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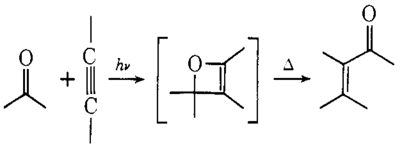
Detection of an Oxetene Intermediate in the Photoreaction of Benzaldehyde with 2-Butyne

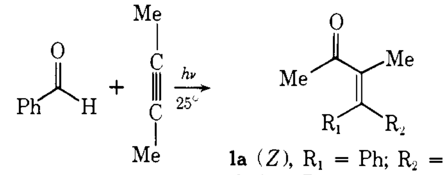
Sir:

Numerous papers dating back to 1956 have been published that describe the photoproduction of enones on irradiation of carbonyl compounds in the presence of acetylenes.[1] In all of these reports, an oxetene intermediate was assumed to have formed which was unstable and fragmented to the enone product. In none of these studies, however, was an oxetene isolated or detected.[2]



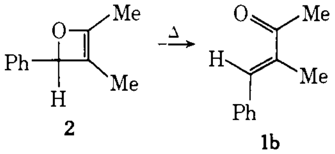
In 1969 the first unfluorinated oxetene, prepared by photolysis of 3,4-dimethyl-3-penten-2-one, was found to be stable at room temperature.[3] We therefore believed that certain stable oxetenes might be detected in the irradiation of carbonyl and acetylenic compounds. One such system is the benzaldehyde–2-butyne pair.[4]

Irradiation[5] of an undegassed CH_2Cl_2 solution containing 0.2 *M* benzaldehyde and 0.5 *M* 2-butyne for 4 hr at 20° gave a *ca.* 24% conversion (43% yield) to the known[6] (*Z*)- and (*E*)-enones, **1a** and **1b**, in a *ca.* 2:1 ratio (nmr). Independent experiments indicated that this ratio was the photostationary state and was not greatly affected by temperatures down to −78°. A similar irradiation at −78°, followed by nmr analysis at room temperature, showed only the *E* isomer **1b**. If this sample of the *E* isomer was cooled to −78° and irradiation continued, the photostationary state of enone **1** was attained. Our conclusion is that enone **1b** was *not* photochemically generated at −78°, but rather was stereospecifically formed from an oxetene in a thermal process on warming.

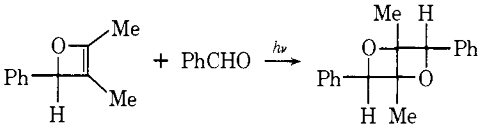


1a (*Z*), R_1 = Ph; R_2 = H
1b (*E*), R_1 = H; R_2 = Ph

Specific attempts to trap the oxetene **2** at −78° or above have failed. In all cases (O_3, Br_2, H_2/Pt, B_2H_6), only the reaction products from enone **1b** were detected. As we expected,[7] however, a [2 + 2] cycloaddition of benzaldehyde with the oxetene **2** was found at low temperature where the oxetene was stable. We have assigned the structure of the novel fused oxetane **3**[8] as containing the 2,5-dioxa[2.2.0]hexane skeleton rather than the 2,6-dioxa[2.2.0]hexane framework because of equivalent methyl signals in the nmr (δ 1.02 (s, 6 H)).



2 **1b**



2 **3**

In an attempt to actually observe the oxetene **2**, a reaction solution was prepared by irradiation at −78°. Most of the CH_2Cl_2 and excess 2-butyne was removed at −45° under reduced pressure. A 100-MHz nmr spectrum at −45° in $CFCl_3$ solution showed two equally intense singlets for oxetene **2** at δ 1.96 and 1.67 ppm[9] that disappeared on warming and did not reappear on cooling.

In their place, singlets appeared at δ 2.44 and 2.07 ppm which correspond to the methyl groups of (*E*)-enone **1b**.[10] The methine hydrogen of oxetene **2** (assigned at δ 5.81) was partially obscured by several minor temperature-independent absorptions that were not investigated.

Oxetene **2** was found to have a half-life of several hours at −35°. From temperature-dependent nmr

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(1) (a) G. Buchi, J. T. Kofron, E. Koller, and D. Rosenthal, *J. Amer. Chem. Soc.*, **78**, 876 (1956); (b) D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *Tetrahedron Lett.*, 2863 (1968); (c) S. P. Pappas and B. C. Pappas, *ibid.*, 1597 (1967); (d) D. Bryce-Smith, G. I. Fray, and A. Gilbert, *ibid.*, 2137 (1964); (e) H. E. Zimmerman and L. Craft, *ibid.*, 2131 (1964); (f) S. Farid, W. Kothe, and G. Pfundt, *ibid.*, 4147 (1968); (g) S. P. Pappas and N. A. Portnoy, *J. Org. Chem.*, **33**, 2200 (1968); (h) H. J. T. Bos, H. T. Van Der Bend, J. S. M. Boleij, C. J. A. Everaars, and H. Polman, *Recl. Trav. Chim. Pays-Bas*, **91**, 65 (1972); (i) H. J. T. Bos and J. S. M. Boleij, *ibid.*, **88**, 465 (1969); (j) H. Polman, J. S. M. Boleij, and H. J. T. Bos, *ibid.*, **91**, 1088 (1972); (k) S. Ficini and A. Krief, *Tetrahedron Lett.*, 2497 (1967); (l) T. Miyamoto, Y. Shigemitsu, and Y. Odaira, *Chem. Commun.*, 1410 (1969); (m) J. A. Barltrop and B. Hesp, *J. Chem. Soc. C*, 1625 (1967).

(2) Some photoreactions evidently by-pass reasonable ground-state intermediates. For example, Buchardt has failed to detect an oxaziridine or any other intermediate with a lifetime greater than 10^{-9} sec in the photolysis of quinoline *N*-oxides to carbostyrils and oxazepines: Organic Colloquium Series, University of Rochester, Rochester, N. Y., Feb 2, 1973. For a recent paper, see O. Buchardt and P. L. Kumler, *Acta Chem. Scand.*, **23**, 2149 (1969). Also, Arnold has suggested that the excess vibrational energy of a generated oxetene may cause fragmentation before collisional deactivation to a stable molecule; see D. R. Arnold, *Advan. Photochem.*, **6**, 341 (1968).

(3) L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, **91**, 7204 (1969).

(4) Irradiation of *trans*-stilbene oxide gave benzaldehyde which added to 2-butyne to yield (*Z*)- and (*E*)-3-methyl-4-phenyl-3-buten-2-one; see H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 1579 (1966).

(5) Hanovia 450-W medium-pressure mercury lamp through Pyrex.

(6) L. E. Hightower, L. R. Glasgow, K. M. Stone, D. A. Albertson, and H. A. Smith, *J. Org. Chem.*, **35**, 1881 (1970), report the *E* isomer. The (*Z*)-enone was apparently uncharacterized until now: nmr (CCl_4) δ 7.07 (s, 5), 6.05 (d, *J* = 1.5 Hz, 1), 1.94 (d, *J* = 1.5 Hz, 3), 1.86 (s, 3).

(7) 2,3,4,4-Tetramethyloxetene reacts with benzophenone triplet to give a [2 + 2] cycloadduct; unpublished results of L. E. Friedrich and G. B. Schuster; see G. B. Schuster, Ph.D. Thesis, University of Rochester, Rochester, N. Y., 1971. Professor J. C. Dalton and S. J. Tremont have prepared the only other known example of this new class of compounds at the University of Rochester, 1973; *Tetrahedron Lett.*, in press.

(8) Oxetane **3**: mp 89–90°; ir (CCl_4) 3065, 3033, 1606, 1493, 1453, 1387, 1137, 979 (very strong), 700 cm^{-1}; nmr (CCl_4) δ 7.44 (s, 10), 6.17 (s, 2), 1.02 (s, 6); mass spectrum (70 eV) 266 (parent, 6), 248 (23), 160 (100), 159 (98), 145 (44), 117 (56), 105 (42), 43 (34). *Anal.* Calcd for $C_{18}H_{18}O_2$ (266.32): C, 81.17; H, 6.81. Found: C, 81.03; H, 6.55.

(9) Relative to CH_2Cl_2 at δ 5.30.

(10) At room temperature in CCl_4 enone **1b** also possesses a vinyl H at δ 7.32, barely distinguishable from the phenyl absorptions at δ 7.21.

studies we estimate that oxetene **2** is *ca.* 10^6 times less stable than 2,3,4,4-tetramethyloxetene[11] at 0°. Care must be taken to exclude acids from oxetene **2**. A small drop of perchloric acid caused a $CFCl_3$ solution of the oxetene to immediately isomerize to enone **1b** at −45°.

Acknowledgment. We thank the National Science Foundation and Merck Chemical Co. Foundation for financial support.

(11) L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, **93**, 4602 (1971).

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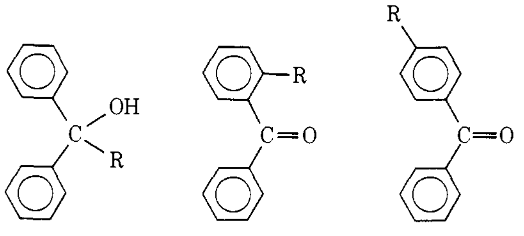
Mechanisms of Wittig Rearrangements and Ketyl–Alkyl Iodide Reactions

Sir:

Radical paths have been implicated for Wittig, Stevens, Meisenheimer, and other "ylide" rearrangements,[1–6] but their extents have been questioned cogently. It is not clear that radical intermediates are entirely consistent with observed high degrees of retention of configuration of migrating groups, and weak and elusive CIDNP from these systems could result from minor paths or side reactions.[7] In fact, the CIDNP reported from a Wittig rearrangement[2] does not appear to be due to a rearrangement product.[8] Further, for a model Stevens rearrangement, a MINDO calculation is said to support an intramolecular migration with no intermediates.[9a]

In the face of such confusion, further detailed study of each reaction is required. We report new evidence that the intermolecular portions of Wittig rearrangements proceed through radicals. Concomitantly, we find that the immediate precursors of intramolecular and intermolecular rearrangement products must differ significantly.

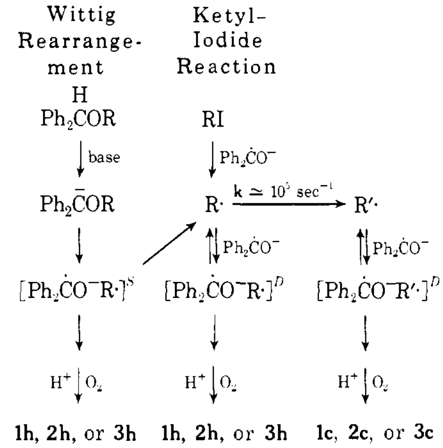
Consider first reactions of lithium benzophenone ketyl with alkyl iodides in THF at room temperature.[9b] Even for *tert*-pentyl iodide, no olefins result.[10a] The absence of elimination militates against initial S_N2–E2 steps, as does the structure-rate trend (*tert*-pentyl iodide reacts four times as rapidly as methyl iodide). For the reaction of 5-hexenyl iodide, the appearance of **1c**, **2c**, and **3c** as products and the dependence of the molar product ratio (**1h** + **2h** + **3h**)/(**1c** + **2c** + **3c**) on the ketyl concentration support the intermediacy of 5-hexenyl radicals which cyclize in competition with coupling with the ketyl (Scheme I). When the initial ketyl concentration is 0.05 *M*, (**1h** + **2h** + **3h**)/(**1c** + **2c** + **3c**) is 12; for 0.001 *M* ketyl, the product ratio is 0.5.



1 **2** **3**

h: R = 5-hexenyl
c: R = cyclopentylmethyl

Scheme I[a]



[a] R· = 5-hexenyl; R'· = cyclopentylmethyl. Lithium counterions are not shown. Ion aggregation must be extensive in THF. No particular states of aggregation are implied by the representations above. *S* pairs are initially electronic singlets. In the above scheme they would be formed with particular initial geometries. *D* pairs are formed when independently generated radicals diffuse together with random geometries.

Turning to the Wittig rearrangement of benzhydryl 5-hexenyl ether promoted by butyllithium in THF at room temperature, we find the same six products, **1h**, **2h**, **3h**, **1c**, **2c**, and **3c**, with the cyclopentylmethylation products accounting for about 15% of these.[10b] Once again, the appearance of **1c**, **2c**, and **3c** suggests intermediate 5-hexenyl radicals which cyclize.

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(1) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966).

(2) (a) U. Schollkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970); (b) U. Schollkopf, *Ind. Chim. Belge*, **36**, 1057 (1971), and references cited therein.

(3) (a) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970); (b) J. E. Baldwin and J. E. Patrick, *J. Amer. Chem. Soc.*, **93**, 3556 (1971), and references cited therein.

(4) V. Rautenstrauch, *Chem. Commun.*, 4 (1970).

(5) (a) A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 1237 (1969); (b) A. R. Lepley, P. M. Cook, and G. F. Willard, *J. Amer. Chem. Soc.*, **92**, 1101 (1970).

(6) Other reviews: (a) G. Tennant, *Annu. Rep. Progr. Chem., Sect. B*, **68**, 241 (1972); (b) A. R. Lepley and A. G. Giumanini in "Mechanisms of Molecular Migrations," Vol. 3, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1971; (c) G. Wittig, *Bull. Soc. Chim. Fr.*, 1920 (1971).

(7) J. Jacobus, *Chem. Commun.*, 709 (1970).

(8) Private communication from A. R. Lepley, 1973.

(9) (a) Calculations presented by M. J. S. Dewar at the 23rd National Organic Symposium of the American Chemical Society, Tallahassee, Fla., June 1973. (b) Dilithium benzophenone was prepared by the reaction of lithium metal with benzophenone in degassed, anhydrous THF. To filtered solutions of dilithium benzophenone, 5–10% excesses of benzophenone were added, giving *ca.* 0.05 *M* solutions of lithium benzophenone ketyl. Approximately equivalent amounts of alkyl iodides were added through serum caps with syringes.

(10) (a) All product analyses were by vpc. Analyses for **1h**, **2h**, **3h**, **1c**, **2c**, and **3c** used internal standard phenyl biphenylyl ketone and two columns, 1/8 in. × 10 ft 10% Carbowax 20M-TPA on 80–100 mesh acid-washed DMCS-treated Chromosorb W and 1/8 in. × 20 ft 20% QF-1 on Chromosorb W, at 240–250°. Products were isolated and characterized by nmr, mass spectra, and ir. Yields, based on benzophenone taken for the dilithium benzophenone preparations, were *ca.* 50%. This probably represents a lower limit, since conversions to dilithium benzophenone could have been incomplete. There were no unaccounted for peaks in the vpc traces. (b) Benzhydryl ethers (0.1–0.2 *M*) were treated with twofold (or greater) excesses of *n*-butyllithium in degassed, anhydrous THF and the resulting solutions were allowed to stand (with stirring) for 1 hr or more. Analyses were as described above. Yields of **1h**, **2h**, **3h**, **1c**, **2c**, and **3c** were *ca.* 90%.