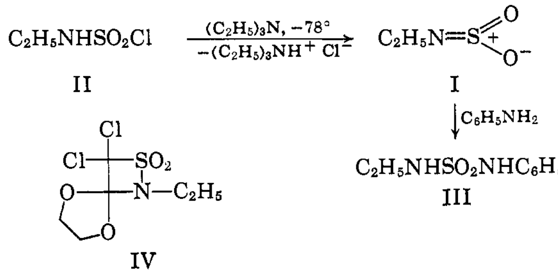
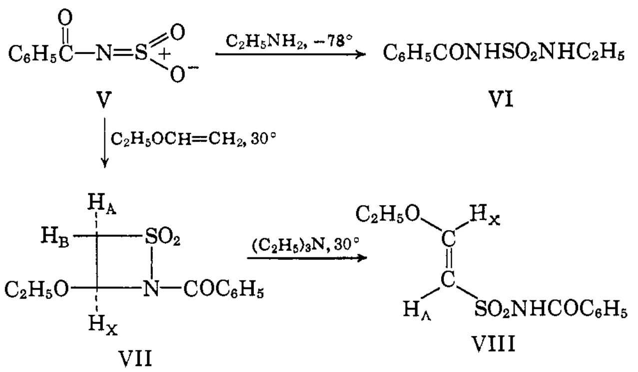
The generation of I at room temperature in the presence of 2-(dichloromethylene)-1,3-dioxalane[5] affords a nearly quantitative yield of a cycloadduct, mp 74–75°, assigned the 1,2-thiazetidine 1,1-dioxide structure IV.[6]



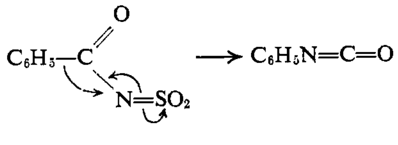
The mass spectrum of IV displayed a molecular ion[7] at *m/e* 262 and prominent ions at *m/e* 107 ($C_2H_5NSO_2^+$) and 154 ($C_4H_4O_2Cl_2^+$) resulting from 1,4 and 2,3 bond cleavage only; therefore our proposed orientation of this cycloadduct rests upon the mechanistic consideration that the transition state polarization of I is $-\bar{N}-S^+O_2$.

More electrophilic[8] N-sulfonylamines such as N-sulfonylbenzamide (V) were prepared in toluene solution at −78° in an analogous manner from benzoylsulfamoyl chloride.[9] The existence of V was likewise established by the formation of N-benzoyl-N′-ethylsulfamide[3] in 66% yield upon quenching with ethylamine at −78°.[10]



The formation of V in the presence of excess ethyl vinyl ether at 30° in benzene solution affords a 71% yield of a cycloadduct, mp 87–88°, for which structure VII is proposed based on the following evidence. The nmr spectrum ($CDCl_3$, 60 Mc) displayed quartets for H_A, H_B, and H_X centered at τ 6.53, 6.20, and 4.07, respectively, with J_{AB} = 14 cps, J_{AX} = 9 cps, and J_{BX} = 3 cps, and the molecular ion appeared at *m/e* 255 in the mass spectrum. Treatment of VII with a benzene solution of triethylamine at 30° provided in nearly quantitative yield an isomer, mp 135–136°, assigned structure VIII.[11] The nmr spectrum ($CDCl_3$, 60 Mc) of VIII indicated a doublet for H_X centered at τ 4.08 coupled (J = 12 cps) with H_A, whose absorption was superimposed on the aromatic and imide proton signals at τ 2.1–2.7. This evidence supports the structural assignment and establishes the orientation of the cycloaddition reaction leading to VII.

If a toluene solution of V at −78° is allowed to warm to room temperature in the absence of a trapping agent exclusive rearrangement to phenyl isocyanate[3] occurs. It is interesting to speculate that this reaction may represent an α elimination of sulfur dioxide, *i.e.*



Studies are in progress on the synthetic usefulness of N-sulfonylamines in elaborating small-ring heterocycles.

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[5] S. M. McElvain and M. J. Curry, *J. Am. Chem. Soc.*, 70, 3781 (1948).

[6] Satisfactory elemental analyses were obtained for all new compounds reported herein.

[7] The appearance of a M + 2 and M + 4 ion resulting from the possible isotopic combinations substantiated the dichloro assignment for IV.

[8] N-Sulfonylethylamine fails to react at room temperature with olefins of low nucleophilicity such as ethyl vinyl ether.

[9] Prepared by the interaction of chlorosulfonyl isocyanate and benzoic acid in benzene solution. See ref 4, p 700.

[10] Currently under investigation is the possibility that the reactive species present is the triethylamine adduct, $C_6H_5CO\bar{N}-SO_2N^+(C_2H_5)_3$. Analogous adducts of certain sulfenes have been reported recently by G. Spitz and D. Bucher, *Tetrahedron Letters*, 43, 5263 (1966).

[11] This imide was isolated as the triethylamine salt which was converted to VIII upon silica gel chromatography. This salt also results from the reaction of ethyl vinyl ether with VI in the presence of excess triethylamine.

Photoreduction of Acetone by Tributylstannane

Sir:

The intermediacy of the triplet states of ketones in their photoreductions is so well established[1–3] that there has been some doubt whether the corresponding excited singlet states have any chemical reactivity in bimolecular reactions in solutions. When it became clear that aliphatic ketones undergo type-II photoelimination from both singlet and triplet excited states,[4] we suggested[5] that the n,π^* excited singlet states of carbonyl compounds may in general be just as reactive

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[1] (a) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961); (b) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); (c) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962); (d) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

[2] G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

[3] P. J. Wagner, *ibid.*, **88**, 5672 (1966).

[4] (a) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); (b) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

[5] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

as the corresponding triplet states but not undergo bimolecular reactions simply because the competing intersystem-crossing process is too rapid. If a bimolecular singlet-state photoreaction is to be observed, it seems obvious that both a very reactive substrate and a ketone with a low rate of intersystem crossing are necessary. Consequently, the photoreduction of acetone by tri-*n*-butylstannane has been studied.

Degassed hexane solutions containing 0.75 M acetone, 0.005 M fluorobenzene as internal standard, 0.38 M freshly prepared tri-*n*-butylstannane, and various concentrations of 2,5-dimethyl-2,4-hexadiene (0–0.10 M) or 1,3-pentadiene (5 M) were subjected to equal intensities of 3130-A radiation. Quantum yields of 2-propanol formation were then determined by glpc analysis. Quite unexpectedly, it developed that a slow dark reaction produces isopropyl alcohol, or at least a compound with the same retention time on a FFAP glpc column, even in the presence of diene. It was at first assumed incorrectly that this unquenchable alcohol formation indicated some singlet photoreduction. However, in experiments in which analysis was performed immediately after irradiation, only traces of alcohol could be detected in samples containing 5 M diene and as much as 1.5 M stannane. Photochemical conversion of acetone to 2-propanol proceeded with unit quantum yield in samples containing no quencher. The 2-hydroxy-2-propyl radical initially formed apparently abstracts a hydrogen atom from a second stannane molecule with very high efficiency. In solutions containing 5 M diene, the quantum yield of 2-propanol formation was <0.01 for both 0.38 and 1.5 M stannane. Moreover, the quantum yield of acetone disappearance was negligible at high piperylene concentrations, indicating that the dienes quench by triplet energy transfer rather than by trapping of intermediate radicals. The possibility of singlet quenching is eliminated by our observation[4] that singlet type-II reactions are not quenched by dienes and by Rebbert and Ausloos' report that dienes do not quench the fluorescence of acetone.[6] Stern–Volmer plots of relative quantum yields yielded a straight line, with a slope equal to $k_q/0.38k_{3h}$, where k_q is the bimolecular rate constant for quenching and k_{3h} is the bimolecular rate constant for hydrogen abstraction from the stannane by triplet acetone. The values of the slope were 32.5 and 29.1 M^{-1} in two separate runs.

That acetone should be photoreduced only from its triplet state by moderately high concentrations of tri-*n*-butylstannane becomes quite striking when the magnitudes of the relevant rate constants are considered. A 10% hexane solution of the stannane is only slightly more viscous than hexane itself, so that k_q can be estimated to equal 1×10^{10} M^{-1} sec^{-1}.[5] The value of k_{3h} thus indicated by the Stern–Volmer slopes is 8×10^8 M^{-1} sec^{-1}. This very large number is not too surprising in view of the ability of the stannane to photoreduce acylnaphthalenes[2] and greatly exceeds the measured rate of decay of triplet acetone in hexane alone,[3,7,8] 1×10^6 sec^{-1}. The actual rate of reaction of triplet acetone with 0.38 M stannane is 3.2×10^8 sec^{-1}. If the rate of intersystem crossing (isc) of acetone is 4×10^7 sec^{-1},[9] and if singlet acetone were just as reactive as triplet acetone, then a quantum yield of unquenchable singlet photoreduction equal to 0.89 ought to be observed. However, since $\Phi_S < 0.01$, even at 1.5 M stannane concentration, $k_{1h} < 0.01$ k_{isc}. Borkman and Kearns estimated k_{isc} as 4×10^7 sec^{-1} from the integrated absorption intensity of acetone and from their measured fluorescence quantum yield in solution of 0.01.[9] Heicklen and Noyes have reported that the quantum yield of acetone fluorescence in the gas phase at 40° is 0.002.[10] There is no reason to suspect that the radiative lifetime estimated from the integrated absorption intensity is in error by more than a factor of 2,[11] and thus it does not seem likely that k_{isc} for acetone exceeds 2×10^8 sec^{-1}. Nor does it seem possible that the stannane might be producing a heavy-atom enhancement of k_{isc}, since theory predicts[12] and experiment confirms[13] that n,π* excited states are not very susceptible to heavy-atom effects. If k_{1h} were to equal k_{3h}, k_{isc} would have to equal at least 10^{11} sec^{-1}. It seems much more likely that the lack of singlet-state reaction is caused by k_{1h} being smaller than 10^6 M^{-1} sec^{-1}, so that it must be concluded that *excited singlet acetone is appreciably less reactive than triplet acetone.*

If excited singlet acetone is only $^1/_{1000}$ as reactive as triplet acetone in hydrogen-abstraction reactions, such should be the case with other aliphatic ketones, in which case the already mentioned intermediacy of both excited states in type-II processes[4,5] requires a new explanation. From the measured singlet-state quantum yields and triplet-state lifetimes of 2-pentanone and of 2-hexanone,[4,5] an assumption of equal reactivity in both states yields an estimate of 3×10^9 sec^{-1} for k_{isc}. This value is larger than what might have been extrapolated from the published value for acetone[9] but convincingly smaller than the value for acetone which results from the assumption of equal singlet and triplet state reactivity. Fortunately, it remains highly possible that type-II photoelimination may proceed by different mechanisms in the two excited states, namely by a concerted six-center process in the singlet and by a perhaps faster intramolecular hydrogen abstraction in the triplet.

There is no good theoretical explanation for n,π* excited states of different multiplicities having different reactivities, and as long ago as 1958 Robinson predicted from a high-resolution spectroscopic investigation of formaldehyde that the two states should have similar reactivities.[14] The prediction was based on the very similar electronic distribution in the two excited states. However, with a little hindsight it might be noted that triplet formaldehyde—and presumedly other carbonyl compounds—comes much closer to assuming a pyramidal (tetrahedral) geometry than does the singlet state.[14] Walling and Gibian have demonstrated the close parallel between the reactivities of

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(6) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 5569 (1965).

(7) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

(8) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(9) R. F. Borkman and D. R. Kearns, *ibid.*, **44**, 945 (1966).

(10) J. Heicklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1959).

(11) *E.g.*, W. R. Ware and B. A. Baldwin, *J. Chem. Phys.*, **40**, 1703 (1964).

(12) M. A. El-Sayed, *ibid.*, **41**, 2462 (1964).

(13) P. J. Wagner, *ibid.*, **45**, 2335 (1966).

(14) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958).

ketone triplet states and of alkoxy radicals,[15] and the most simple minded appraisal might suggest that the alkoxy radical character of the triplet ketone is closely associated with its tetrahedral geometry.

Acknowledgment. Grants from the American Chemical Society Petroleum Research Fund and the National Science Foundation provided financial support for this work, and Dr. William Reusch provided useful discussion.

[15] C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

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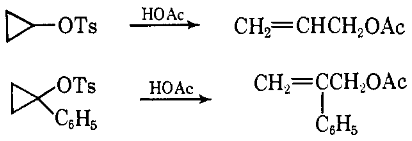
1-Chlorobicyclopropyl. Evidence for the Formation of a Cyclopropanol during the Hydrolysis of a Cyclopropyl Halide

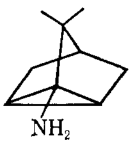
Sir:

We wish to report unprecedented examples of solvolyses of a simple cyclopropyl derivative which result in products that arise from the attack of solvent on an intermediate ion in which the cyclopropane ring is still intact.

Because of the facile rearrangement of the cylopropyl to the allyl carbonium, ion, the only products that have ever been observed in the solvolyses of variously substituted cyclopropyl derivatives have been the open-chain allylic structures.[1,2]



Although reports have appeared that the nitrous acid deamination of apotricyclylamine (**1**),[3] 1-aminonortricyclene (**2**),[4] and 3-amino-1,2-cyclopropanoacenaphthene (**3**)[5] resulted in unrearranged products, the explanation for the lack of rearrangement has been based either on considerations of orbital symmetry during the electrocyclic transformation to the allylic structure[2b,6] or on the assumption that the mechanism may have been free radical in nature[7] rather than involving a carbonium ion.[8]



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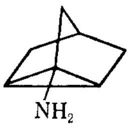

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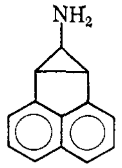
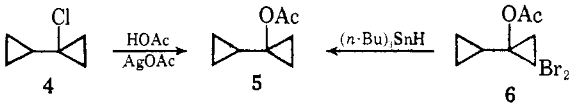
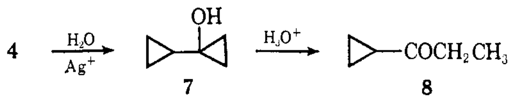


3

In the present study, 1-chlorobicyclopropyl (**4**) was prepared in an over-all yield of 30–44% by vapor phase chlorination of the parent hydrocarbon followed by distillation of the monochloride product fraction which contained about 89% of the desired material.[9]



The acetolysis of chloride **4** in the presence of silver acetate at 115° for 72 hr produced a mixture of products from which a 42.6% component was isolated and identified as the unrearranged 1-acetoxybicyclopropyl (**5**). A direct infrared spectral comparison with a sample prepared by the addition of dibromocarbene to the enol acetate of methyl cyclopropyl ketone, followed by reduction of the resulting dibromoacetate **6** with tri-*n*-butyltin hydride, confirmed the assignment of structure.[10] In a similar experiment, the silver ion assisted hydrolysis of **4** (65°, 24 hr) produced a mixture of several compounds, of which the major component (65%) was identified as ethyl cyclopropyl ketone (**8**) by spectral comparison of the collected peak (vpc) with an authentic sample. No other single component of the product mixture represented more than 24%.[11] In view of the acetolysis results, the presence of ketone **8** as the major product can be readily explained by assuming that 1-bicyclopropanol (**7**) is formed initially and then undergoes an acid-catalyzed ring opening to the ketone, the latter reaction having been well established for a variety of 1-substituted cyclopropanols.[12] If instead of undergoing an attack by water, the initially formed carbonium ion had opened to produce the allylic ion, a process of the type which occurs to the exclusion of all others during the solvolyses of other cyclopropyl derivatives, the expected product would have been β-cyclopropylallyl alcohol, a compound which may yet be identified as a minor constituent of the product mixture.



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[1] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

[2] (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965); (b) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

[3] P. Lipp and C. Padberg, *Chem. Ber.*, **54B**, 1316 (1921).

[4] H. Hart and R. H. Martin, *J. Am. Chem. Soc.*, **82**, 6362 (1960).

[5] R. Pettit, *ibid.*, **82**, 1972 (1960).

[6] S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **88**, 4007 (1966); R. B. Woodward and R. Hoffman, *ibid.*, **87**, 395 (1965).

[7] K. V. Scherer, Jr., and R. S. Lunt, III, *ibid.*, **88**, 2860 (1966).

[8] In the original explanation of the behavior of **2** and **3** by Hart,[4] it was assumed that the unrearranged product formed from the collapse of a diazonium ion pair directly to the product.

[9] Chloride **4** gave the correct analysis for C_6H_9Cl and an nmr spectrum consistent only with the assigned structure.

[10] The nmr spectrum of **5** showed only complex multiplets from τ 8.0 to 8.6 and 9.0 to 9.9 and a sharp singlet at 8.1.

[11] Several other products have only been tentatively identified and will be discussed in detail in a subsequent publication.

[12] C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Am. Chem. Soc.*, **88**, 3347 (1966), and references cited therein.