

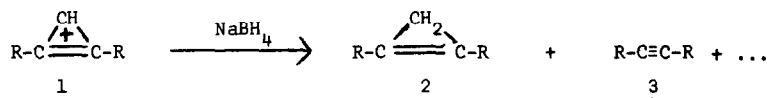
ACETYLENES FROM CYCLOPROPENIUM IONS

Walter J. Gensler and John J. Langone¹

Department of Chemistry, Boston University, Boston, Massachusetts 02215

(Received in USA 9 March 1972; received in UK for publication 3 August 1972)

We had obtained some indication before² that 1,2-dialkylcyclopropenium ions 1 with mixed metal hydrides could give not only the desired 1,2-dialkylcyclopropene 2 but also the corresponding acetylene 3. The work now reported unequivocally establishes this novel process as written, and also explores its unusual scope and generality.³ The fate of the missing carbon atom remains



to be discovered, and further inquiry with this in mind is planned.

Table I, which summarizes some of our results, reveals that a surprising variety of nucleophiles ranging from water to olefins can furnish the acetylenic product. Although an adequate discussion of the tabulated data must be deferred, it is worth pointing out that the starting material in every case is dipropylcyclopropenium perchlorate,⁴ a substrate chosen specifically because it is recrystallizable and sharp-melting. Significantly, quite similar results were found also with solutions of diethyl, dipropyl, and dibutylcyclopropenium ions⁵ derived by zinc chloride decarbonylation of the corresponding cyclopropene acid chlorides.

Although acetylenes have been observed before as products from three-membered unsaturated rings,⁶ the reaction conditions are different from those used here, and we have no reason to believe that the mechanisms are the same. Our results can be accommodated by a working hypothesis in which an early step common to all the reactions adds cyclopropenium ion 1 to an olefinic double bond (4).⁷ The olefinic constituent could be cyclopropenes formed in situ, such as 1,2-dialkylcyclopropene, trialkylcyclopropene, or bis-(1,2-dialkyl-3-cyclopropenyl)ether, or it could be an added olefin such as 2-octene. The resulting protonated cyclopropane 5⁸ is postulated to

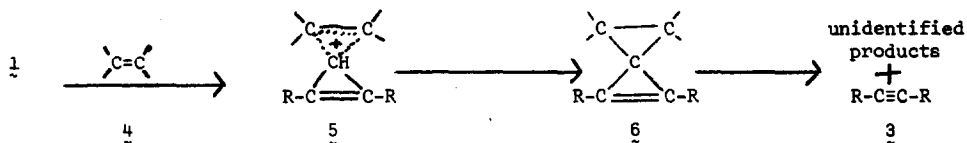
TABLE I
1,2-DIPROPYLCYCLOPROPENIUM PERCHLORATE WITH NUCLEOPHILES

Mode of Mixing	Yield of 4-octyne ^a	Other identified products ^a
dry salt to H ₂ O plus ether (25°)	7%	b
dry salt to 0.2-N HCl plus ether (25°)	6%	-
dry salt to 0.2-N NaOH plus ether (25°)	6	2-propyl-2-hexenal (1%) ^c
dry salt to LiAlH ₄ in ether (25°)	13	1,2-dipropylcyclopropene (44%)
LiAlH ₄ in ether slowly to CH ₂ Cl ₂ solution (25°)	15	no propene
LiAlH ₄ in ether rapidly (10 sec) to ether suspens. (0°)	12	1,2-dipropylcyclopropene (41%)
LiAlH ₄ in ether (3 min) to ether suspens. (25°)	13	1,2-dipropylcyclopropene (30%)
LiAlH ₄ in ether (60-200 min) to ether suspens. (0°)	27	1,2-dipropylcyclopropene (3%)
PrMgBr dropwise to ether suspens. (25°)	16	1,2,3-tri-Pr-cyclopropene ^d
PrLi in ether to ether suspens. (-80°)	0	1,2,3-tri-Pr-cyclopropene (50%)
BuLi in pentane to ether suspens. (-80°)	0	Bu-di-Pr-cyclopropene (20%)
CH ₂ Cl ₂ solution to 2-octene in CH ₂ Cl ₂ (25°)	18	-
2-octene in ether to ether suspens. (-80°)	19	-
CH ₂ Cl ₂ solution to cyclohexene in CH ₂ Cl ₂ (0°)	12	e
CH ₂ Cl ₂ soln. to 1,2-di-Pr-cyclopropene in CH ₂ Cl ₂ (-80°)	12	-

- a) Yields were determined by gas-liquid chromatography with the help of added internal standards, and are given relative to the amount of cyclopropenium ion taken as starting material. In many of the runs, products were isolated as pure materials.
- b) A careful search failed to reveal even traces of formaldehyde. Calibration showed that the method used could detect far less formaldehyde than that corresponding to the amount of acetylene formed.
- c) Production of this aldehyde from 1,2-dipropylcyclopropenium ion is analogous to formation of 2-phenylcinnamaldehyde from diphenylcyclopropenium ion [D.G.Farnum and M. Burr, *J. Amer. Chem. Soc.*, 82, 2651 (1960)], benzylidenedesoxybenzoin from triphenylcyclopropenium ion [R. Breslow and C. Yuan, *ibid.*, 80, 5991 (1958)], or 2,3-dichloracrolein from dichlorocyclopropenium ion [R. Breslow, G. Ryan, and J.T. Groves, *ibid.*, 92, 988 (1970)]. In this connection, we found that adding a more concentrated sodium hydroxide solution (6.3 N) to dipropylcyclopropenium chlorozincate gave higher yields of both 4-octyne (8%) and 2-propyl-2-hexenal (23%).
- d) As a mixture.
- e) Norcarane could not be detected.

lose a proton to give spiro [2,2] pentene 6,⁹ from which the relatively stable acetylene 3 is extruded. The reactions invariably give significant amounts of unidentified high-boiling materials, so that acetylene formation may be only one of several competing paths of breakdown which could involve the reactive intermediates 5 and 6. The postulated sequence fits

the additional fact that the carbon atom lost in forming the acetylene must be derived from the



unsubstituted position of the cyclopropenium ion 1. Thus, treating 1,2-dipropylcyclopropenium-3-¹⁴C perchlorate with lithium aluminum hydride yields, 1,2-dipropylcyclopropene-3-¹⁴C (30%) showing the same radioactivity as the starting perchlorate, whereas the accompanying 4-octyne (20%) shows no activity. The working hypothesis can also accommodate the possibility that a hydrogen atom must be present at the spiro position of 5 in order to allow acetylene formation. This requirement is suggested - but not proved - by the observation that adding lithium aluminum hydride to 1,2,3-tripropylcyclopropenium perchlorate⁴ suspended in ether gives tripropylcyclopropene in good yield (78%) but no trace of 4-octyne.¹⁰

REFERENCES AND NOTES

1. NASA Graduate Trainee, 1967-1970.
2. W. J. Gensler, M. B. Floyd, R. Yanase, and K. W. Pober, *J. Amer. Chem. Soc.*, **92**, 2472 (1970); W. J. Gensler, K. W. Pober, D. M. Solomon, and M. B. Floyd, *J. Org. Chem.*, **35**, 2301 (1970).
3. The single prior example we could uncover that could refer to this kind of reaction appears in a Dissertation by Nordby, in which the author in his Experimental Section mentions without comment that the gas-liquid chromatographic retention time of one of the products obtained when dipropylcyclopropenium perchlorate is treated with lithium aluminum hydride corresponds to that of 4-octyne [H. E. Nordby, Doctoral Dissertation, University of Arizona, 1963, p.80; available as item 63-6726, through University Microfilms, Inc., Ann Arbor, Michigan].
4. R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).
5. We regard these products as ion pairs on the basis of the same pattern of nmr signals observed for dipropylcyclopropenium perchlorate as for the corresponding chlorozincate.
6. Some of the many known examples have been reported by I. S. Krull and D. R. Arnold, *Tetrahedron Lett.*, 1247 (1969); P. Anderson et al., *J. Amer. Chem. Soc.*, **90**, 3888 (1968); R. Breslow and L. J. Altman, *ibid.*, **88**, 504, (1966); and J. Ciabattini and co-workers, *ibid.*, **91**, 4766 (1969); **93**, 4902 (1971).
7. This is also the first step in a mechanism postulated for related reactions of diphenylcyclopropenium ion with cyclopropenes [D. M. Stehouwer and D. T. Longone, *Tetrahedron Lett.*, 5311 (1969); D. T. Longone and D. M. Stehouwer, *ibid.*, 1017 (1970)]. However, the subsequent stages do not lead to diphenylacetylene. Presumably in carbonium ion 5, where R is

is phenyl instead of alkyl, the reaction is steered along other paths. In agreement, we find that diphenylcyclopropenium perchlorate in acetonitrile solution, although reacting vigorously with cyclohexene, produces no sign of diphenylacetylene.

8. Protonated cyclopropanes as products from addition of carbonium ions to olefins have been invoked before [Cf., inter alia, C. C. Lee and Bo-Sup Han, J. Amer. Chem. Soc., 91, 6420 (1969); K. B. Wiberg and J. M. Lavanish, *ibid.*, 88, 365 (1966)]. Protonated cyclopropanes as cyclization products from open carbonium ions have been reviewed by C. C. Lee in Progress in Physical-Organic Chemistry, 7, 129 (1970), and by several contributors to Carbonium Ions, Volume II, G. A. Olah and P. von R. Schleyer, editors, John Wiley and Sons, Inc., 1970.
9. A labile spiro[2,2]pentene has been obtained in low yield from the reaction of diphenylcyclopropenyl N,N-dimethylcarbamate with dimethyl fumarate. However, this spiropentene, instead of releasing diphenylacetylene, isomerizes to a diphenylcyclopropenylidene derivative [W. M. Jones and M. E. Stowe, Tetrahedron Lett., 3459 (1964); W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester, J. Amer. Chem. Soc., 90, 1849 (1968)]. See also E. V. Dehmlow, Chem. Ber., 101, 410, 427 (1968).
10. Also cf. Ciabattini et al. in Footnote 6.