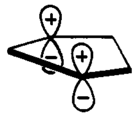
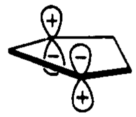
18



18S



18A

the pyrolysis of bicyclo[2.2.0]hexanes[20] (a result superficially similar to that found here for bicyclo[2.1.0]pentanes) can be interpreted on purely conformational grounds with the aid of a hypothetical chair-like cyclohexane-1,4-diyl intermediate,[20] it would seem difficult to extend this rationalization to the case of the rather rigid and nearly planar intermediate **18.** Orbital correlation diagrams, however, predict conrotatory opening of **18**, provided the highest occupied molecular orbital is symmetric (**18S**) rather than antisymmetric (**18A**).

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(20) L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970).

(21) Supported by a NATO Fellowship and grant-in-aid administered by the Deutscher Akademischer Austauschdienst, 1969–1970.

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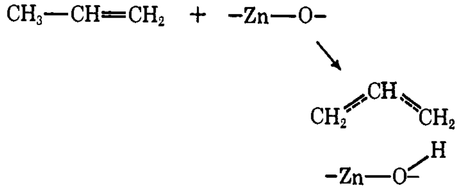
Received October 9, 1970

Intermediates in Allene–Acetylene Isomerization over Zinc Oxide

Sir:

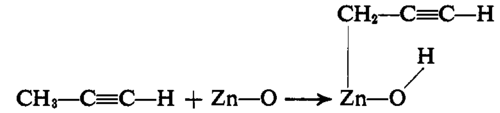
Infrared studies[1] reveal that propylene adsorbs on zinc oxide *via* rupture of the methyl carbon–hydrogen bond. This process can be represented by the equation



where Zn—O represents a limited number of active-pair sites similar to those responsible for dissociative adsorption of hydrogen.[2,3] Data for various adsorbed, deuterium-labeled propylenes[1] show that the hydrogen removed is attached to an oxide ion; the hydrocarbon fragments yield spectra expected for a symmetric π-allyl complex, and it was concluded[1] that this species is probably bound to the zinc half of the active site. Inasmuch as the zinc and oxide ions of the active site are Lewis acids and bases, respectively, we can expect the allyl species to have anionic character and the abstracted hydrogen to have protonic character. Thus, dissociative adsorption of propylene can be viewed as an acid–base reaction involving heterolytic fission of the acidic, allylic hydrogen. From this standpoint, the interactions of hydrocarbons with zinc oxide should resemble the interactions of hydrocarbons with bases in homogeneous systems. Support for this view is offered by recent studies of butene interactions with and isomerization over zinc oxide.[4]

If, indeed, zinc oxide plays the role of a base with propylene, this role should be even more apparent for the more acidic acetylenes. Adsorbed acetylene on zinc oxide[5] is more strongly bound than olefins, and, in contrast to olefins, acetylene is only partially recovered, as such, even after degassing at 300°. Nevertheless, addition of small amounts of acetylene gives rise to the immediate appearance of a band at 3550 cm^{-1}, a region characteristic of an O-H bond, together with bands expected for the hydrocarbon moiety. Adsorption of perdeuterioacetylene gives rise to no new bands in the OH region; hence, the band at 3550 cm^{-1} is *not* due to hydrogen-bonding shifts of the surface hydroxyls evident in the background spectrum.[6] Perdeuterioacetylene does, however, give rise to an OD band at 2622 cm^{-1}, a position very close to that expected (2623 ± 3 cm^{-1}) for a normal[7] isotope shift of the 3550-cm^{-1} band. Thus, it seems clear that the expected dissociative adsorption of acetylene on zinc oxide does occur.

Adsorption of methylacetylene, as expected, gives rise to an OH band (at 3515 cm^{-1}). *Adsorption of* $CH_3{-}C{\equiv}C\cdot D$, *however, also gives rise to an OH band at 3515 cm^{-1} and* (at least initially) *no corresponding (2598 cm^{-1}) OD band is observed.* This result suggests that the following process occurs



If, however, the hydrocarbon fragment is essentially the propargyl anion, there are two contributing forms to the resulting resonance hybrid[8]

$$\bar{C}H_2{-}C{\equiv}C{-}H \longleftrightarrow CH_2{=}C{=}\bar{C}{-}H$$

Then one might expect that the spectrum of adsorbed allene would be essentially the same as that of adsorbed methylacetylene. In fact, the initial spectra of adsorbed methylacetylene and allene are essentially indistinguishable and markedly different from that of either of the parent molecules.[9] Thus, it seems likely that methylacetylene (and allene) adsorbs on zinc oxide to form a propargyl anion.

The propargyl anion is the presumed intermediate in the homogeneous, base-catalyzed, allene–acetylene isomerization.[10] Thus, if the above view is correct, one would expect zinc oxide to be an effective catalyst for isomerization of allene to methylacetylene. In line

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(1) A. L. Dent and R. J. Kokes, *J. Amer. Chem. Soc.*, **92**, 6709, 6718 (1970).

(2) R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catal.*, **1**, 180 (1962).

(3) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772, 3781 (1969).

(4) (a) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, in press; (b) W. C. Conner and R. J. Kokes, unpublished results.

(5) Experimental procedures for the spectroscopic measurements and the pretreatment of the zinc oxide (Kadox 25, New Jersey Zinc Co.) were those given in ref 1. All experiments reported herein were carried out at room temperature.

(6) D. J. C. Yates and P. J. Lucchesi, *J. Chem. Phys.*, **35**, 243 (1961).

(7) The "normal" isotope shift is that observed when surface hydroxyls are exchanged with deuterium.

(8) As written, the two forms imply different nuclear geometries. Clearly, a common compromise geometry is required if this is resonance rather than tautomerism.

(9) We cannot rule out rapid surface isomerization of allene to methylacetylene, but details of the spectra make this unlikely.

(10) I. Iwai in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1969, p 73.

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.

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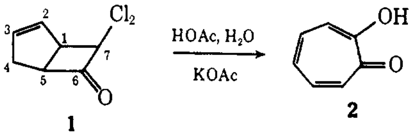
Mechanism of the Conversion of the Dichloroketene–Cyclopentadiene Adduct into Tropolone

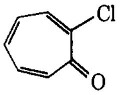
Sir:

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)

1 **2**



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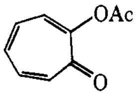

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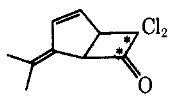

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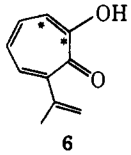

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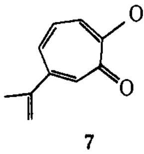
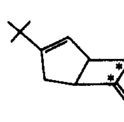


7

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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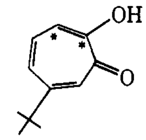
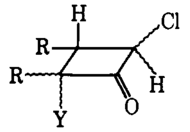


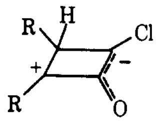
9

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.

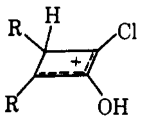
Previous work in this laboratory[6] has shown that monocyclic 2,2-dichlorocyclobutanones undergo rapid rearrangement in the presence of bases to mixtures of stereoisomeric 2,4-dichlorocyclobutanones (**13a**) and, in the presence of a nucleophile, such as methanol, they also yield stereoisomeric mixtures 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$_3$



14



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).