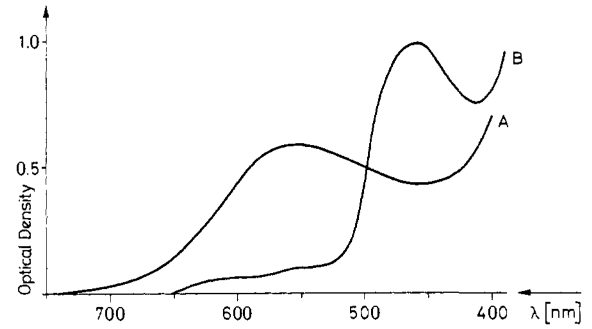
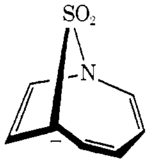


Figure 3. Visible spectra of 5^{2-} (A) and 4^{2-} (B) recorded at −80° in tetrahydrofuran solution.

sitions ($\pi^* \leftarrow n_a$ and $\pi^* \leftarrow n_s$) of low energy are expected. Also for the transition of lowest energy ($\pi^* \leftarrow n_a$) a smaller ϵ value is predicted than for the one with higher energy ($\pi^* \leftarrow n_s$) as is seen.

Significantly, the qualitative picture arising from the EH calculations denotes unequivocally that *the color observed for* 5^{2-} *is not due to any transition involving the sulfur atom of the* SO_2 *group.* Rather, the role of the sulfone function is merely to render the bridgehead positions acidic. Successive replacement of the bridgehead positions of 5^{2-} by nitrogen atoms to yield 6^- and 7 has also been considered. As anticipated from first-order perturbation theory,[18] the positions of the lone pairs on the energy scale are now lowered, while the π and π^* orbitals remain approximately constant. The calculated values for 6^- are $n_a = -10.62$ and $n_s = -12.14$ eV and for 7 $n_a = -12.53$ and $n_s = -13.87$ eV on the EH energy scale. Thus, in 7 the transitions of lower energy are predicted to be $\pi^* \leftarrow \pi$ in nature.



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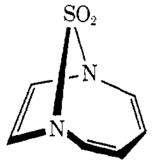

7

(18) E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendung," Vol. 1, Verlag Chemie, GmbH, Weinheim/Bergstr., 1968.

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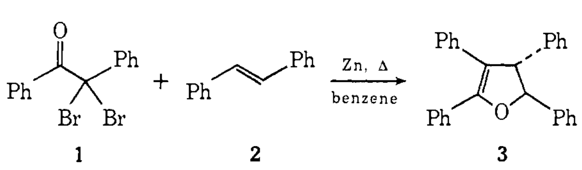
Received April 19, 1973

Ketocarbenoids by α Elimination. Intermolecular Trapping by Olefin Cycloaddition

Sir:

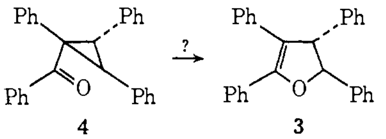
Since the classic work of Buchner and Curtius in 1885,[1] diazo esters and ketones have remained nearly the exclusive source of carbonyl-conjugated carbenes and carbenoids.[2] Recently, however, we described the first example of a ketocarbenoid generated by α elimination in high yield and the efficient trapping of that intermediate by intramolecular C–H insertion.[3] We should now like to report the successful intermolecular trapping by olefin cycloaddition of a ketocarbenoid so generated.[4]

Treatment of an equimolar mixture of α,α-dibromodesoxybenzoin (**1**)[5] and *trans*-stilbene (**2**) with excess zinc dust in refluxing benzene for 1 day gives the dihydrofuran **3** in 27% yield as the major, isolable product (eq 1). The dihydrofuran structure of this 1:1 adduct follows directly from its spectral properties[6] and from its facile conversion to tetraphenylfuran by bromination–dehydrobromination[7] (85% yield). Assignment of the trans stereochemistry rests on nmr coupling constant arguments[8] and should be considered tentative. Attempts to prepare the diastereomer of **3** from *cis*-stilbene by an identical procedure gave the same *trans*-dihydrofuran (**3**); no conclusion may be drawn about the stereospecificity of this reaction, however, since recovered stilbene was shown to be partially isomerized.



(1)

Dihydrofuran **3** represents the product of formal dipolar addition of benzoylphenylcarbene to stilbene. Although not without precedent, the trapping of ketocarbenes as 1,3 dipoles has been reported only rarely.[9] One must appreciate, however, that the observed product of such apparent dipolar additions may in fact derive from rearrangement of an initially formed cyclopropyl ketone (see eq 2). Zinc bromide, a presumed



(2)

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[1] E. Buchner and T. Curtius, *Chem. Ber.*, **18**, 2371, 2377 (1885).

[2] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971; V. Dave and E. W. Warnhoff, *Org. React.*, **18**, 217 (1970).

[3] L. T. Scott and W. D. Cotton, *J. Amer. Chem. Soc.*, **95**, 2708 (1973).

[4] The preparation of cyclopropyl ketones and esters by the reaction of *polarized* double bonds with α-haloenolates is generally regarded as a two-stage process involving Michael addition followed by SN2 cyclization, *e.g.*, F. Gaudemar-Bardone and M. Gaudemar, *C. R. Acad. Sci., Ser. C*, **274**, 991 (1972). We have purposely avoided the use of trapping agents which might qualify as good Michael acceptors.

[5] Dibromodesoxybenzoin was prepared by the acid-catalyzed bromination of desoxybenzoin in ether and recrystallized from ethanol, mp 112° (lit. mp 112°, J. R. A. Pollock and R. Stevens, Ed., "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965, p 939).

[6] Compound **3**: mp 118–120° (pentane); ir (CCl_4) 1645 (C=C) and 1240 cm^{-1} (C—O), no carbonyl; nmr (CCl_4) δ 7.70–6.90 (m, 20), 5.42 (d, 1, J = 6.0 Hz), and 4.35 ppm (d, 1, J = 6.0 Hz); uv max (EtOH) 298 mμ (ϵ 9400); mass spectrum (70 eV) M^+ at m/e 374. *Anal.* Calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92. Found: C, 89.67; H, 5.79.

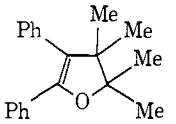
[7] Bromination of **3** at room temperature with 1.0 equiv of bromine in 1:1 ether–carbon tetrachloride followed by dehydrobromination with refluxing ethanolic potassium hydroxide for 1 hr gave tetraphenylfuran (85% yield) which was identical with an authentic sample.

[8] The coupling constant between the benzylic hydrogens in **3** (J = 6.0 Hz) agrees well with the corresponding coupling constant in the structurally similar heterocycles *trans*-2,3-diphenyl-2,3-dihydro-4,5,6,7-tetrachlorobenzo[*b*]furan (J = 5.7 Hz) and *trans*-3,4,5-triphenyl-4,5-dihydroisoxazole (J = 5.6 Hz); the cis isomer of the latter has a much larger coupling constant (J = 9.7 Hz): G. Binsch, R. Huisgen, and H. König, *Chem. Ber.*, **97**, 2893 (1964).

[9] R. Huisgen, G. Binsch, and H. König, *Chem. Ber.*, **97**, 2868, 2884, 2893 (1964), and references cited therein.

by-product in our reaction, would likely catalyze the rearrangement of **4** to **3**.[10,10a]

Treatment of dibromodesoxybenzoin (**1**) with excess zinc dust in refluxing tetramethylethylene for 2 days provides the fully substituted dihydrofuran **5**[11] in 37% yield. Analogous reactions in benzene with 1,1-diphenylethylene or diphenylacetylene produce the corresponding heterocycles **6**[12] and **7**, albeit in lower yield.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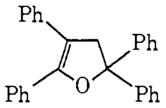
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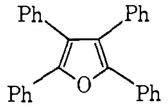
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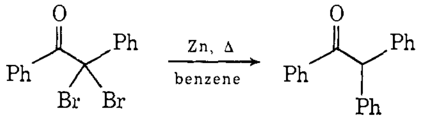
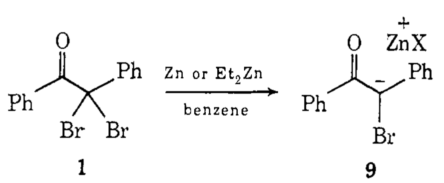
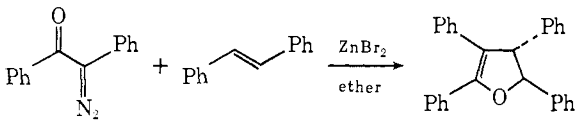
In the absence of other trapping agents, benzhydryl phenyl ketone (**8**) constitutes the major product (20–30% yield) from α debromination of **1** with zinc in refluxing benzene (eq 3). Simple insertion of the ketocarbenoid into a C–H bond of benzene satisfactorily accounts for the formation of **8**, although other mechanisms may be imagined. The possibility of Wolff rearrangement to diphenylketene followed by acylation of the solvent (zinc bromide catalyzed) was easily disproved by repetition of this reaction in benzene-d_6 which afforded **8** with all the deuterium in the benzhydryl portion of the molecule.[13] In the other trapping experiments run in benzene, ketone **8** generally appears as a by-product; desoxybenzoin and benzil have also been isolated in variable yield.


1 **8** (3)

We believe the zinc-induced α elimination of bromine from **1** involves the intermediacy of bromoenolate **9** (X = Br), formed by a process which parallels the first step of a Reformatsky reaction.[14] The related enolate **9** (X = Et) can be prepared rapidly and efficiently by the reaction of **1** with diethylzinc in benzene at 5° (eq 4); subsequent quenching with chlorotrimethylsilane, even after 24 hr at room temperature, furnishes the corresponding trimethylsilyl enol ether in high yield and attests to the stability of this α bromoenolate.[15] Complete generation of the enolate from **1**, in fact, requires only 0.5 molar equiv of diethylzinc. The α-bromoenolate formed in this manner also gives the dihydrofuran **3** with *trans*-stilbene in refluxing benzene; however, ethyl bromide, the by-product of enolate formation, interferes with olefin trapping and must first be removed by evaporation and replaced with fresh solvent.


1 **9** (4)

The classical diazo ketone route to benzoylphenylcarbene, starting from azibenzil (**10**), has been known for many decades,[16] but previous attempts to intercept this ketocarbene with olefins have failed.[17] We have found that decomposition of **10** with zinc bromide in the presence of *trans*-stilbene produces the same dihydrofuran (**3**) obtained earlier by the α-elimination route (eq 5; *cf.* eq 1). Bromoenolate **9** (X = Br), a plausible common intermediate in the production of **3** by both the diazo route and the α-elimination route, undoubtedly accounts for the monobromodesoxybenzoin isolated also from the azibenzil decomposition.


10 **2** **3** (5)

The results described herein not only provide a second example of α elimination adjacent to a ketone but also demonstrate for the first time the feasibility of trapping the resulting ketocarbenoids intermolecularly with olefins, with an acetylene, and with benzene. Efforts to develop synthetically useful α-elimination routes to carbonyl-conjugated carbenes and carbenoids for the cyclopropanation of olefins continue in our laboratories.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of California—Los Angeles Research Committee for financial support of this work.

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[10] Related rearrangements have been reported by M. I. Komendantov, T. S. Smirnova, I. N. Domnin, and L. A. Krakhmal'naya, *J. Org. Chem. USSR*, 2551 (1971).

[10a] NOTE ADDED IN PROOF: Cyclopropyl ketone **4**, prepared by another method, can be recovered quantitatively after treatment with zinc bromide in refluxing benzene for 3 days. Furthermore, when the reaction in eq 1 is run in the presence of independently prepared **4**, the cyclopropyl ketone is not consumed. These experiments support the dipolar addition mechanism for the formation of dihydrofuran **3**, since **4** never appears among the normal products of that reaction.

[11] Compound 5: ir (CCl_4) 1650 (C=C) and 1250 cm^{-1} (C—O), no carbonyl; nmr (CCl_4) δ 7.30–7.05 (m, 20), 1.35 (s, 6), and 1.02 ppm (s, 6); uv max (EtOH) 285 mμ (ε 11,000); mass spectrum (70 eV) M$^+$ at *m/e* 278. *Anal.* Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.04; H, 7.82.

[12] Compound **6** had spectral properties in agreement with those reported by R. E. Lutz and D. W. Boykin, Jr., *J. Amer. Chem. Soc.*, **86**, 5046 (1964).

[13] Benzhydryl phenyl ketone (**8**) fragments in the mass spectrometer (70 eV) to give major peaks at *m/e* 167 (PhCH$^+$Ph) and 105 (Ph-C≡O$^+$). In the mass spectrum of 8 obtained from the benzene-d_6 trapping, only the former peak appears at higher *m/e*. The nmr signal for the two hydrogens ortho to the carbonyl group in **8** (δ 8.05–7.75 ppm) appears well separated from that of the other aromatic hydrogens (δ 7.50–7.15 ppm) and remains unchanged in the nmr spectrum of benzhydryl phenyl ketone obtained from the benzene-d_6 experiment.

[14] R. L. Shriner, *Org. React.*, 1, 1 (1942).

[15] Other α-haloenolates show similar stability; see ref 3.

[16] G. Schroeter, *Ber. Deut. Chem. Ges.*, 42, 2336, 3356 (1909).

[17] R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, 73, 368 (1961).

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Received April 18, 1973

[4 + 2] Cycloadditions of a Vinylketenimine. A New Route toward Functionalized Cyclohexenone Derivatives

Sir:

Vinylheterocumulenes **1a** and **b** offer synthetic potentialities which have been little explored. One at-