by the unknown differences in σ bond energies of the isomers and intermolecular solvent associations.[17]

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Photochemistry of Olefins. Radical-Cation Behavior

Sir:

Recent studies in these laboratories and others have shown that either photosensitized or direct irradiation of medium-sized cycloalkenes in protic media results in light-induced protonation of the olefin followed by subsequent ground-state reactions of the resulting carbonium ion intermediate.[1-3] This process, which is thought to involve protonation of the highly strained trans isomer of the starting olefin,[1] is specific to six-, seven-, and eight-membered cyclic olefins and is not shared by acyclic, exocyclic, or smaller and larger ring cyclic olefins.[1]

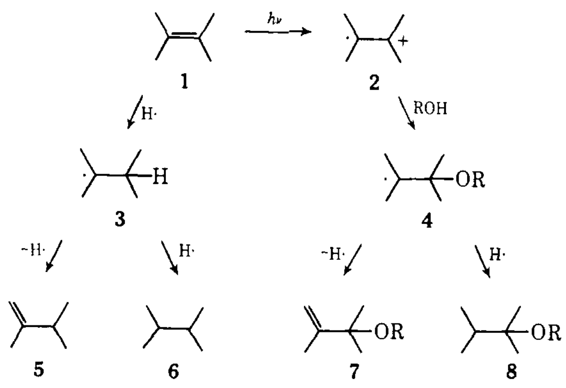
We now wish to report a new photochemical process for olefins, involving direct irradiation, which occurs with both acyclic and cyclic olefins, regardless of ring size. It is illustrated by 2,3-dimethyl-2-butene (**1**), which on irradiation in alcoholic solvents readily affords principally a mixture of the ethers **7** and **8**,[4] accompanied by lesser amounts of the hydrocarbons **5** and **6** (see Table I). Similarly, in aqueous acetonitrile the corresponding alcohols **7** and **8** (R = H) are obtained. Analogous behavior is exhibited by the cyclic analogs 1,2-dimethylcyclopentene and -hexene.

Table I. Irradiation of 2,3-Dimethyl-2-butene (**1**)[a]

Solvent	Time, hr	Yield, %[b] **1**	**5**	**6**	**7**	**8**	**9**	**10**
H_2O, CH_3CN[c]	4	3	1.5	1	16	23	*d*	*d*
CH_3OH	4	6	4	16	30	37	*e*	*e*
CH_3OH[f]	128	42	1	2	2.5	3	*d*	*d*
C_2H_5OH	4	35	5	6	20	12	*e*	*e*
	8	3	5.5	6.5	23	16	*e*	*e*
n-C_4H_9OH	4	60	4	3	10	2	1	1
	16	5	7	7	23	10	4	4

[a] Unless otherwise indicated, irradiations were conducted with 3.40 g of **1** in 200 ml of solvent using a Hanovia Type L 450-W lamp and a water-cooled quartz immersion well. [b] Determined by gas-chromatographic analysis of aliquots removed from the reaction mixture relative to a saturated hydrocarbon internal standard. [c] 30% aqueous solution. [d] None detectable. [e] Trace. [f] A circular array of 16 G8T5 lamps, which emit principally at 253.7 nm, was used as the light source. The slowness of the reaction under these conditions is due in large part to the very small absorption by **1** at this wavelength.

The formation of both saturated and unsaturated adducts suggests a mechanism involving the intermediacy of a radical cation of type **2** or, at least, a species exhibiting similar behavior, which undergoes nucleophilic trapping by the solvent to afford the alkoxy radical **4**. The hydrocarbon products **5** and **6** apparently arise *via* attack of H· on the starting olefin **1** as indicated. A principal source of H· appears to be from reaction of the ejected electron with solvent as shown in eq 1.[5] This is corroborated by the finding

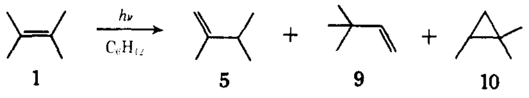


$$e^- + CH_3OH \longrightarrow CH_3O^- + H\cdot \qquad (1)$$

that irradiation of **1** in methanol-*O-d* resulted in extensive incorporation of deuterium in products **5** and **6** but only minor incorporation in the ethers **7** and **8** (R = CH_3).

The radical-cation behavior is markedly sensitive to the degree of alkyl substitution. The trisubstituted analog 2-methyl-2-butene undergoes much slower reaction in methanol than does **1** under the same conditions and after 72 hr is only 80% converted, affording principally a mixture of hydrocarbons and ethers (yields of 42 and 9%, respectively). The radical-cation behavior is also markedly sensitive to the nature of the medium. This can be seen in Table I by the decrease in the rate of disappearance of **1** on going from water to 1-butanol. In aprotic media **1** undergoes instead a slow isomerization to a mixture of the isomers **5**, **9**, and **10**.[3] In 1-butanol, in which the rate of reaction *via* the radical-cation pathway is slow, appreciable amounts of the isomers **9** and **10** are formed in competition with the products **5**–**8**.

The conversion of **1** to photoproducts **5**–**8** is apparently a singlet-state reaction since attempts to induce reaction of **1** by triplet sensitization with *p*-xylene have been unsuccessful. It is not yet clear whether the radical-cation intermediate arises from direct photoionization of the olefin or whether it involves the singlet Rydberg excited state of the olefin. However, the ionization potential of **1** in hydroxylic media, which can be estimated from the Born equation to be about 2 eV lower than the gas-phase ionization potential of 8.30 eV,[6] is not sufficient to account for the fact that reaction can be effected at 253.7 nm (4.88 eV). On the other hand, the Rydberg excited state (λ_{max} 5.4 eV), although little studied,[7] has been assigned as the lowest lying



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[1] P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **91**, 7466 (1969), and references cited therein.

[2] For a recent review, see J. A. Marshall, *Science*, **170**, 137 (1970).

[3] Unpublished results from these laboratories.

[4] Satisfactory analytical and spectral data have been obtained for all new compounds.

[5] A. Habersbergerova, Lj. Josimovic, and J. Teply, *Trans. Faraday Soc.*, **66**, 656, 669 (1970).

[6] J. P. Teegenand and A. D. Walsh, *ibid.*, 47, 1 (1951).

[7] To the best of our knowledge there is only one example in which photochemical behavior has been assigned to an olefin Rydberg state. This assignment, involving various gas-phase fragmentations, was made by default when it was found that the reactions occurred under conditions in which there was no concomitant cis–trans isomerization; see P. Borrell and F. C. James, *ibid.*, **62**, 2452 (1966); P. Borrell and P. Cashmore, *ibid.*, **65**, 2412 (1969).

singlet excited state of simple olefins and is thought to involve the promotion of a π electron to a molecular orbital so large that the resulting excited state is expected to display behavior resembling that of a radical cation.[8]

Previous studies on the photoprotonation of olefins have afforded several reactions having important synthetic applicability.[1] The discovery of radical-cation behavior opens yet a new vista of synthetic applications, since trapping of the radical-cation intermediate with any one of a number of nucleophiles should be possible. Moreover, the reaction has the advantage of not being limited to certain cyclic systems. Further work is in progress to explore the full synthetic potential, as well as the mechanistic details, of this new reaction.

Acknowledgment. Support of this work through the Science Development Program of the National Science Foundation at the University of North Carolina is gratefully acknowledged.

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[8] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

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Synthesis of (+)- and (−)-7-Oxaprostaglandin $F_{1\alpha}$ and Their 15-Epimers

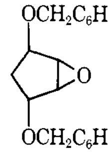
Sir:

We recently reported the synthesis of 7-oxa derivatives of $PGF_{1\alpha}$[1] and PGE_1[2] as well as of skeletally identical but less oxygenated derivatives.[3] Some of these showed prostaglandin-like activity,[4] others were prostaglandin antagonists,[3,5–7] and some combined both activities. The substances originally synthesized and tested were racemic and consisted of mixtures of 15-epimers. The overlap of agonist and antagonistic properties made it imperative that the pure enantiomers of known absolute configuration be available for biological evaluation.

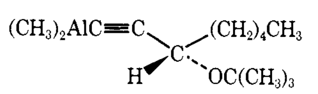
We now wish to report the synthesis of (+)-7-oxa-$PGF_{1\alpha}$ (**9a**)[8] and (+)-7-oxa-15-epi-$PGF_{1\alpha}$ (**9b**) and their enantiomers, as well as preliminary biological data showing that only **9a** possessing the absolute configuration of the prostaglandins exhibits typical prostaglandin-like activities.

The novel feature of this synthesis, which as the key step utilizes the opening of a *meso*-cyclopentene oxide with a dialkylalkynylalane,[1] is the introduction of the completely functionalized eight-carbon side chain in optically active form, leading to two diastereomers, which can be readily separated by chromatography. Such a procedure has the advantage of requiring but one resolution of a simple acetylenic alcohol, which then serves to resolve the remaining chiral portion of the molecule. It also possesses generality in that other analogs can be prepared without additional resolutions. Application of this principle to the synthesis of the prostaglandins themselves will be reported later.

all-cis-Cyclopentene 3,5-dibenzyloxyepoxide (**1**) was condensed with dimethyl (*S*)-(−)-3-*tert*-butyloxy-1-octynylalane (**2**)[9] (2 equiv) in toluene at 70–80° for 24 hr and the resulting mixture of diastereomeric butyl ethers (**3a** + **3b**, 72%), [α]D −28.6°,[10] debutylated with trifluoroacetic acid at 0° for 2 hr to the acetylenic alcohols (**4a** + **4b**, 98%),[11] [α]D +1.33°, which could



1



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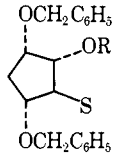
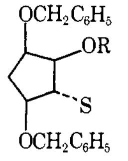
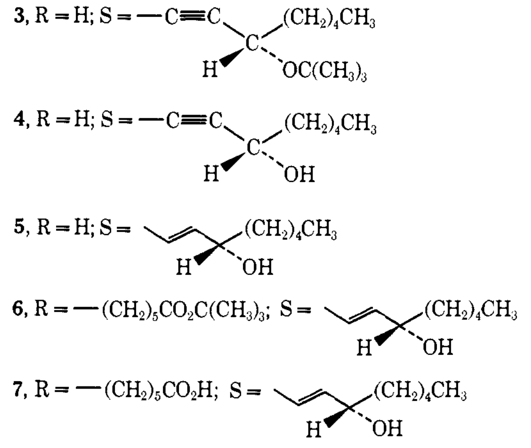


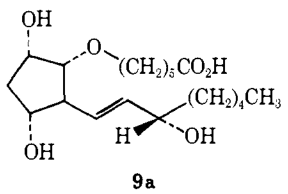
a



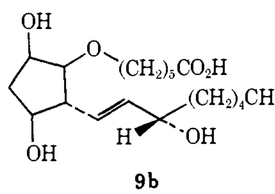
b



8, R = H; S = $—C{\equiv}C(CH_2)_5CH_3$



9a



9b

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[4] S. H. Ford and J. Fried, *Life Sci.*, **8**, 983 (1969).

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[6] F. A. Kuehl, Jr., J. Humes, J. Tarnoff, V. J. Cirillo, and E. A. Ham, *Science*, **169**, 883 (1970).

[7] W. Vale, C. Rivier, and R. Guillemin, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **30**, 960 (1971).

[8] Compound numbers refer only to the absolute configuration represented in the structural formulas. To designate racemates or enantiomers the prefixes (±), (+), or (−) precede the numbers. Thus, **9a** and **9b** possess the absolute configuration of *nat*-$PGF_{1\alpha}$ and *ent*-15-epi-$PGF_{1\alpha}$, respectively.

[9] Prepared from (*S*)-(−)-3-hydroxy-1-octyne (*cf.* ref 5) with isobutylene in methylene chloride in the presence of BF_3–etherate and phosphoric acid, $[\alpha]^{\text{ether}}_{D}$ −70°, followed by lithiation (BuLi) and reaction with dimethylchloroalane.

[10] Rotations in chloroform.

[11] All yield figures refer to chromatographically purified fractions.