with this it is found that when 15 cm^3 STP of allene is circulated over 10 g of activated zinc oxide[5] for 5 hr, at least 90% of it is converted to the more stable methylacetylene.[11]

In conclusion, then, we believe that these data strongly support the developing view that zinc oxide acts as a base in the catalysis of isomerization reactions of unsaturated hydrocarbons. Moreover, for the particular example of methylacetylene–allene isomerization, it appears quite likely that propargyl ion is the intermediate.

Acknowledgment. This work was aided by funds from the NSF under Grant No. GP-22830.

(11) At equilibrium the gas phase should be 96% methylacetylene: R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952).

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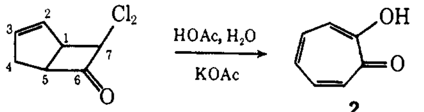
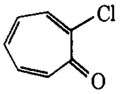
Mechanism of the Conversion of the Dichloroketene–Cyclopentadiene Adduct into Tropolone

Sir:

This conversion (eq 1)[1] has several peculiarities showing that it does not proceed by any of certain obvious paths, such as a simple 4,7 elimination of HCl with fragmentation. (1) Neither 2-chlorotropone (**3**) nor 2-acetoxytropone (**4**) lies on the reaction path, since neither one yields tropolone at the required rate under the conditions of eq 1. (2) Basic reagents more prone to produce elimination reactions than the reagent of eq 1 yield not tropolone, but products of the opening of the four-membered ring.[1,2] (3) The product **5** of addition of dichloroketene to dimethylfulvene is converted, by triethylammonium acetate in aqueous acetone, into α-dolabrin (**6**) rather than β-dolabrin (**7**).[3]



1 **2** (1)



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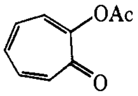

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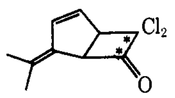

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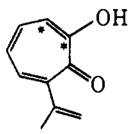

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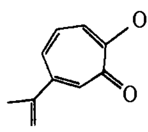
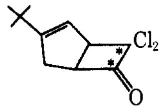


7

Moreover, ^{14}C placed at the 7 position of **1** appears at the α carbon of **2** and not as either of the oxygenated carbon atoms.[4]

In accord with this observation, we have recently found that the bicycloheptenone **8**,[5a] in which *tert*-butyl is separated from the nearest oxygenated carbon atom by three other carbon atoms, is opened to β-*tert*-butyltropolone (**9**)[5a] and not to its γ isomer.[5b]



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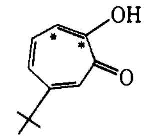
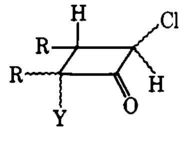


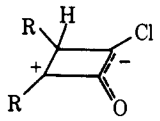
9

In this communication we report evidence that in the conversion of **1** to **2** a necessary intermediate is the rearranged chloro alcohol **18d** or **19d**, which is formed best through hydrolysis of an initially formed carboxylic ester of corresponding structure.

Previous work in this laboratory[6] has shown that monocyclic 2,2-dichlorocyclobutanones undergo rapid rearrangement in the presence of bases to mixtures of stereoisomeric 2,4-dichlorocyclobutanones (**13a**) and, in the presence of a nucleophile, such as methanol, they also yield stereoisomeric mixtures of structure **13b**.[7] Evidence will be presented elsewhere that these rapid equilibrations proceed by way of a planar intermediate such as the 1,3 dipole[7–11] **14** or the enol allylic cation[10,11] **14H**. 1,3-Dipolar species like **14** have been considered in cycloaddition reactions of cyclopropanones.[12]



13a, Y = Cl
b, Y = OCH$_3$



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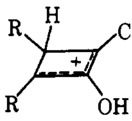

14H

Acetate ion in the presence of water appears to be an especially effective reagent for the conversion of **1** to tropolone. Whereas triethylamine in aqueous acetic acid gives tropolone in good yield, sodium methoxide opens the ring. Triethylammonium acetate in aqueous acetone affords a 37% yield of tropolone, accompanied by 21% lactone **16**,[5a] derived from the ring-cleavage product **15**. Triethylamine in methanol–chloroform gives cleavage to the cis methyl ester **17**, the trans isomer of which was reported by Ghosez, Montaigne, and Mallet.[2] **16** showed the following spectral characteristics: nmr methylene multiplet at δ 2.80, one-

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(1) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

(2) L. Ghosez, R. Montaigne, and P. Mallet, *Tetrahedron Lett.*, 135 (1966).

(3) T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *Chem. Commun.*, 89 (1970); T. Nozoe, private communication.

(4) Y. Kitahara, private communication; T. Asao, T. Machiguchi, and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **43**, 2662 (1970).

(5) (a) These compounds were analyzed and yielded satisfactory analyses. (b) P. D. Bartlett and T. Ando, to be published.

(6) H. Knoche, H. Griengl, and T. Ando, to be published.

(7) Similar 2,4 rearrangements and displacements in 2,2-dichlorocyclobutanones have been observed by V. R. Fletcher and A. Hassner, *Tetrahedron Lett.*, 1071 (1970).

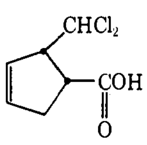
(8) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 806 ff.

(9) F. G. Bordwell, R. G. Scamehorn, and W. R. Springer, *J. Amer. Chem. Soc.*, **91**, 2087 (1969).

(10) F. G. Bordwell, R. G. Scamehorn, and A. C. Knipe, *ibid.*, **92**, 2172 (1970).

(11) F. G. Bordwell and M. W. Carlson, *ibid.*, **92**, 3370, 3377 (1970). The conditions of our rearrangements correspond to the less basic ones under which Bordwell and collaborators present evidence for the intermediacy of enol cations. However, **14** must be substantially less basic than their enolates, and **14H** correspondingly less favored under any basic conditions.

(12) N. J. Turro, *Accounts Chem. Res.*, **2**, 28 (1969).



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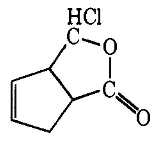

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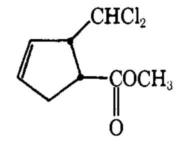
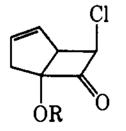


17

proton multiplets at 3.39, 3.87, 5.74, 5.94, 1-H singlet at 6.22; ir $\nu_{C=O}$ 1810 cm^{-1} (compare γ-chloro-γ-butyrolactone, $\nu_{C=O}$ 1810 cm^{-1}).[13]

On treatment with triethylammonium acetate in dry acetone, **1** reacted slowly to form two isomers[14] of the 5-acetate, **18a**[5a] and **19a**, in yields of 40 and 9%, respectively, together with a small amount of tropolone equal only to the possible amount of water present. **18a** and **19a** were converted into **2** rapidly by triethylammonium acetate in aqueous acetone at room temperature, the conversion of **1** under these conditions being relatively slow. **18a** showed the following spectral characteristics: nmr δ 2.13 s (3 H), 2.78 dm (1 H, J = 18 Hz), 2.91 dm (1 H, J = 18 Hz), 4.03, broad doublet (1 H, J = 9 Hz), 5.61 d (1 H, J = 9 Hz), ~5.72 m (1 H), ~5.93 m (1 H); ir $\nu_{C=O}$, 1735, 1795 cm^{-1}.



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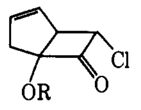
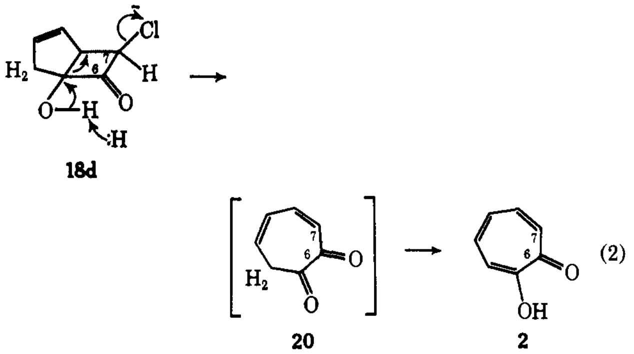


19

a, R = COCH$_3$
b, R = COC$_6$H$_4$NO$_2$(*m*)
c, R = COC$_6$H$_2$(CH$_3$)$_3$(2, 4, 6)
d, R = H

19a showed the following spectral characteristics: nmr 2.11 s (3 H), 2.74 dm (1 H, J = 18.5 Hz), 2.94 dm (1 H, J = 18.5 Hz), 3.74 broad doublet (1 H, J = 4 Hz), 4.12 d (1 H, J = 4 Hz), ~5.85 m (1 H), ~6.03 m (1 H); ir $\nu_{C=O}$ 1750, 1800 cm^{-1}.

The summation of these results suggests that the oxygen atom at position 5 in **18a** and **19a** is present in the product tropolone, but that tropolone acetate is never an intermediate. The key to the rearrangement is hydrolysis of **18a** or **19a** to the chloro alcohol **18d** or **19d**. Evidently the eliminative fragmentation which produces tropolone is triggered by ketonization of the tertiary OH group (eq 2) more effectively than by proton abstraction from the CH$_2$ of the ring. The numbers of carbons 6 and 7 in eq 2 indicate the functional shift involved in the rearrangement. In this case formation of the aromatic system of tropolone can provide no driving force for the reaction since the fragmentation proceeds in the first instance to the keto tautomer of tropolone (**20**). With part aqueous triethylamine some **18d** appears to be formed, and to lead to tropolone; but because of the ease with which the hydroxyl ion attacks the carbonyl group of **1**, the **18**–**19** system is not formed in really good yield except through nucleophilic attack of a carboxylate ion on an intermediate similar to **14**.



18d **20** **2**

Not surprisingly, we were unable to isolate the alcohols **18d** or **19d**. In fact, the acetates (**18a** and **19a**) and *m*-nitrobenzoates (**18b**[5a] and **19b**) in the presence of triethylammonium acetate reacted to give tropolone directly. To test the requirement of hydrolysis of **18a** to **18d** we treated **1** with triethylammonium mesitoate in dry acetone. The mesitoate ion, which is very little hindered in acting as a nucleophile, formed **18c**,[5a] mp 106–107°, in 72% yield together with a lesser amount of **19c**. These compounds were stable to the conditions which converted the acetate and *m*-nitrobenzoate to tropolone, and in fact the mesitoates could be isolated under the wet conditions which gave only tropolone from **1** in the presence of anions of the unhindered acids.

This experiment distinguishes between the two mechanisms (acyl–oxygen fission as in normal ester hydrolysis and solvolytic alkyl–oxygen fission) for conversion of the carboxylic esters **18a**–**c** and **19a**–**c** into the alcohols **18d** and **19d**. The pK_a's of benzoic, mesitoic, and *m*-nitrobenzoic acids in 55% ethanol are 5.83, 5.32, and 4.76, respectively.[15] The mesitoate esters should therefore be about as readily solvolyzable as the acetates (pK_a of acetic acid in water, 4.75), though of course far less readily attacked in normal ester hydrolysis. The result shows that the alcohols must be formed by that mechanism which is strongly hindered in the mesitoate, namely, attack of water at the carbonyl group.

Kitahara, *et al.*,[3] proposed a mechanism for the formation of **2** from **1** which involved attack of base on the methylene group of **1** and valence isomerization to chloronorcaradienone with expulsion of one chlorine atom. Such a mechanism is reasonable and accommodates the positional history of C$_7$ in the rearrangement; but even if we modify this mechanism by allowing **18a**, **b**, or **c** to react in this way, the mechanism embodies no visible requirement that an ester group undergo hydrolysis before the reaction can proceed. We therefore think it highly probable that eq 2 represents the process and that a norcaradienone is not involved.

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[14] For a discussion of the assignment of configurations to bicyclo-[3.2.0]heptenones, see M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970).

[15] (a) F. M. Beringer and S. Sands, *J. Amer. Chem. Soc.*, **75**, 3319 (1953); (b) "Constants of Organic Compounds," M. Kotake, Ed., Asakura Publishing Co., Tokyo, 1963, p 637 ff.

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