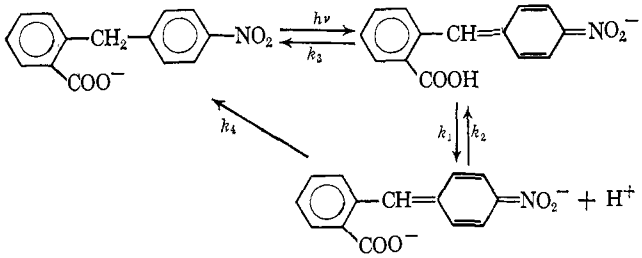
from the p-carboxylate structure (IV) as from the o-carboxylate structure (III). Also, the undissociated carboxylic acid form of III yields very little transient species compared to the carboxylate ion form; photolysis at pH 2 yields only about 1% as much transient absorption as is formed at pH 7 or greater. These observations indicate that the photochromic reaction is probably favored by an intramolecular reaction mechanism in which a six-membered ring pathway facilitates hydrogen transfer[6] from the methylene group to the carboxylate ion and then into solution.



In O_2-free solutions the kinetics of the decay of the transient species from III is consistent with this mechanism over seven orders of magnitude (milliseconds to hours) in the pH range 3 to 11. If values typical[7] of aromatic carboxylic acids are assumed for k_1 and k_2, then $K = k_1/k_2 \cong 10^{-4}$, where $k_1 \cong 5 \times 10^6$ sec^{-1} and $k_2 \cong 5 \times 10^{10}$ M^{-1} sec^{-1}. The intramolecular proton-transfer back-reaction represented by k_3 is probably the dominant transient decay process, and $k_3 \cong 2.5 \times 10^3$ sec^{-1} if $k_4 < 10^3 k_3$. On the other hand, if $k_4 > 10^5 k_3$ the intermolecular proton-addition back-reaction (k_4) would be dominant, with $k_4 \cong 2.5 \times 10^7$ M^{-1} sec^{-1}. In either case the equilibrium process represented by k_1 and k_2 would be about 10^3 more rapid than the transient decay reaction.

The rate of decay of the photolysis transients from I, II, III, and IV is dependent upon the presence of oxygen in the solutions as well as on the pH. Oxygen increases the fading rate markedly in the more basic solutions, while it has only a small effect in the lower pH range. Since the photochromic repeatability is better in the absence of oxygen and in less basic solutions, it appears that oxygen enhances nonreversible reactions of the *aci*-nitro anions, and that these compete with the reversible protonation reaction. Our attempts to check the photochromic mechanism by carrying out photolyses in D_2O have as yet been inconclusive because of analytical difficulties in the infrared analysis of the C–H and C–D bands in these acids. However, the starting material has been recovered in high yield after long periods of photolysis in the lower pH range.

Acknowledgment. The authors are indebted to the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1264, for financial support.

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(6) It is convenient to consider this as a proton transfer in an excited-state acid–base reaction, but a hydrogen atom transfer could give the same results.

(7) A. F. Scott, Ed., "Survey of Progress in Chemistry," Vol. 2, Academic Press Inc., New York, N. Y., 1964, p 81.

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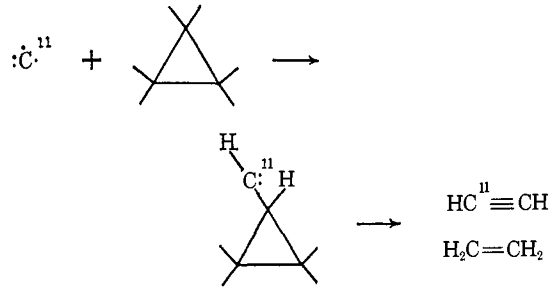
The Reactions of Cyclopropylcarbinyl Carbene Produced Photolytically in the Gas Phase[1]

Sir:

The reactions of energetic carbon atoms with cyclopropane produce acetylene and ethylene as major products.[2] It was suggested[2] that the carbon atom in colliding with a cyclopropane molecule inserts in a C–H bond yielding a short-lived cyclopropylcarbinyl carbene which by simple electronic rearrangement decomposes to give acetylene and ethylene.

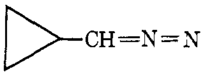


(1)

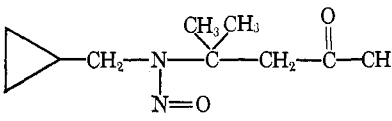
The cyclopropane system is particularly well suited for energetic carbon atom studies because the yields of products are high and the numbers of products produced are small.[3] In particular, bond reorganization reactions[4] and pressure dependence studies[5] have been and are still being carried out on this sytem.

In a recent communication Engel and Skell[6] have reported on the products of reaction between carbon atoms and cyclopropane when these are simultaneously "condensed" on a cold surface. No acetylene or ethylene was obtained as product. Since both the reaction at low temperatures involving carbon atoms on a cold surface and the gas-phase reactions of energetic and discrete carbon atoms presume the intermediacy of cyclopropylcarbinyl carbene, we chose to prepare cyclopropylcarbinyl carbene by a chemical method in which the geometric structure of this intermediate is perhaps less questionable.

Accordingly we have prepared cyclopropyldiazomethane (I)[7] *via* N-nitroso-N-(isobutyl methyl ketone)-N-cyclopropylmethylamine (II). Cyclopropylamine hydrochloride was prepared by the method of Mazur,



I



II

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

(3) For a review of energetic carbon atom reactions, *cf.* (a) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 202 (1964); (b) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 99 (1965).

(4) H. J. Ache and A. P. Wolf, "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna, 1964, pp 107–120.

(5) H. J. Ache and A. P. Wolf, *J. Am. Chem. Soc.*, **88**, 888 (1966).

(6) R. R. Engel and P. S. Skell, *ibid.*, **87**, 4663 (1965).

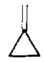
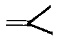
(7) H. A. Moss and F. C. Shulman, *Chem. Commun.*, **12**, 373 (1966), have recently reported the preparation of this compound *via* the nitrosourethan.

Table I. Yields[a] of Products from the Gas-Phase Photolysis of Cyclopropyldiazomethane

c-$C_3H_5CHN_2$ mmole	Total pressure,[b] mm	% yield C_2H_2	C_2H_4		
4.55×10^{-2}	1.38	31.2	31.2	28.8	0.24
3.14×10^{-2}	13.30	31.8	31.8	30.8	0.19
4.73×10^{-2}	93.43	30.7	30.7	31.3	0.19
2.53×10^{-2}	708.7	30.1	30.1	25.3	0.81

[a] Methylenecyclopropane can only be present in low yield, if at all. Another major product (~35% yield) as yet unidentified was obtained by separation on a carbowax column. Yields of each compound are based on the millimoles of starting material. If one includes the unknown compound it can be seen that >90% of the starting material is accounted for. [b] Nitrogen was added to the system to achieve the total pressures listed.

Table II. Products from Reactions Which May Go through Cyclopropylcarbinyl Carbene

System	Phase in which reaction takes place	Major products, % yield HC≡CH	$H_2C\equiv CH_2$				
1. △ + [C] energetic atom;[a] oxygen scavenged	g	49.5	*b*	5	*c*	*c*	*c*
2. △ + [C] energetic atom[d]	l	34.7	*b*	*c*	*c*	*c*	*c*
3. △ + [C] atom on cold[e] surface	s	0	0	0	1	65	18
4. Cyclopropanecarboxaldehyde[f] tosylhydrazone decompn	l	11.5	11.5	5.6	63.5	0	*c*
5. Cyclopropyldiazomethane[g]	g	30.1	30.1	25.3	0.81	0	*c*

[a] *Cf.* ref 2, 4, and 5. [b] The ethylene cannot be detected in the energetic atom case since it is not labeled with carbon-11; *cf.* ref 3. [c] No assay made for these compounds. [d] G. Stöcklin and A. P. Wolf, unpublished results. [e] *Cf.* ref 6. [f] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960), first reported on this compound. Subsequent work on this compound and on closely related systems has amplified the understanding of these reactions: J. A. Smith, H. Schechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965); J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, **87**, 661 (1965), H. M. Frey and D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964), and K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 365 (1965), have also reported on related work. [g] Results from the last row of Table I are used for comparison.

et al.[8] Compound II was prepared from the amine hydrochloride by the method of Adamson and Kenner.[9] The nmr of this product was consistent with the assigned structure. We used the revised method of Adamson and Kenner[9a] to prepare the diazo compound.

Compound I was purified by bulb-to-bulb distillation in a vacuum system (constructed with Teflon stopcocks in order to avoid decomposition of the diazo compound). Compound I is a red-orange liquid[7] which can be successfully put in the gas phase. A well-defined infrared spectrum of the compound was obtained with a diazo band at 2075 cm^{-1} and complex bands centering at 1100 and 745 cm^{-1}. The photolysis of I was accomplished in a Pyrex cylindrical vessel (494 cc) with a water-cooled photolysis well in the center. A Hanovia (No. 654A36) high-pressure lamp was used. Photolysis was complete in 30 min in all cases investigated. The products were separated by glpc and identified by comparison of their infrared spectra with those of authentic samples and by retention times of two glpc columns. Results of the photolyses are given in Table I. A comparison with previous work is shown in Table II.

It is clear from the results shown in Table I that cyclopropylcarbinyl carbene produced in the gas phase decomposes to give acetylene and ethylene. Since a similar product spectrum is observed in both gas- and liquid-phase reactions of cyclopropane with energetic carbon atoms it is reasonable to suppose that the structures of the short-lived intermediates produced are similar.

It has been suggested[10] that acetylene produced from the energetic carbon atom plus ethylene reaction arises primarily by the insertion of a triplet carbon atom into the C–H bond with subsequent decomposition of the adduct. The spin state of the carbon atom which inserts into the C–H bond of an alkane is an open question.[3]

A number of factors will determine the fate of a carbene such as cyclopropylcarbinyl carbene formed in a hot-atom reaction. Among these are the spin state of the carbene itself, the vibrational energy in the carbene and whether that energy is localized or equilibrated before decomposition takes place, and the general relation between total energy content of the intermediate and the function of a third body in the product-determining reaction.

The photochemically produced carbene herein described is probably a mixture of the low-lying triplet and singlet states. A detailed study of the photochemically produced cyclopropylcarbinyl carbene should be most fruitful in facilitating the elucidation of the mechanism involved in the hot-atom case.[11] For example, if further research on the photochemical case should prove that *only* the *singlet* carbene leads to acetylene and ethylene, then doubt can be raised as to whether attack by an energetic triplet carbon atom is involved in the hot-atom case.[12]

It is probable that the photolytically produced carbene is energetically different from the carbene

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(8) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

(9) (a) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 1551 (1937); (b) *ibid.*, 286 (1935).

(10) J. Dubrin, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4747 (1964).

(11) Detailed pressure dependence studies, bond reorganization reactions, and scavenger reactions are being used in the energetic atom case to further explore the carbon atom reaction. Bond reorganization, scavenger, pressure, moderator, and wavelength studies are being applied to the gas-phase reactions of cyclopropyldiazomethane.

(12) The same reasoning applies to the converse case. The simplest explanation would argue for spin conservation in the insertion–decomposition sequence. It must also be pointed out that spin conservation can occur but is not *a priori* demanded in the hot-atom case. Furthermore it needs to be shown that no multiplicity change takes place during the lifetime of the intermediate.

produced in the heterogeneous reaction of Engel and Skell.[6,13] Present evidence from a consideration of the energetic atom case, the condensed-phase surface reaction, and the photolytic case would suggest that a proper combination of spin state and kinetic energy will allow a carbon atom to insert in a C–H bond.

[13] Other things being equal, any spin restriction in the product-determining step would apply to all three methods of producing cyclopropylcarbinyl carbene.

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Microbiological Synthesis of 16-Keto Steroids from Steroidal Sapogenins

Sir:

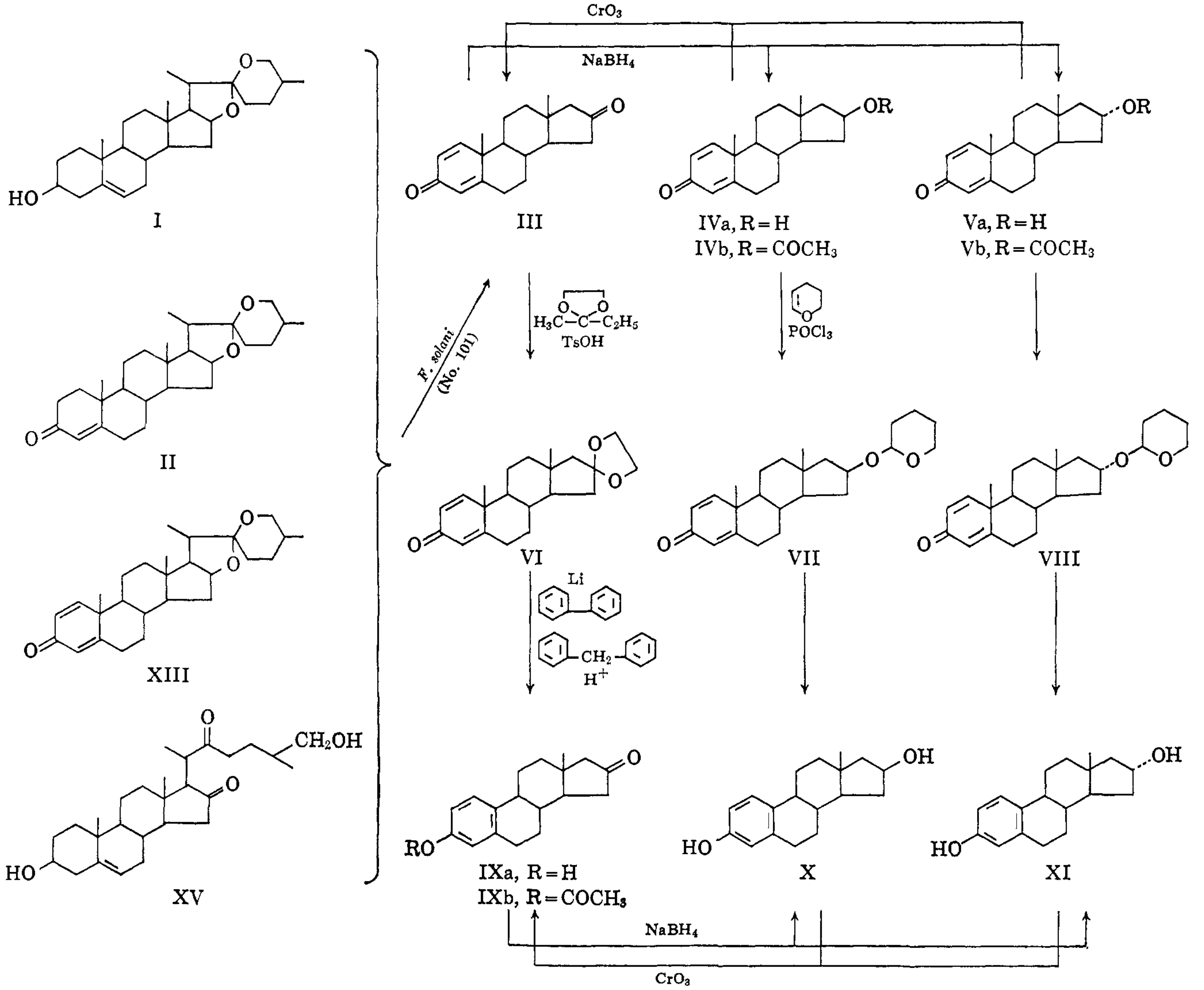
It has long been known that the steroidal sapogenins are good sources for chemical preparation of steroidal hormones. As far as the microbiological utilization of sapogenins is concerned, however, only a few investigations have been reported.

Mininger and his co-workers[1] attempted to transform commonly occurring sapogenins with microorganisms and concluded that steroidal sapogenins are not readily attacked. The first successful microbiological hydroxylation (7β and 11α) of diosgenin (I) was reported by Hayakawa and Satoh.[2] Dehydrogenation of I to form 25D-spirost-4-en-3-one (II, diosgenone) and 25D-spirosta-1,4-dien-3-one (XIII, 1-dehydrodiosgenone) was recently announced by Iizuka and Iwafuji.[3]

We wish to report a new microbiological transformation of sapogenins dealing with the degradation of the spiroketal ring in the initially formed Δ^1-dehydrogenation products (Scheme I).

Incubation of II with *Fusarium solani* (No. 101)[4] afforded three crystalline compounds, III, IVa, and Va, in yields of about 65, 5, and 5%, respectively. These compounds were also obtained from I, but the yields were very low. Analytical samples showed the following constants:[5] III ($C_{19}H_{24}O_2$), mp 140–141°, $[\alpha]^{24}D$ −204.2°, $\lambda_{max}^{95\% EtOH}$ 245 mμ (ϵ 15,400), ν_{max}^{Nujol}

Scheme I



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[1] R. F. Mininger, M. E. Wall, R. G. Dworschack, and R. W. Jackson, *Arch. Biochem. Biophys.*, **60**, 427 (1956).

[2] S. Hayakawa and Y. Satoh, *J. Org. Chem.*, **28**, 1742 (1963).

[3] H. Iizuka and Iwafuji, Meeting of the Agricultural Chemical Society, Japan, April 1965.

[4] The medium consisting of 3.5% glucose, 2% peptone, and 0.3% corn steep liquor is suitable for growth.

[5] Elemental analyses of the described compounds gave satisfactory values. Unless otherwise noted, optical rotations were determined in chloroform containing 1% ethanol.