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.

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Received July 21, 1973

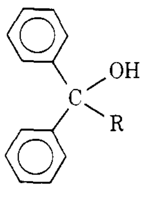
Mechanisms of Wittig Rearrangements and Ketyl–Alkyl Iodide Reactions

Sir:

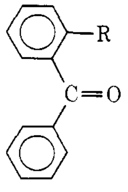
Radical paths have been implicated for Wittig, Stevens, Meisenheimer, and other "ylide" rearrangements,[1–6] but their extents have been questioned cogently. It is not clear that radical intermediates are entirely consistent with observed high degrees of retention of configuration of migrating groups, 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.

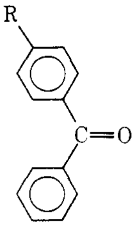
Consider first reactions of lithium benzophenone ketyl with alkyl iodides in THF at room temperature.[9b] Even for *tert*-pentyl iodide, no olefins result.[10a] The absence of elimination militates against initial SN2–E2 steps, as does the structure-rate trend (*tert*-pentyl iodide reacts four times 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



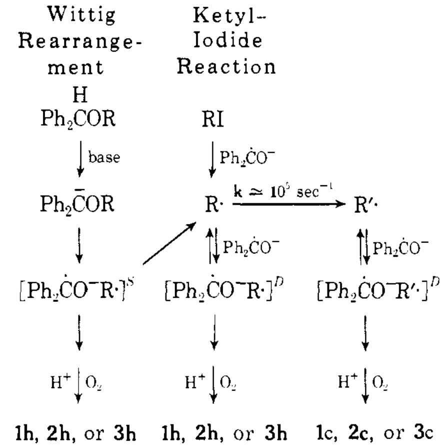
2



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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(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%.

This relationship between the ketyl–5-hexenyl iodide reaction and the Wittig rearrangement of benzhydryl 5-hexenyl ether is further confirmed by the ratios **1c**:**2c**:**3c**, which are 41:5:54 for the ketyl reaction and 46:5:49 for the Wittig rearrangement, the same within experimental error. It is clear that these products result from the same process in the two reactions, collapse of cyclopentylmethyl–ketyl radical pairs. Since the cyclization of 5-hexenyl radicals is too slow ($k \simeq 10^5$ sec^{-1})[11] to compete with cage reactions (which must occur within about 10^{-9} sec),[12] **1c**, **2c**, and **3c** are intermolecular Wittig rearrangement products (Scheme I).

The ratios **1h**:**2h**:**3h** are 45:8:47 from the ketyl–5-hexenyl iodide reaction but 77:13:10 from the Wittig rearrangement of benzhydryl 5-hexenyl ether. Since a large fraction of the 5-hexenyl radicals escaping reaction with their geminate partners must cyclize,[13] **1h**, **2h**, and **3h** must be primarily intramolecular rearrangement products. Thus, the immediate product precursors must be significantly different for the intramolecular and intermolecular portions of the Wittig rearrangement.

There are three *limiting* descriptions of the intramolecular Wittig rearrangement path which incorporate factors that could be held solely responsible for the intramolecular and intermolecular product differences. (1) Radical pairs are not intermediates. (2) Radical pairs are intermediates, but their collapse to product competes effectively with mutual reorientation of the radicals, giving preferential coupling at the sites of the ketyl which are initially near the alkyl radical. (3) Radical pairs are intermediates, but different states of ion aggregation and solvation or the different initial electronic spin characters of the collapsing radical pairs for the intramolecular and intermolecular pathways give rise to different product distributions.

Possibility 1 is the least attractive limiting description of the intramolecular process. Since the fragments to which the ether anions separate at large distances are radicals, it is unreasonable to suppose that they are not radicals at separations of one or two molecular diameters. Yet, appreciable fractions of radical pairs at these smaller separations should be expected to diffuse together and react. Thus, there should be some secondary recombination[12] contributing to the intramolecular reaction.

Possibilities 2 and 3 are more reasonable limiting descriptions, with possibility 2 especially accounting nicely for the observed intramolecular product distribution. However, it must be recognized that a considerable fraction of the intramolecular reaction could occur through primary recombination, in which the radicals never separate by so much as a molecular diameter.[12] In fact, if we assume that possibility 2 obtains and that secondary recombination should give the same ratios **1h**:**2h**:**3h** as the ketyl–alkyl iodide reaction then we calculate that at least 0.8 of the intramolecular pathway must be described as primary recombination.[14] Since primary recombination of radical pairs,[15] rearrangements through tight particle pairs describable (possibly) as radical–nonradical resonance hybrids,[17] and concerted migrations may all give retention of configuration of migrating groups without generating CIDNP, it is problematical whether these will be operationally distinguishable.

Occam's razor, considered in conjunction with the intermolecular rearrangement mechanism, supports a radical pair description of the intramolecular rearrangement as well, with the possibility that a substantial fraction might be considered as primary recombination of geminate radicals.

Acknowledgment. We are grateful to the National Science Foundation for grants supporting this research.

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(13) Kinetic analysis of the reaction, using mostly known rate constants, indicates that at least 90% of the 5-hexenyl radicals escaping geminate recombination should cyclize, probably more. The concentration of ketyl in these reactions is, of course, quite low.

(14) This presumes that relative rotational relaxation of the radical partners is essentially complete between encounters.

(15) Only secondary recombination gives CIDNP.[16]

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Received April 10, 1973

Molybdenum(IV) in Aqueous Solutions

Sir:

The role of molybdenum in enzymatic reactions recently aroused interest in the nature of the aquo ions of molybdenum in its various oxidation states.[1,2] Bowen and Taube[1] demonstrated the existence of the molybdenum(II) aquo ion Mo_2^{4+} and of the molybdenum(III) hexaaquo ion $Mo(H_2O)_6^{3+}$. Molybdenum(V) was recently shown to exist in aqueous solutions of noncomplexing acids as a binuclear cation of ionic charge +2, with a di-μ-oxo structure.[2] Whereas the existence of molybdenum aquo ions in oxidation states +2, +3, and +5 (and +6) has been established, there has been no indication, so far, of the existence of molybdenum(IV) as a stable aquo ion in solution. Except for a few complex ions of molybdenum(IV), such as the octacyano ion and its derivatives,[3] the chemistry of molybdenum(IV) in aqueous solution is virtually unknown. The accepted view[4] of this oxidation state is that molybdenum(IV) cannot exist in aqueous solution and that if it is formed as a transient intermediate during reduction of molybdenum(VI) or molybdenum(V) it would undergo rapid disproportionation to molybdenum(III) and molybdenum(V).

We wish to report the discovery of a stable aquo ion of molybdenum(IV) in aqueous solution. While investigating substitution reactions of $Mo(H_2O)_6^{3+}$, we observed that an almost colorless solution of this ion in *p*-toluenesulfonic acid[1] (HPTS) acquired a pinkish tint after prolonged storage under a paraffin protective layer (used to prevent exposure to the atmosphere). Absorption of this aged solution on a cation-exchange column (Dowex 50X-2) revealed a sharp dark red band above the light yellow band of hexaaquomolybdenum-

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