ethoxide ion. This is in qualitative agreement with recently reported measurements of hydrogen bond energies to Cl^- ions.[10]

A wide variety of negative cluster ions can be generated in the pulsed icr spectrometer. In favorable cases it may be possible to measure the free energy of dissociation for cluster ions containing more than one solvent molecule. By measuring the thermodynamics for sequential solvation of ions in the gas phase, the process of ion solvation can be studied at its most fundamental level.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Conselho Nacional de Pesquisas of Brazil for support of this research.

(10) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **93**, 7139 (1971).

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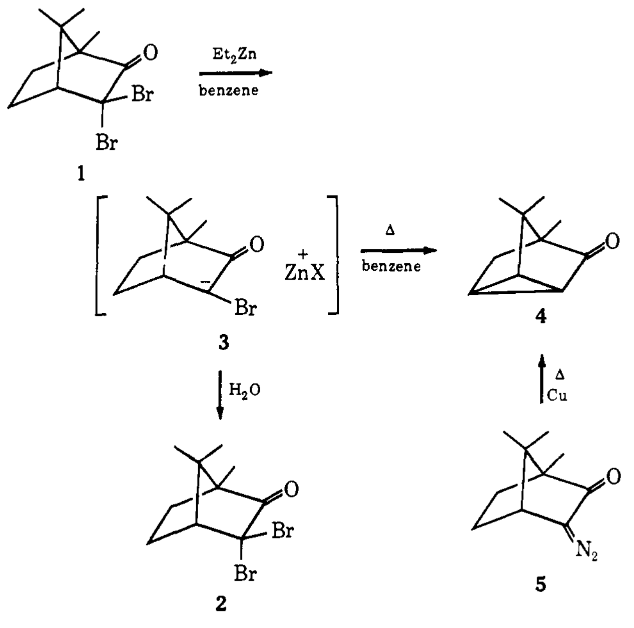
Ketocarbenoids by α Elimination. Intramolecular Trapping by Carbon–Hydrogen Insertion

Sir:

Although α-elimination reactions provide the best route to most classes of carbenes and carbenoids, the decomposition of diazo ketones has stood for over half a century as the sole source of *keto*carbenes.[1] The lack of synthetically useful alternatives to this frequently unsatisfactory diazo route, together with the mechanistic mysteries surrounding the metal-catalyzed decomposition of diazo ketones, has sparked substantial recent activity in this area of carbene chemistry.[2,3] We should now like to report the first example of a ketocarbenoid generated by α elimination in high yield and the efficient trapping of this intermediate by intramolecular C–H insertion.

Treatment of α,α-dibromocamphor (**1**)[4] with 1 molar equiv of diethylzinc in anhydrous benzene causes a rapid disappearance of starting material. Quenching the reaction mixture with water at this stage gives *endo*-α-bromocamphor (**2**) quantitatively,[5] suggesting the initial formation of bromoenolate **3** (see Scheme I). If the reaction mixture is refluxed for 22 hr before quenching, however, tricyclic ketone **4** is produced in 80% yield,[6,8] while the yield of **2** drops to 10%. Longer reaction times give slightly more **4** at the expense of **2**. When considered with respect to Bredt's preparation of the same tricyclic ketone[9] by C–H insertion of the ketocarbene derived in the classical way from diazo ketone **5**, our results argue convincingly for the intermediacy of a ketocarbenoid[10] in this α elimination.

Scheme I



The use of only 0.5 molar equiv of diethylzinc in the above reaction changes the product distribution very little (60% **4**:11% **2**:5% **1**). Evidently the α elimination does not require an ethyl group as ligand X in intermediate **3**. The formation of tricyclic ketone **4** from dibromocamphor (**1**) in *ca.* 35% yield by the action of either zinc dust or zinc–copper couple[11] in hot dimethylformamide supports this conclusion, although both reactions fail in benzene or ether solvents.

In accord with the α elimination of Br_2 adjacent to a ketone, the corresponding α elimination of HBr likewise yields a ketocarbenoid (Scheme II). Thus, the relatively slow reaction between diethylzinc and *endo*-α-bromocamphor (**2**) in refluxing benzene furnishes **2**, **4**, and **7** in comparable amounts after 48 hr. Production of the tricyclic ketone **4** again implicates most likely the bromoenolate **3**, formed in this instance by deprotonation of the starting material. Competitive removal of the bromine from **2** by diethylzinc undoubtedly accounts for the camphor **7** found in this reaction, whereas the bromocamphor **2** may either

(1) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(2) H. O. House, W. F. Fischer, Jr., M. Gall, T. E. McLaughlin, and N. P. Peet, *J. Org. Chem.*, **36**, 3429 (1971).

(3) B. W. Peace and D. S. Wulfman, *Tetrahedron Lett.*, 3799 (1971); B. W. Peace and D. S. Wulfman, *Chem. Commun.*, 1179 (1971); D. S. Wulfman, B. W. Peace, and E. K. Steffen, *ibid.*, 1360 (1971); B. W. Peace, F. Carman, and D. S. Wulfman, *Synthesis*, 658 (1971); D. S. Wulfman and B. W. Peace, *Tetrahedron Lett.*, 3903 (1972).

(4) Dibromocamphor was prepared from *d*-camphor by a modification of the procedure of B. Shive, W. W. Crouch, and H. L. Lochte, *J. Amer. Chem. Soc.*, **63**, 2979 (1941).

(5) Identified by comparison with an authentic sample.

(6) The combustion analysis, ir, nmr, and mass spectral properties of this compound are all consistent with the structure assigned; mp 165–166° (lit.[7] 168–170°); oxime mp 127–129° (lit.[7] 132°).

(7) J. R. A. Pollock and R. Stevens, Ed., "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965, p 3190.

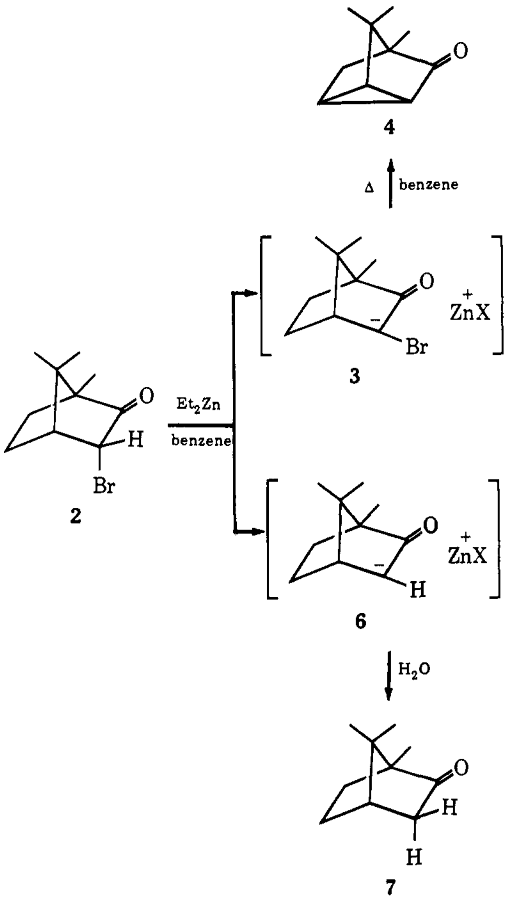
(8) Yields based on dibromocamphor were determined by vpc, using α-methylnaphthalene as internal standard, and have been corrected by the detector response factor for each compound.

(9) The correct structure for tricyclic ketone **4** was first assigned by J. Bredt and W. Holz, *J. Prakt. Chem.*, **95** (2), 133 (1917), although the compound had been prepared previously by R. Schiff, *Chem. Ber.*, **14**, 1375 (1881). See also P. Yates and S. Danishefsky, *J. Amer. Chem. Soc.*, **84**, 879 (1962), for a more recent examination of diazocamphor (**5**) and related diazo ketones.

(10) We support the commonly accepted definition of "carbenoid" found on p 6 in ref 1. The ketocarbenoids (metal-complexed carbenes) formed by copper-catalyzed decomposition of diazo ketones and by our α eliminations are clearly distinct from the "free" ketocarbenes generated by diazo ketone photolysis, for only the latter suffer Wolff rearrangement.[1]

(11) The zinc–copper couple was prepared by the method of E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

Scheme II



come from **3** or simply represent virgin starting material.

It is for good reasons that the α-elimination route to ketocarbenoids remained unknown for so many years. Generation of the requisite α-haloenolates is often complicated by competing Favorskii rearrangement, Darzens-type condensation, or alkylation of the newly formed enolate by neutral starting material. We have overcome these difficulties with a hindered, nonenolizable dibromo ketone as the substrate and point out here that our method may be confined to systems having these characteristics. Enolates of other α-halo ketones[2] and α-halo esters[12,13] have also been prepared recently by different methods.

The final expulsion of halide represents a more serious problem with this route to ketocarbenoids, for α-haloenolates, once formed, exhibit a relatively high degree of stability.[2,12] No doubt the carbonyl group diminishes greatly the electron density at the site of halogen attachment. Indeed, House has reported[2] that the lithium enolates of several α-chloro ketones survive virtually unchanged after 24 hr at room temperature in dimethoxyethane and fail to give carbenoid products; our own haloenolate **3** loses bromide only slowly at 80° with a half-life of several hours. Certainly the nature of both the halide and the metal should affect the ease of this reaction quite markedly, as with other α eliminations,[1,14] and the search for milder methods of producing carbonyl-conjugated carbenes and carbenoids in this manner continues in our laboratories.

With the feasibility of α elimination adjacent to a ketone now established, the intermolecular trapping of a ketocarbenoid so generated becomes a realistic goal. Not surprisingly, added olefins fail to intercept the camphor carbenoid which possesses an efficient internal trap. We have achieved some success in this regard, however, with another dibromo ketone and shall report on these findings shortly.

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[12] D. Seyferth, D. C. Mueller, and R. L. Lambert, Jr., *J. Amer. Chem. Soc.*, **91**, 1562 (1969).

[13] R. F. Borch, *Tetrahedron Lett.*, 3761 (1972).

[14] W. Kirmse, *Angew. Chem., Int. Ed. Engl.*, **4**, 1 (1965); G. Köbrich, *ibid.*, **6**, 41 (1967); G. Köbrich, *20 [Zwanzig] Jahre Fonds Chem. Ind. Beitr. Wiss. Veranst.*, 101 (1970); G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **11**, 473 (1972).

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Reinterpretation of "Nonvertical" Triplet–Triplet Energy Transfer and the Photoisomerization of Stilbene

Sir:

The idea of "nonvertical" triplet–triplet energy transfer introduced by Hammond and Slatiel[1] is not a well substantiated concept and deserves further investigation. The mechanism which led these authors[1] to the above concept may be abstracted as follows

$$\mathrm{D^* + c \longrightarrow D + T} \qquad k_1$$
$$\mathrm{D^* + t \longrightarrow D + T} \qquad k_2$$
$$\mathrm{T \longrightarrow c} \qquad k_3$$
$$\mathrm{T \longrightarrow t} \qquad k_4$$

where D and D* are respectively the ground and the triplet states of sensitizer, c and t are respectively *cis*- and *trans*-stilbene, and T is its triplet state. Then, the photostationary ratio of isomers, expressed by

$$[\mathrm{c}]_\mathrm{s}/[\mathrm{t}]_\mathrm{s} = (k_2/k_1)(k_3/k_4)$$

reflects the "activation ratio" (k_2/k_1) which is expected to increase as the sensitizer triplet energy is lowered. Experimentally, however, as the triplet excitation energy of the sensitizer decreases below 17 kK, the activation ratio drops.[2,3] This unexpected finding was rationalized by postulating "nonvertical" and "nonspectroscopic" excitation of *cis*-stilbene to triplet state, and the term "nonvertical energy transfer" was introduced. The importance of this concept lies in the nature of the excitation of stilbene. Hammond and Saltiel stressed that *the excitation process is neither spectroscopic nor thermal.* However, it is exactly this excitation mechanism which is not easily understood

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[1] G. S. Hammond and J. Saltiel, *J. Amer. Chem. Soc.*, **85**, 2516 (1963).

[2] J. Saltiel and G. S. Hammond, *J. Amer. Chem. Soc.*, **85**, 2515 (1963).

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).