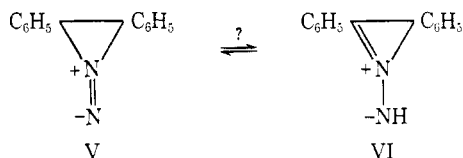


cis-stilbene is not isomerized under the reaction conditions there is no certainty that the *cis*-azamine intermediate (V) is not isomerized to the *trans* isomer prior to fragmentation. A possible intermediate which could account for such an isomerization is the azirine imine VI. Related species have been implicated in other



reactions of azamines,¹⁸ although the mild conditions used in the present oxidation would appear to discount this possibility. Evidence on this point is being sought through deuterium-substitution studies as well as by generation of VI in other ways.

Of perhaps greater novelty than their oxidative behavior is the fact that both *cis*- and *trans*-I undergo thermal fragmentation readily. As expected¹⁹ the *trans*-N-aminoaziridine is less stable than the *cis* isomer and undergoes decomposition to *trans*-stilbene on attempted recrystallization from ethanol or by brief heating at the melting point. Experiments are under way to determine whether the transient by-product of this fragmentation is the long-sought hydronitrogen, azamine (H₂NN).

Acknowledgment. This study was supported by a grant (GP-4283) from the National Science Foundation.

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(19) A similar marked difference in stability has been observed for the corresponding episulfones.¹⁰ The difference can be rationalized on the basis of smooth fragmentation, in the case of the *trans* isomer, to the highly conjugated *trans*-stilbene system.

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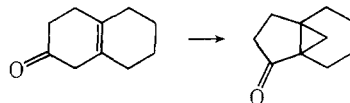
Photochemical Rearrangement of an Acyclic β,γ -Unsaturated Ketone to a Conjugated Cyclopropyl Ketone. An Oxa-di- π -methane Rearrangement¹

Sir:

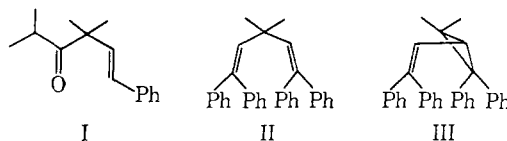
The photochemistry of 1,3-dienes and their related α,β -unsaturated ketone analogs has been studied in order to correlate the mechanistic aspects of the two chromophores.^{2,3a} In continuation of this type of investigation, we wish to report the photochemical rearrangement of β,γ -unsaturated ketone (I) to α,β -cyclopropyl ketone (VIII), a rearrangement which is directly analogous to the di- π -methane rearrangement found in 1,4-dienes (II to III).^{3b} Furthermore, the rearrangement of I to VIII occurred only on sensitized irradiation, and the absence of acyl cleavage or de-

carbonylation products under such conditions suggests a mechanism involving initial vinyl-carbonyl bridging. In striking contrast, direct irradiation of I gave isomeric ketone IV and decarbonylation products V-VII. In ketone photochemistry, such a clean separation of reaction pathway depending upon method of excitation is rarely found.

Various β,γ -unsaturated ketones upon irradiation rearrange to cyclopropyl-conjugated ketones.⁴⁻¹² It



has been suggested^{6,11} that such a rearrangement proceeds *via* initial ketonic α cleavage but doubts have been cast on the occurrence of *free radical* intermediates in the rearrangement step.¹² Recently, the rearrangement of benzobicyclo[2.2.0]octadienone has been suggested to proceed *via* carbonyl-vinyl bridging.¹³ To investigate the possibility of the generality of an "oxa-di- π -methane" rearrangement pathway for all β,γ -unsaturated ketones, the photochemistry of the acyclic 1-phenyl-3,3,5-trimethylhex-1-en-4-one (I), a ketone structurally similar to the diene II which has been shown to undergo a di- π -methane rearrangement to III,^{3b} has been examined.



The starting ketone I was prepared in the following manner. Selective oxidation of 2,2,4-trimethyl-3-hydroxyvaleraldehyde (aldol of isobutyraldehyde) with a sixfold excess of isolated dry CrO₃-(pyridine)₂ complex in methylene chloride at room temperature^{14,15} yielded 2,2,4-trimethyl-3-oxovaleraldehyde. This aldehyde upon reaction with benzylidenetriphenylphosphorane yielded a *cis-trans* (1:1) mixture of I; I_c and I_t were separately characterized by their uv, ir, nmr, and mass spectral properties.

The rearrangement of 1,4-diene II to cyclopropane ene III proceeded under both direct and sensitized irradiation conditions, the process being more efficient under direct irradiation conditions.^{3b} The related "oxa-di- π -methane" rearrangement of ketone I would not be expected to proceed by direct irradiation, however, since under such conditions β,γ -unsaturated ketones are known to undergo facile ketonic α cleavage^{7,12} and decarbonylation.¹⁶ Indeed, when I was directly

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(5) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967).

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(7) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, **90**, 5153 (1968).

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(9) J. Ipaktschi, *Tetrahedron Lett.*, 215 (1969).

(10) K. Kojima, K. Sakai, and K. Tanabe, *ibid.*, 1925 (1969).

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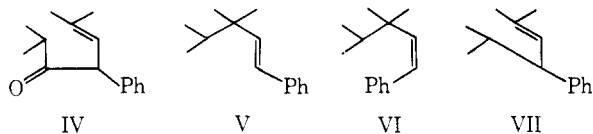
(16) J. E. Starr and R. H. Eastman, *ibid.*, **31**, 1393 (1966).

(1) This work was supported in part by Public Health Service Grant No. AM 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

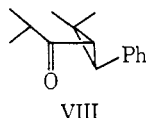
(2) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967).

(3) (a) W. G. Dauben and W. A. Spitzer, *ibid.*, **90**, 802 (1968); (b) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969), and references cited therein.

irradiated in ethanol using a mercury source and a Pyrex filter, the isomeric photoproduct IV formed; prolonged irradiation gave the decarbonylation products V–VII.

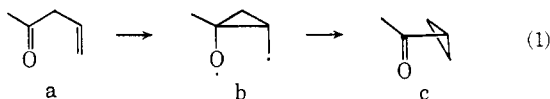


When 1 g of I [$\lambda_{\text{max}}^{\text{EtOH}}$ 248 nm (ϵ 9300), 284 nm (ϵ 47), 292 nm (ϵ 89); I_2 , $\lambda_{\text{max}}^{\text{EtOH}}$ 253 nm (ϵ 14,950), 285 nm (ϵ 292), 293 nm (ϵ 376)] was irradiated in 100 ml of benzene using a Nonex filter ($\lambda > 310$ nm) and 25 ml of acetophenone as a sensitizer (E_t 74), it disappeared at a much slower rate than under direct excitation conditions. After 60 hr all the starting material had been consumed, and a single isomeric photoproduct, *trans*-2,2-dimethyl-3-phenylcyclopropyl isopropyl ketone (VIII), was obtained in 93% yield. Careful monitoring of the course of the photolysis by glpc showed that no other products, such as IV through VII, were ever formed in detectable amounts. The spectral properties of VIII are as follows: nmr (δ , CCl_4), 7.00 (5 H, s, phenyl), 2.67 (1 H, sept, $J = 7$ cps, $-\text{CH}-(\text{CH}_3)_2$), 2.47 (2 H, q, $\delta_A - \delta_B = 0.56$ ppm, $J_{AB} = 6$ cps, *trans*-cyclopropyl), 1.20 (3 H, s, methyl), 1.10 (6 H, $J = 7$ cps, $-\text{CH}-(\text{CH}_3)_2$), 1.06 (3 H, s, methyl); ir (CCl_4) 1700 cm^{-1} ; uv max (EtOH) 220 nm (ϵ 11,700); mass spectrum (m/e) 216 (parent ion), 145 (base peak). The rearrangement of I to the cyclopropyl ketone VIII also



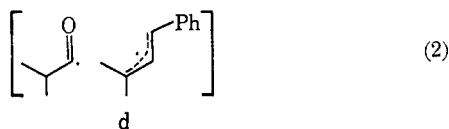
proceeded when benzophenone (E_t 69) and 1-acetonaphthone (E_t 56) were used as sensitizers.

The direct analogy between the photochemical rearrangement of β,γ -unsaturated ketone I and its 1,4-diene analog II suggests similar mechanisms for the two processes (eq 1 for the ketone): (1) vinyl–carbonyl bridge-



ing of a to give biradical b, (2) radical rearrangement and reclosure of b to cyclopropane c.¹⁷

It has previously been suggested that rearrangements of β,γ -unsaturated ketones to cyclopropyl-conjugated ketones proceed *via* ketonic α cleavage (see eq 2) to a biradical d which then recloses at the center of the allylic



system. From an energetic standpoint, bonding to the central carbon of an allylic system or the rearrangement

(17) Normally, all β,γ -unsaturated ketone rearrangements to cyclopropyl ketones stem from the triplet state.¹² Since in any synchronous rearrangement process, the multiplicity of the state should not change, [$\sigma^2 + \pi^2$] cycloaddition mechanisms require that the product be formed in the triplet state. Such is not energetically possible in the rearrangement of I to VIII and thus a stepwise process seems indicated.

of an allyl radical to a cyclopropyl radical is the least favorable of the pathways available to radical species d. Closure of this species to give compounds I and IV would be expected to take precedence.¹⁸ The absence of formation of a detectable amount of IV in the sensitized excitation and the effective use of a low energy sensitizer (E_t 56) further indicate that an initial acyl cleavage is not likely and that 2,4 bonding between the carbonyl and vinyl groupings¹⁹ precedes α cleavage.

The concept of the oxa-di- π -methane process can be extended to 2,4-cyclohexadien-1-ones which rearrange, photochemically, to a bicyclo[3.1.0]hex-3-en-2-one ring system.⁸ Furthermore, initial formation of a 2,4 bond in a variety of 1,4-di- π systems appears to be a general phenomenon, a typical example being the ring closure of an acyclic 4,6-heptadien-2-one.^{20,20a}

(18) O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46**, 1317 (1968).

(19) Formally nonconjugated β,γ -unsaturated ketone systems exhibit remarkable uv, cd, and ORD properties, indicating an interaction between the double bond and the carbonyl moiety (see D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., B*, 215 (1967), and references cited therein). The concept of 2,4-carbonyl–vinyl bridging in the photochemistry of such systems is in accord with these spectral properties.

(20) J. Meinwald and J. W. Kobzina, *J. Amer. Chem. Soc.*, **91**, 5177 (1969).

(20a) NOTE ADDED IN PROOF. Since the submission of this manuscript, the possibility of vinyl–carbonyl 2,4 bridging has also been suggested by K. Schaffner and coworkers, *Helv. Chim. Acta*, **52**, 2436 (1969).

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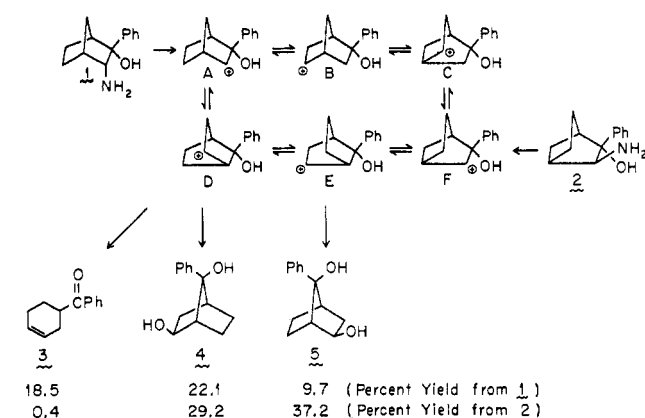
Received December 22, 1969

Anion Control of Stereoselectivity During Deaminations¹

Sir:

We wish to report a striking difference in stereoselectivity exhibited by presumably identical carbonium ions (D in Chart I) which have been indirectly formed during

Chart I



the deaminations of two different reactant amines (1 and 2). We tentatively ascribe this stereoselectivity to partial control of product formation by the counter-

(1) (a) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.; (b) presented in an address to the Gesellschaft Deutscher Chemiker, Ortsverband Süd-Württemberg, Tübingen, May 30, 1969.