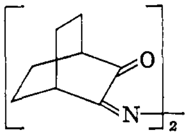
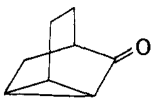
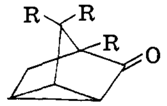
244 (molecular ion), 216, 188, and 122 (base peak, M/2). The occurrence of the M/2 peak as the base peak has recently been shown to be characteristic of the mass spectra of ketene dimers; it presumably arises by cleavage to the monomer.[11] The mass spectrum of V is also analogous to the spectra of ketene dimers[11] in showing peaks at M − 28 and M − 56. Irradiation[12] of V in aqueous tetrahydrofuran gave bicyclo[2.2.1]heptane-7-carboxylic acid[13] (VII; 53%), mp 75–76.5° (lit.[13,14] mp 77.5–78.5°, 76–77°), identified by infrared spectral comparison.[15] Irradiation[12] of the diazo ketone I in aqueous tetrahydrofuran containing sodium bicarbonate[16] also gave VII (82%), mp and mmp 76–77°. The spectroscopic data for V and its photochemical conversion to VII, which finds analogy in the case of other ketene dimers,[17] make the structural assignment secure. In addition, we find that irradiation of I in benzene also leads to the formation of V (62%),[18] mp and mmp 224.5–226°.



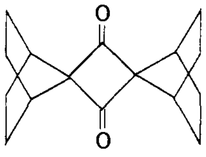
III



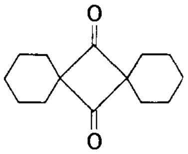
IV



X, R = CH_3
XI, R = H



V



VI

The Wolff rearrangement of α-diazo ketones in hydroxylic solvents under the influence of ultraviolet radiation is well known,[19] although the demonstration of the formation in inert medium of a ketene dimer appears to be novel. However, the catalysis of the Wolff rearrangement of I by copper is extraordinary,[20] particularly in relation to the behavior of 3-diazocamphor (VIII) and 3-diazonorcamphor (IX). It has long been known that VIII gives high yields of cyclocamphanone (X) on treatment with copper,[21] and we have now found that decomposition of a 0.1% solution of IX in benzene with coppper gives nortricyclanone (XI; 60%),[22] identified by comparison with an authentic sample.[23] Thus in the cases of the diazo ketones VIII and IX the major reaction product is the tricyclic compound, which can be considered to arise by an intramolecular insertion reaction of a keto carbene formed by loss of nitrogen from the diazo ketone; as in almost all other cases of copper catalysis[2] no Wolff rearrangement products were detected. In the case of I, the corresponding insertion product, IV, is formed in only 5% yield, while bimolecular reaction (formation of III) and Wolff rearrangement take precedence. We interpret the difference in behavior between the diazo ketones in the [2.2.2] and [2.2.1] series in terms of geometrical factors which favor the insertion reaction in the latter case because of the closer approach of the diazo carbon to the C–H bond into which insertion occurs. More generally, we suggest that a keto carbene or its copper complex formed by copper-catalyzed loss of nitrogen from an α-diazo ketone can undergo the Wolff rearrangement, but normally does not because of successful competition by intermolecular or other intramolecular reaction modes.[24]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for support of this research.

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[11] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *J. Am. Chem. Soc.*, **87**, 4097 (1965).

[12] All irradiations were carried out in Pyrex vessels with a Rayonet photochemical reactor.

[13] H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4072 (1954).

[14] R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 1685 (1964).

[15] We thank Professor H. Kwart, University of Delaware, for providing us with the infrared spectrum of this compound.

[16] Sodium bicarbonate was added because of the sensitivity of I to traces of acid.

[17] N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Am. Chem. Soc.*, **87**, 2613 (1965).

[18] The conditions for this reaction were not optimized; in a small-scale run carried out in a sealed tube the yield was almost quantitative.

[19] *Cf.*, for example, J. Meinwald and E. G. Miller, *Tetrahedron Letters*, 253 (1961); L. Horner, D. W. Baston, W. Dürckheimer, and H. G. Schmelzer, *Chem. Ber.*, **98**, 1252 (1965).

[20] In the absence of copper, the thermal decomposition of I in benzene gives only III.

[21] P. Yates and S. Danishefsky, *J. Am. Chem. Soc.*, **84**, 879 (1962); although X has been subsequently obtained as the major product, it has not been possible to reproduce the very high yields previously reported, perhaps because of the difference in the copper samples used as catalysts.

[22] This represents a minimum yield since the high volatility of XI leads inevitably to losses in its isolation.

[23] We thank Mr. L. Kilmurry for providing this sample.

[24] A recent observation[4] lends strength to this view; decomposition of 2-diazoacetophenone by copper in acetonitrile in the presence of restricted amounts of methanol gives methyl phenylacetate, the Wolff rearrangement product, as the major product. However, in methanol alone, where competition between Wolff rearrangement and attack by methanol on a keto carbenoid intermediate may be expected to be resolved in favor of the latter, it gives 2-methoxyacetophenone[25] as the major product.

[25] P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).

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An Oxacarbene as an Intermediate in the Photolysis of Cyclocamphanone

Sir:

We recently reported[1] a novel photochemical reaction in which *d*-cyclocamphanone (I) on irradiation in alcohols gives ring-expanded products of type II.[2] It was suggested at that time[1] that the reaction proceeds *via* cleavage of the 1–2 C–C bond followed by bond formation between C-1 and the oxygen atom of the carbonyl group, *i.e.*, *via* an intermediate species III. We now report evidence which relates to this proposal.

Irradiation of a 1% solution of I in dry cyclohexene with a 450-w Hanovia high-pressure lamp and fractionation of the product mixture by chromatography on Florisil followed by molecular distillation gave a colorless oil in low yield, which after repeated redis-

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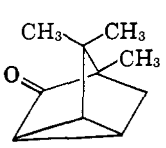
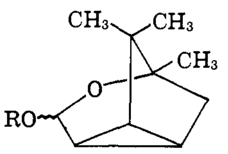
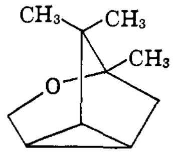
[1] P. Yates and L. Kilmurry, *Tetrahedron Letters*, 1739 (1964).

[2] An analogous reaction in the case of 7,7-dimethylbicyclo[3.2.0]hept-2-en-6-one has been reported subsequently by H. U. Hostettler, *Tetrahedron Letters*, 687 (1965); *cf.* also A. G. Brook and J. B. Pierce, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p 12P.

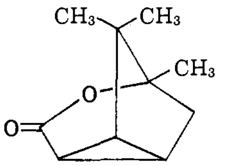

I

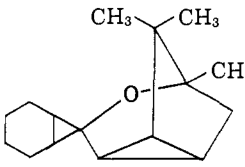

II

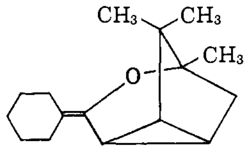

III

tillation yielded a crystalline solid, $C_{16}H_{24}O$, mp 37–39° (sealed capillary). *Anal.* Found: C, 82.43; H, 10.34; mol wt, 232 (mass spectrum).[3] This product, whose molecular formula showed it to be an adduct of I and cyclohexene, had bands in its infrared spectrum at 3.26 (sh), 3.38, 9.00, and 9.16 μ, but no bands in the hydroxyl stretching region or in the carbonyl or ethylenic double bond stretching regions. The oil, whose infrared spectrum was identical with that of the crystalline solid, showed in its nmr spectrum a complex group of signals with δ 0.25–2.0 ppm, superimposed upon which were three sharp singlets at δ 0.87, 0.97, and 1.06 ppm; there were no signals with $\delta > 2.00$ ppm. The ultraviolet spectrum of the crystalline solid had no maximum in the region 214.5–350 mμ; it showed end absorption with $\epsilon_{214.5}$ 290. Oxidation of the adduct with sodium dichromate and sulfuric acid gave the lactone IV[1,4,5] (22%) and adipic acid (14%).

These data require the assignment of structure V to the adduct. The closely related, alternative structure VI is excluded on the basis of the spectroscopic data, for, while the infrared spectrum of the adduct shows no band in the C=C stretching region, enol ethers are known to give rise to unusually strong C=C stretching bands.[6] Further, the end absorption in the ultraviolet spectrum of the adduct at 214.5 mμ is less than one-tenth of that reported for simple enol ethers.[7]


IV


V


VI

The formation of V is best interpreted as involving the formation of the carbene III followed by its addition to the double bond of cyclohexene[8] and lends strong support to the postulated intermediacy of this carbene in the formation of products of type II when I is irradiated in alcohols.[9]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for support of this research.

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[3] We thank Professor D. B. MacLean and Dr. A. F. A. Wallis, McMaster University, for this spectrum.

[4] Due to miscalibration, the nmr signals previously reported for this compound are in error; we now find a complex group of signals at δ (CCl_4) 1.5–2.3 ppm with three sharp signals at 0.93, 0.98, and 1.20 ppm.

[5] This compound has recently been obtained also by H. E. Conrad, J. Hedegaard, I. C. Gunsalus, E. J. Corey, and H. Uda, *Tetrahedron Letters*, 561 (1965).

[6] G. D. Meakins, *J. Chem. Soc.*, 4170 (1953).

[7] G. Eglinton, E. R. H. Jones, and M. C. Whiting, *ibid.*, 2873 (1952).

[8] *Cf.* W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 207.

[9] NOTE ADDED IN PROOF. Since the submission of this paper, two reports have appeared in which it is postulated that the photolysis of benzocyclobutene-1,2-dione involves formation of a carbenoid intermediate analogous to that proposed by ourselves: R. F. C. Brown and R. K. Solly, *Tetrahedron Letters*, 169 (1966); H. A. Staab and J. Ipaktschi, *ibid.*, 583 (1966). The latter workers have also succeeded in trapping this intermediate.

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On Molecular Orbital Correlation Diagrams, the Occurrence of Möbius Systems in Cyclization Reactions, and Factors Controlling Ground- and Excited-State Reactions. I

Sir:

Recently Woodward and Hoffmann[1] and Longuet-Higgins and Abrahamson[2] have presented some intriguing discussion of literature and theory. In three of these papers[1c,e,2] correlation diagrams[3] were used, while in two others[1a,b] the bonding or antibonding tendency of the highest occupied MO was considered as controlling reactions. These approaches are limited to symmetrical systems and require knowledge of the symmetry and energy of the reactant and product MO's.

The present papers (i) present another approach for symmetrical cyclic systems, (ii) suggest a method applicable to nonsymmetrical as well as symmetrical reacting systems, (iii) offer an interpretation relevant to photochemistry, and (iv) note the limitations of using only the highest occupied MO and comment on the bond-order criterion used earlier by the author.[4,5]

Some time ago Heilbronner[6] presented the fascinating idea that large-ring polyenes might be twisted once to give Möbius systems. He observed that a single sign inversion between a pair of adjacent p orbitals is characteristic of such Möbius systems and presented a formula for the MO energies.

In the case of Hückel cyclic systems, Frost and Musulin[7] have put forth the simple circle mnemonic (*cf.* Figure 1a) which gives the MO energies. Here the appropriate polygon is inscribed with one vertex down in a circle of radius 2β,[8] centered at zero (energy of an

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[1] (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965); (b) *ibid.*, 87, 2511 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, 87, 2046 (1965); (d) *ibid.*, 87, 4388 (1965); (e) *ibid.*, 87, 4389 (1965).

[2] H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2046 (1965).

[3] *Cf.*, e.g., C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp 93, 100–101.

[4] H. E. Zimmerman, Abstracts, 17th National Organic Symposium, Bloomington, Indiana, June 1961, p 31.

[5] (a) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964); (b) H. E. Zimmerman, *Pure Appl. Chem.*, 493 (1964).

[6] E. Heilbronner, *Tetrahedron Letters*, 1923 (1964).

[7] A. Frost and B. Musulin, *J. Chem. Phys.*, **21**, 572 (1953).

[8] The circle radii will be 2β only if the overlap between adjacent orbitals is ethylenic. In Figures 1a and 1b it is approximated that all