusive evidence in support of a biradical intermediate.

In order to identify the excited state of biacetyl which is involved in these reactions, the emission of biacetyl (0.05 *M*) in the presence of Id (1.0 *M*) was examined in degassed benzene at room temperature. The phosphorescence of biacetyl was completely quenched but the fluorescence was unaffected,[14] which indicates that the reactions are derived from the n–π^* triplet of biacetyl.

In the most reasonable mechanism which satisfies the above results, attack of the carbonyl oxygen of excited biacetyl (T; n–π^*) on olefins produces a biradical intermediate which either cyclizes to form oxetanes or disproportionates intramolecularly to give II. Table I shows that the ratio of cyclization to disproportionation varies with the type of olefin. Though further evidence might be necessary to explain these phenomena clearly, the decrease in cyclization for Ic and Id may be caused by steric hindrance,[15] mainly 1,3-diaxial interactions which have been reported to decrease the formation of cyclobutanes from the biradical intermediate formed upon δ-hydrogen abstraction by the carbonyl excited state.[16]

The occurrence of II and the absence of 1,4 cycloadducts (dioxenes)[4] in these reactions indicate unambiguously that the photochemical behavior of biacetyl toward olefins is different from that of monoketones or *o*-quinones such as phenanthrenequinones. Further studies will resolve these problems. The generality of this reaction and the nature of the biradical intermediate are under current investigation.



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and the recovered olefin were deuterated the same per cent as the starting olefin (87% D), and no scrambling occurred in them.

[14] The emission of biacetyl in the presence of olefin was compared with that in the absence of it taken under similar conditions.

[15] It is well known that the free energy of activation for cyclization is governed mainly by a strain factor and by the probability of the two active centers meeting each other: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 198.

[16] F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970).

Monodehydro[26]annulene. The Demonstration of a Diamagnetic Ring Current in a 26-Membered Macrocycle[1]

Sir:

The question of the exact limit for aromaticity in $[4n + 2]$annulenes is an interesting one. It has been calculated that the limit lies between the 22- and the 26-membered rings.[2] In agreement with this is the finding that [22]annulene[3] and monodehydro[22]-annulene[4] show a diamagnetic ring current in the nmr spectra, but tridehydro[26]annulene[5] (the only previously known [26]annulene derivative) shows no ring current.

Of course, the possibility existed that the lack of a diamagnetic ring current in tridehydro[26]annulene is due to the perturbation of the three acetylenic linkages, which causes the nondelocalized alternate bond structure to be energetically preferred to the delocalized system. This perturbation is likely to become of importance in rings of this size, since the difference in energy between the two forms is predicted to be small.[2] In order to test this possibility, it was desirable to synthesize [26]annulene itself, or a dehydro[26]annulene containing fewer acetylenes than the tridehydro compound. We have now succeeded in synthesizing monodehydro[26]annulenes (*e.g.*, **5**), containing only one acetylenic bond. This substance was indeed found to possess a diamagnetic ring current, and it is, therefore, presumably aromatic. This is the largest macrocycle for which a ring current has been observed,[6,7] and the limit for aromaticity in $[4n + 2]$-annulenes appears to lie above the 26-membered ring.

Reaction of *trans,trans*-1,6-dibromo-2,4-hexadiene (**1**)[4] with an excess of ethynylmagnesium bromide[8] in tetrahydrofuran in the presence of cuprous chloride[9]

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[1] Unsaturated Macrocyclic Compounds. LXXXV. For part LXXXIV, see P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *Chem. Commun.*, 947 (1971).

[2] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965). See also H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc., Ser. A*, **251**, 172 (1959); **257**, 445 (1960); C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962).

[3] R. M. McQuilkin, B. W. Metcalf, and F. Sondheimer, *Chem. Commun.*, 338 (1971).

[4] R. M. McQuilkin and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 6341 (1970).

[5] C. C. Leznoff and F. Sondheimer, *ibid.*, **89**, 4247 (1967).

[6] See R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 105 (1971).

[7] Evidence for a diamagnetic ring current in the dianion of 1,3,7,9,-13,15,19,21-octadehydro[24]annulene, a 26-π-electron system, has been obtained previously (R. M. McQuilkin, P. J. Garratt, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 6682 (1970)).

[8] E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); *Org. Syn.*, **39**, 56 (1959).

[9] See J. P. Danehy, D. B. Killian, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **58**, 611 (1936).