fold more slowly than 1-phenylpropyne.[4] The ratio of chloride to ketone is found to increase substantially with the HCl concentration for 3-hexyne but was shown to undergo no significant change for 1-phenylpropyne.[4] These observations indicate that a different mechanism operates for addition to 3-hexyne than for 1-phenylpropyne.

As the results in Table I show, TMAC greatly enhances the rate of formation of *trans* chloride but has little effect on the rate of formation of ketone. At 25° the rates for product formation can be expressed approximately as

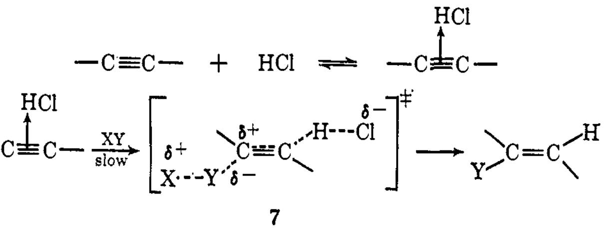
$$d[\mathbf{4}]/dt = kA[\mathrm{HCl}]^{2.6} + k'A[\mathrm{TMAC}][\mathrm{HCl}]^{1.4}$$

$$d[\mathbf{6}]/dt = k''A[\mathrm{HCl}]^{1.8}$$

where A is the concentration of 3-hexyne. The numerical values of the rate constants for these expressions are probably not meaningful since it is not yet clear whether the fractional orders in HCl should be associated with changes in the solvent character at the high concentrations employed here or with rate expressions involving first-, second-, and third-order terms in HCl. In either case it is clear that chloride formation in the absence of TMAC is associated with a rate equation approximately one order higher in HCl than that for ketone formation or for the TMAC-catalyzed reaction. These results are unexpected for a mechanism involving the formation of a cationic intermediate but are in accord with a mechanism involving synchronous formation of the C–H and C–X bonds.

The mechanism can be formulated as shown in Scheme I. Since acetylenes[9] and other unsaturated hydrocarbons[10] are known to form weak complexes with HCl, the first step in the reaction is postulated as rapid, reversible complex formation. Competing attack on the complex by HCl, TMAC, and HOAc leads, *via* transition state **7**, to *trans* adduct. The vinyl acetate is then rapidly converted to ketone. The fractional order in HCl may result from solvation of the highly charge-separated transition state **7** or from competing reactions in which hydrogen dichloride ion, rather than chloride ion, is produced in the rate-limiting step. The results show that, in the apparent rate equation, k' is over 100 times larger than k, which is consistent with TMAC being a better nucleophile than HCl.

Scheme I



7

X = H; Y = OAc or Cl
X = $(CH_3)_4N$; Y = Cl

The observation that 3-hexyne in refluxing trifluoracetic acid undergoes nonsterospecific addition[3] suggests that the stepwise vinyl cation mechanism and the synchronous mechanism are both accessible for addition to 3-hexyne depending upon the reaction conditions. Trifluoroacetic acid, being polar and strongly acidic but weakly nucleophilic, should favor addition *via* a vinyl cation intermediate. There is, in fact, evidence suggesting that a vinyl cation mechanism may be competitive with the synchronous process for the hydrochlorination in acetic acid. Thus, although chloride **5** is a negligible product for addition at 25°, we find that at 80° it amounts to 5% of the total reaction product under kinetically controlled conditions. The present study is being extended to lower acid concentrations and higher temperatures in order to further delineate this apparent competition between stepwise and synchronous addition mechanisms.

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[9] D. Cook, Y. Lupien, and W. G. Schneider, *Can. J. Chem.*, **34**, 957 (1956).

[10] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, 71, 3573 (1949).

[11] Alfred P. Sloan Foundation Research Fellow, 1966–1968.

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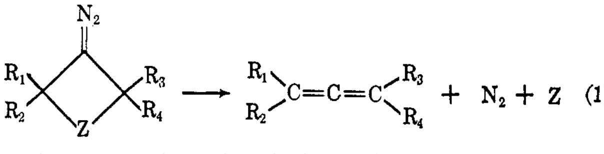
Synthesis of Allenes by Means of Cycloelimination Reactions

Sir:

Although cycloeliminations of the type shown in eq 1 would be of synthetic and theoretical interest, no such reactions have been recorded in the literature. We wish to report the first examples of this type of reaction.



(1)

When an ethereal solution of 4-keto-3,3,5,5-tetramethylpyrazoline hydrazone[1] (**1**) was treated at room temperature, under nitrogen, with a 10–20% molar excess of nickel peroxide,[2] a transient yellow color was formed and vigorous nitrogen evolution ensued, ceasing after *ca.* 10 min. Analysis of the colorless supernatant by glpc[3] indicated the presence of tetramethylallene (**2**) in yields of 87–91% (eq 2). Freshly prepared silver(I) oxide is less effective, allene **2** being produced in poor (2.5–3.5%) yield. The tetramethylallene thus produced was identified by comparing its glpc retention times (three different columns) and its infrared, nmr, and mass spectra with those of authentic tetramethylallene. Solutions of the intermediate diazo compound **3** are stable at 0° for at least 30 min, **3** being detectable by its yellow color and by the presence of a strong infrared diazo absorption[4] (2075 cm^{-1} in *n*-decane; 2060

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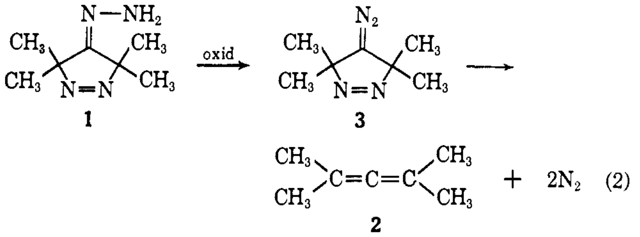
[1] W. L. Mock, Ph.D. Thesis, Harvard University, Cambridge, Mass., Sept 1964. A referee has suggested that, owing to the general inaccessibility of this thesis, the general procedures developed by Mock for the preparation of **1** and **4** be outlined. The 4-keto-3,3,5,5-tetramethylpyrazoline precursor of **1** is obtained from the hypobromite oxidation of the 2,4-diamino ketone resulting from reduction of 2,4-diazido-2,4-dimethyl-3-pentanone with hydrogen sulfide. The diazide may be prepared from the corresponding dibromo ketone [A. Favorsky and A. Umnova, *J. Prakt. Chem.*, **88**, 679 (1913)]. Compound **4** may be prepared from the corresponding ketone which is obtained from the peracetic acid oxidation of the known 2,2,4,4-tetramethyl-3-thietanone [G. Claeson, A. Thalén, and L. Schotte, *Arkiv Kemi*, **21**, 295 (1963)].

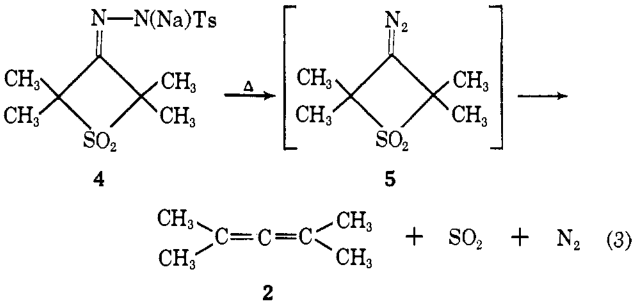
[2] (a) K. Nakagawa, H. Onoue, and K. Minami, *Chem. Commun.*, 730 (1966); (b) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

[3] Glpc analysis was done on an Aerograph A 90-P3 gas chromatograph using a 5 ft × 0.25 in. column of 20% SE-30 on 60–80 mesh Chromosorb W. Both tetramethylallene and toluene, the internal standard used for the yield determinations, are stable to nickel peroxide under the reaction conditions.



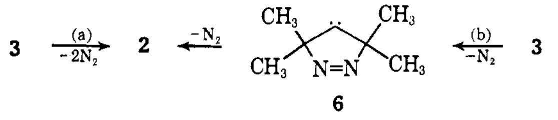
cm^{-1} in cyclohexene) which fades rapidly if the solution is allowed to warm. Although hydrazone **1** is less soluble in hydrocarbon solvents than it is in ether, the yields of allene **2** are but little affected, averaging *ca.* 82% in tetramethylethylene and cyclohexene and 77% in *n*-hexane and *n*-decane.

Cycloelimination leading to the formation of tetramethylallene can also be effected when one of the leaving groups is sulfur dioxide (eq 3). When the dry sodium salt, **4**, of the tosylhydrazone of 2,2,4,4-tetramethyl-3-thietanone dioxide,[1] prepared by treatment of a tetrahydrofuran solution of the tosylhydrazone with excess sodium hydride, was pyrolyzed *in vacuo* at *ca.* 110–160° according to the method of Shechter, *et al.*,[5] a 54–56% yield of tetramethylallene was obtained (presumably *via* diazo compound **5**) along with sulfur dioxide (identified by its glpc retention time on two different columns and by its infrared spectrum) and sodium *p*-toluenesulfinate (identified by its infrared spectrum).



Preliminary attempts to extend this cycloelimination reaction to the sodium salt of 2,2,4,4-tetramethylcyclobutanedione monotosylhydrazone (elimination of carbon monoxide) have not yielded sufficient tetramethylallene to be detectable by glpc.[6]

Since the two cycloelimination reactions would appear to be mechanistically similar, only the first will be discussed. It is clear that diazo compound **3** is a precursor of allene **2**. Whether the two nitrogen molecules are lost simultaneously (pathway a) or stepwise (pathway b) is yet unknown.[7,8] Preliminary attempts



to trap carbene **6** with cyclohexene or with tetramethylethylene have been unsuccessful; high yields of tetramethylallene are obtained in these solvents and only trace amounts (<2%) of additional reaction products are detectable by glpc.[9] While failure to trap carbene **6** cannot be used as evidence against its existence,[10] the absence of intramolecular C–H insertion products, expected for a dialkylcarbene with available β-hydrogen atoms,[11,12] suggests that carbene **6**, if formed at all, is extremely short-lived, cycloelimination of nitrogen being faster than intramolecular C–H insertion or intermolecular addition to olefins. Possibly both pathways a and b may be operative.[13]

Experiments designed to test the generality and stereochemical course of this type of cycloelimination reaction are in progress.

Acknowledgment. This research was partially supported by a grant from the Research Corp.

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(4) P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, 79, 5756 (1957).

(5) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *ibid.*, 87, 936 (1965).

(6) The products of this reaction are under investigation. See G. Maier and M. Strasser, *Tetrahedron Letters*, 6453 (1966), and references cited therein, for the pyrolysis of similar systems in which cycloelimination does not occur.

(7) For possibly related reactions involving the formation of olefins, see (a) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965); (b) D. M. Lemal and E. H. Banitt, *Tetrahedron Letters*, 245 (1964).

(8) Allenes and other cumulenes have been synthesized by means of carbenic rearrangements. See (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 61–64, and references cited therein; (b) L. Skattebøl, *Acta Chem. Scand.*, 17, 1683 (1963); (c) L. Skattebøl, *J. Org. Chem.*, 31, 2789 (1966); (d) K. G. Untch, D. J. Martin, and N. T. Castellucchi, *ibid.*, 30, 3572 (1965). For the synthesis of optically active allenes, see (e) W. M. Jones, J. W. Wilson, Jr., and F. B. Tutwiler, *J. Am. Chem. Soc.*, **85**, 3309 (1963); (f) W. M. Jones and J. W. Wilson, Jr., *Tetrahedron Letters*, 1587 (1965). For the synthesis of strained cyclic allenes, see (g) E. T. Marquis and P. D. Gardner, *ibid.*, 2793 (1966). For the synthesis of higher cumulenes, see (h) F. T. Bond and D. E. Bradway, *J. Am. Chem. Soc.*, **87**, 4977 (1965); (i) G. Maier, *Tetrahedron Letters*, 3603 (1965); (j) L. Skattebol, *ibid.*, 2175 (1965).

(9) In some reactions small (*ca.* 4–5%) amounts of 4-keto-3,3,5,5-tetramethylpyrazoline were detected, presumably formed by hydrolysis of hydrazone 1 by the hydrated nickel peroxide.

(10) The 2,2-diphenylcyclopropylidene has been trapped by olefins; see W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

(11) See ref 8a, pp 52–57.

(12) Treatment of 1,1-dibromotetramethylcyclopropane with methyllithium gives no tetramethylallene, instead yielding 1-methyl-1-isopropenylcyclopropane (95%) whose formation is attributed to intramolecular C–H insertion by initially formed tetramethylcyclopropylidene.[8b] For another viewpoint, see M. J. Goldstein and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **87**, 2293 (1965).

(13) W. M. Jones and M. H. Grasley, *Tetrahedron Letters*, 927 (1962).

(14) National Science Foundation Teaching Assistant, summer 1966; National Science Foundation Predoctoral Fellow, 1966–1968.

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The Rearrangement of Phosphorane Boranes

Sir:

The numerous examples of substituent rearrangement from negatively charged boron,[1] and the previously observed[2] reduction of triphenylphosphine oxide by organoboranes, suggested that phosphorane boranes might undergo similar reactions. Although these 1,3-dipolar adducts are in general sufficiently stable to allow isolation under normal conditions,[3,4] rearrangement does in fact occur at higher temperatures.

When triphenylphosphinemethyleneborane[3] (I) is refluxed in chlorobenzene (bp 131°) for 40 min, a clear

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(1) For an analogous rearrangement involving a sulfur ylide and leading references, see J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966).

(2) R. Köster and Y. Morita, *Angew. Chem. Intern. Ed. Engl.*, **4**, 593 (1965).

(3) M. F. Hawthorne, *J. Am. Chem. Soc.*, 80, 3480 (1958); **83**, 367 (1961).

(4) D. Seyferth and S. O. Grim, *ibid.*, **83**, 1613 (1961).