similarity between its subsequent fragmentation and that of the benzofuran molecular radical cation.[2] We wish to emphasize that structural conclusions so reached must be accepted cautiously.

As an instance where similar indirect evidence leads to a demonstrably erronous conclusion, the electron impact fragmentation of 2-pyrone (I) is cited. 2-Pyrone, on electron impact, loses carbon monoxide[3,4] to yield abundantly a $C_4H_4O$ radical cation whose subsequent fragmentation leads to a mass spectrum similar to that of furan.[5] From this, it could be inferred that the $C_4H_4O$ radical cation has the furan structure II, for which a number of canonical resonance structures may be written. Most of these resonance structures place the positive charge on oxygen, a comparitively stable arrangement. It is generally accepted that the formation of stable oxonium ions plays an important role in controlling fragmentation processes[6a,b]; therefore, a priori, II seems quite reasonable. However, deuterium labeling studies clearly show the $C_4H_4O$ radical cation does not have structure II.[7]



II
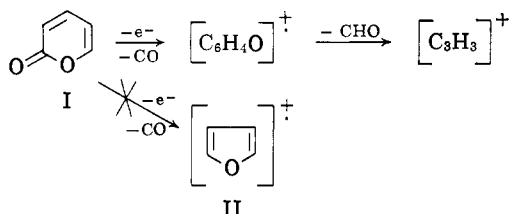
In the mass spectrum of 2-pyrone, the most abundant fragment is a $C_3H_3$ cation[8] formed either by loss of a formyl radical[9] or by stepwise loss of carbon monoxide[4] and a hydrogen atom from the $C_4H_4O$ radical cation.

(2) While this assignment may be correct, it must be pointed out that the structure of the benzofuran radical cation is itself unknown.

(3) It appears likely that it is the carbonyl which is expelled. While no direct evidence of this is presently offered, there is ample precedent for it [J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, 63, 1861 (1959); J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, 85, 1739 (1963); C. Djerassi, et al., *Tetrahedron*, 19, 2247 (1963); P. Beak, T. H. Kinstle, and G. A. Carls, *J. Am. Chem. Soc.*, 86, 3833 (1964)].

(4) The metastable peak for this transition is observed.

(5) The formation and subsequent fragmentation of a substantial amount of M − 1 ion complicates somewhat the mass region of interest. However, the observation that all peaks in the furan spectrum are present in at least as great an intensity in the 2-pyrone spectrum and the exact correspondence of all furan metastable peaks (masses 22.4, 23.7, 25.8, 35.2, and 38.8) with those observed in the same region of the 2-pyrone spectrum is strong evidence for the similarity of fragmentation paths of the furan molecular ion and the $C_4H_4O$ ion derived from 2-pyrone.

(6) (a) C. H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structural Elucidation of Natural Products by Mass Spectroscopy," Vol. 2, Holden-Day, Inc., San Francisco, Calif., 1964; (b) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p. 315.

(7) In a paper which has appeared since the completion of this work [H. Nakata, Y. Hirata, and A. Tatematsu, *Tetrahedron Letters*, No. 2, 123 (1965)] the claim is made that explusion of carbon monoxide from the molecular ions of a number of substituted 2-pyrones results in furan-like ions. It is not, however, essential to invoke such ions to account for the fragmentation observed by these workers. In view of the present work, this assumption must be regarded as unwarranted.

(8) Presumably, this ion is the cyclopropenium cation [see F. W. McLafferty in "Determinations of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p. 93, and the paper by K. B. Wiberg, W. J. Bartley, and F. D. Lossing, *J. Am. Chem. Soc.*, 84, 3980 (1962)].

(9) Although both the $C_4H_4O$ and $C_3H_3$ ions give rise to intense peaks, the metastable peak for the transition between them is of rather low intensity. It should be noted, however, that a number of substituted 2-pyrones give rise to substituted cyclopropenium ions in a two-step process with both metastable peaks being easily observed (see Nakata, et al.[7]; W. H. Pirkle, unpublished work.).

**Table I[a]**

| m/e | Furan | 2-Pyrone | 2-Pyrone-3-d | 2-Pyrone-6-d |
|---|---|---|---|---|
| | | Relative intensities (5% or greater) | | |
| 97 | | | 79 | 52 |
| 96 | | 72 | 19 | |
| 95 | | 18 | | 8 |
| 69 | | | 94 | 83 |
| 68 | 85 | 88 | | 13 |
| 42 | 7.4 | 17 | 13 | |
| 41 | | | 39 | 50 |
| 40 | 13 | 32 | 100 | 59 |
| 39 | 100 | 100 | 31 | 100 |
| 38 | 14.5 | 24 | 14 | 42 |
| 37 | 8.3 | 13 | | 34 |
| 29 | 13 | 13 | 12 | 7.0 |
| 28 | | 8.2 | | 17 |
| 27 | | | 5.0 | 15 |
| 26 | | 7.3 | | 8.4 |

[a] Spectra were obtained at 70 e.v. in an Atlas CH 4 spectrometer.

Replacement of either the C-3 or the C-6 hydrogen in 2-pyrone by deuterium would lead, were structure II correct, to the same ion in both instances. The observation of gross differences in the distribution of deuterium among the fragments of these labeled pyrones[10] indicates that the furan ion II is not an important contributor in the fragmentation of 2-pyrone. Moreover, it is obvious from Table I that C-3 deuterium is preferentially incorporated into the cyclopropenium ion while C-6 deuterium is preferentially excluded.

Reduction of ionizing voltage to the appearance potential of the three-carbon ion does not lead to label scrambling. Apparently, the $C_4H_4O$ radical cation does not cyclize to generate a furan-like fragment even when formed with as little excess energy as possible.[11] Whether the $C_4H_4O$ radical cation is acyclic or has closed to yield a formyl-substituted cyclopropene radical cation cannot be determined from the present experiment.[12] Moreover, the significance of the similarity between the mass spectra of furan and the $C_4H_4O$ fragment cannot be stated with certainty. A possible inference is that the furan molecular radical cation is identical with the $C_4H_4O$ fragment from 2-pyrone and hence no longer retains the furan ring.

(10) The synthesis of these specifically deuteriated 2-pyrones will be published elsewhere.

(11) A referee has suggested that accurate appearance potentials of the furan molecular ion and the 2-pyrone $C_4H_4O$ ion would be of interest. Unfortunately, accurate appearance potentials cannot yet be determined in this laboratory.

(12) A referee has suggested that the mass spectra of the two isomeric formylcyclopropenes would be a useful addition to the paper. However, these compounds are as yet unreported.

W. H. Pirkle

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## Kinetic Evidence for 1,3-Diradicals from the Thermal Decomposition of 1-Pyrazolines

Sir:

We wish to present conclusive evidence for the formation of an intermediate in the thermal decomposition of 1-pyrazolines. The trimethylene diradical has been frequently postulated as an intermediate in the thermal
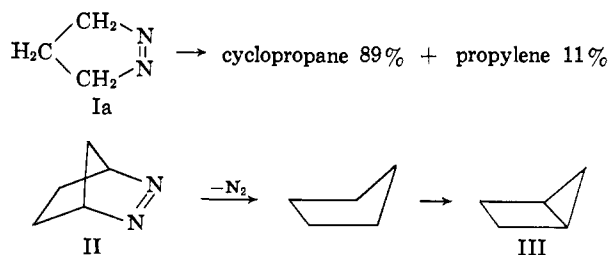
isomerizations of cyclopropane[1]; pyrazolines (I) have also been considered to proceed through 1,3-diradicals on conversion to cyclopropanes,[2] but a concerted process has also been suggested.[3]

1-Pyrazoline was prepared by the silver oxide oxidation of pyrazolidine[4] in methanol at 0° for 15 min. The solids were removed by filtration and the solvent was removed using a Vigreaux column. The residue was distilled at reduced pressure giving a major fraction boiling at 61° (80 mm.), $n^{25}D$ 1.4360; $\lambda_{max}$ 315 m$\mu$ ($\epsilon$ 446, methanol). The compound showed infrared absorption at 1545 cm.$^{-1}$ (N=N), while no absorption appeared in the 3600–3100 and 2700–1600 cm.$^{-1}$ region. The n.m.r. spectrum shows a triplet at $\tau$ 5.73 and a quintet at 8.54 (ratio of areas 2:1, respectively). The product was readily converted by acid or base to the known 2-pyrazoline.[5] All other pyrazolines in Table I were prepared in a similar manner and were further purified by preparative gas chromatography using a 20-ft. Ucon on Fluoropak column.

Table I. Kinetic Parameters

| Substituted 1-Pyrazolines | $E_a$, kcal./mole | $\Delta S^*_{250°}$, e.u. |
|---|---|---|
| Ia, unsubstituted | 42.4 ± 0.3 | 11.2 ± 0.6 |
| b, 3-methyl | 41.0 ± 0.3 | 10.5 ± 0.7 |
| c, 4-methyl | 42.2 ± 0.2 | 10.8 ± 0.5 |
| d, 3,3-dimethyl | 40.0 ± 0.2 | 10.8 ± 0.4 |
| e, 3,5-dimethyl (cis) | 40.3 ± 0.3 | 9.4 ± 0.5 |
| f, 3,5-dimethyl (trans) | 40.2 ± 0.3 | 10.0 ± 0.5 |
| g, 3,3,5-trimethyl | 38.9 ± 0.4 | 8.9 ± 0.6 |
| h, 3,3,5,5-tetramethyl | 37.7 ± 0.4 | 4.6 ± 0.7 |
| II, this work | 36.9 ± 0.3 | 5.7 ± 0.4 |
| II, ref. 2a | 37.3 ± 0.3 | 6.3 ± 0.5 |

The kinetics were measured by following the pressure increase in the range 100–200 mm. at 170–290°. The sample was injected into a stainless steel cell, and the pressure was continuously recorded using the system of Smith.[6] Each compound was measured at six temperatures over a 40° temperature change. First-order kinetics were observed to greater than 95% completion in all cases. The reaction was shown to be independent of the nature of the surface by using a glass ampoule technique and by comparing the rates with that of the previously studied[2a] pyrazoline (II).



$$H_2C \underset{CH_2-N}{\overset{CH_2-N}{\diagup}} \longrightarrow \text{cyclopropane } 89\% + \text{propylene } 11\%$$
Ia



II $\xrightarrow{-N_2}$ → III

The data in Table I indicate a continuous decrease in activation energy as each additional methyl group is placed on to the nitrogen-bearing carbons. The comparison of Ib with Ie and If, and that of Id with Ig and Ih, suggests that both carbon–nitrogen bonds are being ruptured in the transition state. The low activation energy of II in comparison with Ie suggests that strain is relieved in the transition state for II; however, if the process is concerted, to produce bicyclo[2.1.0]pentane (III), the reverse would be expected. The order of reactivity in Table I is the converse of that expected for a dipolar[3] transition state.

The $\Delta S^*$ terms decrease regularly as one proceeds from the pyrazoline that would produce two primary radicals, Ia and Ic, to that producing two tertiary radicals, Ih. This is as would be expected if the transition state in the pyrazoline decompositions more closely resembles the starting materials as we proceed to the ditertiary species.

The product proportions from the 4-methyl-1-pyrazoline are such that a suitable test for the intervention of an intermediate may be carried out.



| | $10^4k$ | | |
|---|---|---|---|
| Ic | 64.1 ± 0.6 sec.$^{-1}$ | 52% | 48% |
| Ic-4-$d_1$ | 59.5 ± 0.6 | 66%[7] | 34% |

$k_H/k_D = 1.07 ± 0.03$

While the rate-determining step has remained essentially unchanged upon deuterium substitution at the 4-position of Ic, the product proportions have changed markedly, a condition requiring the existence of an intermediate. From the rate data in Table I and the experiments with Ic we conclude that the intermediate is the isobutylene diradical (IV) and that the product-determining step is that of hydrogen migration vs. ring closure. That a "hot methylcyclopropane" is not the intermediate is suggested by the products of decomposition of Ic being different from those of Ib (methylcyclopropane 93.3%, cis-2-butene 1.8%, trans-2-butene 1.2%, and 1-butene 3.7%), only isobutene from the former and unbranched butenes from the latter.

The isotope effect in the product-determining step gives a value, $k_H/k_D = 1.80$ (assuming that the isotope
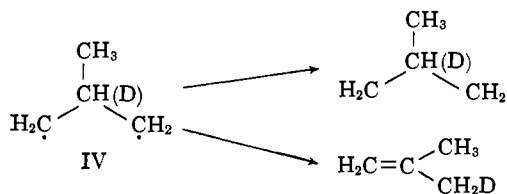


effect in the cyclization process is unity), which is well within the range 1.59–2.36 previously observed[1a] in cyclopropane isomerization studies.

It is of interest to note that the product proportions from the thermal decomposition of Ia are cyclopropane 89% and propylene 11%. This is the same value that one obtains using the data of Setser and Rabinovitch[1a]

(1) (a) D. W. Setser and B. S. Rabinovitch, J. Am. Chem. Soc., 86, 565 (1964); (b) S. W. Benson, J. Chem. Phys., 34, 521 (1961); (c) W. B. DeMore and S. W. Benson, Advan. Photochem., 2, 255 (1964).

(2) (a) S. G. Cohen, R. Zand, and C. Steel, J. Am. Chem. Soc., 83, 2895 (1961); (b) C. G. Overberger, N. Weinshenker, and J. P. Anselme, ibid., 86, 5364 (1964).

(3) T. V. Van Auken and K. L. Rinehart, Jr., ibid., 84, 3736 (1962); D. E. McGreer, et al., Can. J. Chem., 43, 1407 (1965).

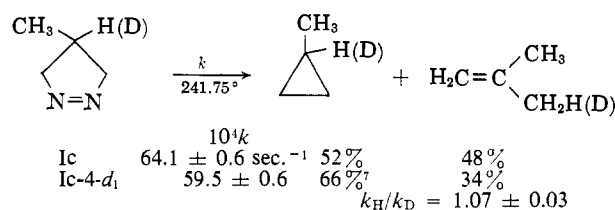(4) E. L. Buhle, A. M. Moore, and F. Y. Wiselogle, J. Am. Chem. Soc., 65, 29 (1943).

(5) A satisfactory elemental analysis was obtained for each new compound reported herein.

(6) G. G. Smith, F. D. Bagley, and R. Taylor, ibid., 83, 3647 (1961).

(7) These results have been corrected, from the observed values of 64 and 36% methylcyclopropane and isobutylene, respectively, for the 17% protium species present in the sample as determined from a 100 Mc. n.m.r. spectrum. The methyl group in the deuterio compound consists of an equal intensity triplet at $\tau$ 9.12 ($J$ = 0.9 c.p.s.).

from the thermal isomerization of *cis*-1,2-dideuterio-cyclopropane and is similar to the product proportions obtained from the addition of methylene to ethylene at high pressures,[8] and suggests that the trimethylene species is an intermediate in these reactions.

(8) B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *J. Am. Chem. Soc.*, **81**, 1083 (1959).
(9) National Research Council of Canada Scholarship holder, 1964–1965.

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## Ozonides from Aldehydic Zwitterions and Acetone

*Sir:*

Recent reports[1-3] have confirmed the implication of the Criegee mechanism of ozonolysis[4] that unsymmetrical olefins should give three ozonide pairs. The formation of two zwitterion and two carbonyl fragments requires the observed results when ·recombination occurs in a random fashion (*e.g.*, see Figure 1). Earlier reports[5] that only a single ozonide is formed under these conditions were regarded as consistent with the over-all mechanism provided that one invoked the operation of a cage mechanism which prevented exchange of zwitterion and carbonyl fragments. The presence and extent of a cage mechanism and its influence on ozonide distribution has been discussed by Loan, Murray, and Story.[3]

The nature of the zwitterion and carbonyl fragments also influences ozonide formation. Thus, while aldehydes react easily with aldehydic zwitterions[5] and can be used to demonstrate the presence of ketonic zwitterions[6] in trapping experiments, it has been reported that *simple ketones do not react with zwitterions*.[5,7,8] This last conclusion appears to be based on the reported failure of tetramethylethylene to give an ozonide upon treatment with ozone.[6] The presence of ketonic zwitterions in this last ozonolysis was confirmed by a trapping experiment with formaldehyde to give isobutylene ozonide.[6] The failure of tetramethylethylene to give an ozonide could be due, however, to the relative nonreactivity of acetone toward a *ketonic zwitterion*. There has been no clear evidence that simple ketones, such as acetone, will not react with *aldehydic zwitterions*. There are a number of reports of reactions of activated, that is, negatively substituted ketones, with zwitterions, to give ozonides.[9] Also, *intramolecular*

(1) O. S. Privett and E. C. Nickell, *J. Am. Oil Chemists' Soc.*, **41**, 72 (1964).
(2) G. Riezebos, J. C. Grimmelikhuysen, and D. A. Van Dorp, *Rec. trav. chim.*, **82**, 1234 (1963).
(3) L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737 (1965).
(4) For a thorough discussion of the mechanism of ozonolysis see P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).
(5) R. Criegee, *Record Chem. Progr.* (Kresgee-Hooker Sci. Lib.), **18**, 111 (1957).
(6) R. Criegee, G. Blust, and H. Zinke, *Chem. Ber.*, **87**, 766 (1954).
(7) G. Lohaus, *Ann.*, **583**, 6 (1953).
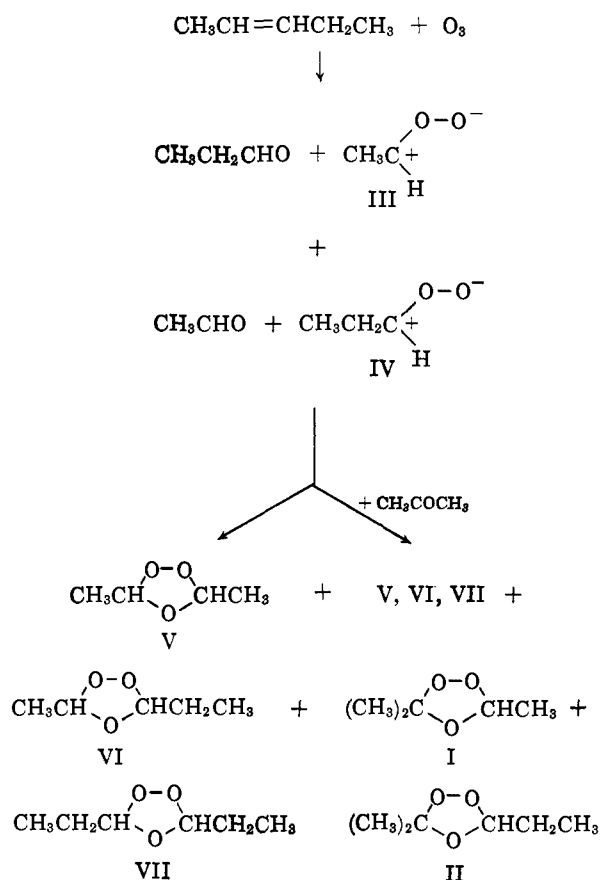(8) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963).



Figure 1.

*reactions* to give ozonides from simple ketones have been reported. For example, 1,2-dimethylcyclopentene gives a good yield of its normal ozonide.[10] These latter observations suggested to us that the long-standing view[5,9] that simple ketones do not react with zwitterions should be re-examined.

We wish to report the formation of ozonides from the reaction of acetone and aldehydic zwitterions. When pentene-2 is ozonized in the presence of excess acetone, the ozonides of 2-methylbutene-2 (I) and 2-methylpentene-2 (II) are produced, in addition to the previously reported[3] ozonides of butene-2, pentene-2, and hexene-3. It is proposed that ozonides I and II arise from the reaction of acetone with aldehydic zwitterions III and IV, respectively.

In a typical reaction 5 g. (71.4 mmoles) of pentene-2 in 50 g. of acetone was ozonized to 61.8% completion. The reaction mixture was analyzed by g.p.c. which showed the presence of two new peaks in addition to those previously shown to be due to the ozonides of butene-2, pentene-2, and hexene-3. The two new peaks were identified as the ozonides of 2-methylbutene-2 and 2-methylpentene-2 on the basis of chemical analysis (*Anal.* Found for I: C, 50.1; H, 7.99; O, 41.7.[11] Found for II: C, 54.5; H, 9.05; O, 36.4), infrared spectra (strong band at 1080–1110 cm.$^{-1}$, no OH or carbonyl), and n.m.r. spectra. The n.m.r.

(9) R. Criegee, S. S. Bath, and B. V. Bornhaupt, *Chem. Ber.*, **93**, 2891 (1960).
(10) R. Criegee, P. de Bruyn, and G. Lohaus, *Ann.*, **583**, 19 (1953).
(11) Because of the instability of the ozonide we were unable to obtain a completely satisfactory analysis. The analysis obtained is most consistent with the proposed structure, however.