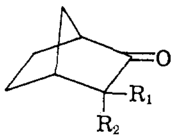
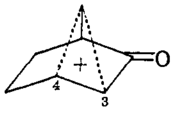
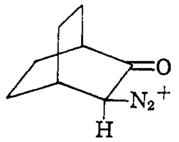
with bond migration and loss of nitrogen could also account for the formation of III from VIII. It seems unlikely that the *exo*-diazonium ion X is formed to any appreciable extent since no significant amounts of nortricyclanone or *exo*-2-hydroxy-7-norbornanone could be detected among the products.[11] Although rearrangement of the bicyclo[2.2.1]heptane system to the bicyclo[3.1.1]heptane system has been postulated previously as an intermediate step in certain cationic processes,[13] the isolation of III represents the first example of the isolation of such a rearrangement product. The well-known reverse process is normally favored because of relief of strain in the bicyclo[3.1.1]heptane system.[14] In the present case the increase in strain energy resulting from the delocalization of the electrons of the C-4–C-7 bond as in IX is compensated by reduction of unfavorable electrostatic interaction.



VIII, $R_1 = H$, $R_2 = N_2^+$
X, $R_1 = N_2^+$, $R_2 = H$



IX



XI

Similar acid-catalyzed decomposition of 3-diazobicyclo[2.2.2]octan-2-one[15] has been shown to give 4-cycloheptenecarboxylic acid (31%),[16] tricyclo-[2.2.2.0^{2,6}]octan-3-one (16%),[17,18] *exo*-2-hydroxybicyclo-[3.2.1]octan-8-one (34%),[18a,19] and bicyclo[3.2.1]oct-2-en-8-one.[20,21] These are considered to be formed *via* XI, the sole diazonium ion derivable from this diazo ketone by protonation on carbon.[22]

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Peter Yates, Robert J. Crawford
Lash Miller Chemical Laboratories
University of Toronto, Toronto, Canada
Received December 23, 1965

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[11] Products analogous to these have been obtained by the acid-catalyzed decomposition of 3-diazocamphor, together with products derived by cleavage of the C-4–C-7 bond;[12] this difference can be interpreted in terms of steric and electronic effects engendered by the C-7 methyl groups.

[12] O. E. Edwards and M. Lesage, *Can. J. Chem.*, **41**, 1592 (1963); J. C. Crano, W. P. Wetter, and R. L. Litle, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 30.

[13] W. Hückel and U. Ströle, *Ann.*, **585**, 182 (1954); W. Hückel and H. Wolowski, *Ber.*, **80**, 39 (1947); D. S. Noyce, *J. Am. Chem. Soc.*, **72**, 924 (1950); S. G. Levine, *ibid.*, **82**, 2556 (1960); R. P. Lutz and J. D. Roberts, *ibid.*, **84**, 3715 (1962).

[14] P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964).

[15] P. Yates and R. J. Crawford, *ibid.*, **88**, 1562 (1966).

[16] G. Stork and H. Landesman, *ibid.*, **78**, 5129 (1956).

[17] (a) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963); (b) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

[18] (a) We thank Professor N. A. LeBel, Wayne State University, for providing us with the infrared spectrum of this compound. (b) We thank Mr. L. Kilmurry for providing a sample, prepared by the method of ref 17b.

[19] N. A. LeBel and L. A. Spurlock, *J. Org. Chem.*, **29**, 1337 (1964).

[20] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964); N. A. LeBel and L. A. Spurlock, *ibid.*, **20**, 215 (1964).

[21] This product was isolated only by vpc of the product mixture; it constituted 6% of the total eluate.

[22] NOTE ADDED IN PROOF. Since the submission of this paper, another report on the acid-catalyzed decomposition of 3-diazonorcamphor has appeared: M. Hanack and J. Dolde, *Tetrahedron Letters*, 321 (1966). The conditions used were different from those in the present work, and although the formation of I and II together with other products is reported, the formation of III was not observed.

Decomposition of 3-Diazobicyclo[2.2.2]octan-2-one. A Copper-Catalyzed Wolff Rearrangement

Sir:

Yates and Fugger[1] have reported that cuprous iodide in methanol–acetonitrile catalyzes the Wolff rearrangement of 2-diazoacetophenone. As has been emphasized recently,[2] this observation is highly unusual in that copper catalysts, unlike silver and platinum catalysts, normally convert α-diazo ketones to unrearranged products.[3] We report now a Wolff rearrangement which is catalyzed by copper metal.

3-Diazobicyclo[2.2.2]octan-2-one (I), mp 71–72° (*Anal.* Found: C, 63.85; H, 6.69; N, 18.89), λ_{max} (CCl_4) 4.79, 6.02, and 7.31 μ, δ (CCl_4) 1.80 (8 H), 2.37 (1 H), and 3.02 (1 H) ppm, was prepared[5] by the action of aqueous NaOH on bicyclo[2.2.2]octane-2,3-dione monotosylhydrazone, mp 133–134° (*Anal.* Found: C, 58.83; H, 6.06; N, 9.24; S, 10.43), itself obtained from bicyclo[2.2.2]octane-2,3-dione (II).[6] A solution of the diazo ketone (0.51 g) in anhydrous benzene (1 l.) was stirred with copper powder[7] (11 g) under nitrogen at reflux for 21 hr, by which time all of the diazo ketone had been consumed. The products obtained were the azine III (28%), the tricyclic ketone IV (5%), and the ketene dimer V (46%).

The azine III, mp 247–248° dec, was identified by comparison with an authentic sample, prepared by treatment of II with hydrazine: λ_{max} ($CHCl_3$) 5.81, 6.19, and 6.26 (sh) μ, δ ($CDCl_3$) 1.87 (16 H), 2.62 (2 H), and 3.00 (2 H) ppm (*Anal.* Found: C, 70.55; H, 7.46; N, 10.05). The ketone IV[2,8] was identified by spectral and R_f comparison with an authentic sample.[9]

Compound V, mp 225.5–226.5° (*Anal.* Found: C, 78.63; H, 8.50), had λ_{max} (CCl_4) 5.78, 5.80 (sh), and 5.86 (w) μ, λ_{max} (EtOH) 232 (ϵ 336), 287 (ϵ 39), 301 (ϵ 66), 309 (ϵ 32), and 345 (ϵ 20) mμ, δ ($CDCl_3$) 1.1–2.3 (16 H) and 2.68 (4 H) ppm. These data may be compared with those for the ketene dimer VI:[10] λ_{max} (CCl_4) 5.76 and 5.89 (w) μ, λ_{max} (EtOH) 233 (ϵ 194), 288 (ϵ 25), 301 (ϵ 39), 311 (ϵ 32), and 341 (ϵ 20) mμ. The mass spectrum of V included peaks with m/e

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[1] P. Yates and J. Fugger, *Chem. Ind.* (London), 1511 (1957).

[2] W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, 21, 25 (1965).

[3] Subsequent investigation[4] has shown that the Wolff rearrangement of α-diazo ketones of type $RCOCHN_2$ by cuprous iodide in methanol–acetonitrile is general.

[4] P. Yates and F. X. Garneau, unpublished results.

[5] *Cf.* M. P. Cava, R. L. Litle, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

[6] K. Alder, H. K. Schäfer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

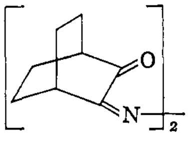
[7] Fisher electrolytic copper dust, washed with ether and pentane and vacuum dried, was used.

[8] N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).

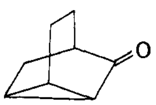
[9] We thank Professor N. A. LeBel, Wayne State University, for providing us with the infrared spectrum of this compound, and Mr. L. Kilmurry for providing a sample, prepared by the method in ref 2.

[10] H. M. Walborsky and E. R. Buchman, *J. Am. Chem. Soc.*, **75**, 6339 (1953); we thank Mr. A. G. Fallis for providing a sample of this compound.

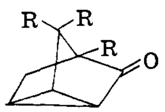
244 (molecular ion), 216, 188, and 122 (base peak, M/2). The occurrence of the M/2 peak as the base peak has recently been shown to be characteristic of the mass spectra of ketene dimers; it presumably arises by cleavage to the monomer.[11] The mass spectrum of V is also analogous to the spectra of ketene 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°.



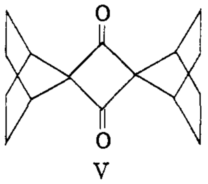
III



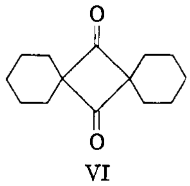
IV



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).

Peter Yates, Robert J. Crawford
Lash Miller Chemical Laboratories
University of Toronto, Toronto, Canada

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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.