the rapid passage technique in order to observe the B^{11} resonance at +20 p.p.m. in the same medium.

The study of photochromism in mesomeric phosphonium salts and other organophosphorus compounds is continuing.

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THE PREPARATION, PYROLYSIS AND PHOTOLYSIS OF CHLORODIAZOMETHANE[1]

Sir:

Halogen derivatives of diazomethane are of interest as potential precursors of divalent carbon intermediates. Particularly, comparison of reactivities of halomethylenes derived from such diazocompounds with those of the formally identical carbenes generated by α-eliminations promises to give new insights into some problems of carbene chemistry.[2] We wish to report the preparation of solutions of chlorodiazomethane and some of their physical and chemical properties.

Reactions of *t*-butyl hypochlorite with dilute solutions of diazomethane in ether or hydrocarbons at −100° give solutions of a red compound which we believe to be chlorodiazomethane on the basis of the following observations: The electronic absorption spectrum in pentane exhibits a bathochromic shift relative to diazomethane with three maxima of about equal intensities at 485, 518 and 545 mμ (ϵ about 15),[3] respectively. The infrared spectrum shows a strong band at 2066 cm.$^{-1}$ attributed to the stretching vibration of a diazo group (*vs.* 2097 cm.$^{-1}$ for diazomethane). The solutions slowly decolorize with loss of nitrogen at temperatures above −40°. Reactions with carboxylic acids lead to rapid nitrogen evolution and decolorization. Chloromethyl acetate and chloromethyl propionate have been prepared in this way.

Confirming evidence for the structure of the chlorination product was obtained from the pyrolytic (−20°) and photolytic (−80°) decompositions of these solutions. Using olefins as solvents, satisfactory (30–40%) yields of chlorocyclopropanes were isolated. Thus, *trans*-2-butene reacted stereospecifically to give 1-chloro-*trans*-2,3-dimethylcyclopropane while *cis*-2-butene gave the two epimeric 1-chloro-*cis*-2,3-dimethylcyclopropanes in equal quantities. Similarly, with cyclohexene both 7-chloronorcarenes were formed in a 1:1 ratio.[4] From reactions in *n*-pentane the three possible carbon–hydrogen insertion products, 1-chlorohexane, 1-chloro-2-methylpentane and 1-chloro-2-ethylbutane, have been identified.[5] Vapor phase chromatographic analysis indicated a ratio of insertion into primary *vs.* secondary carbon–hydrogen bonds of 0.05 for both photolysis and pyrolysis.

The remarkable reactivity differences of chlorocarbene derived from the diazocompound and of the formally identical intermediate in α-elimination from methylene chloride[4] is noteworthy. The failure of the latter intermediate to insert into carbon–hydrogen bonds and its relatively high steric discrimination in additions to olefins[6] (*e.g.*, ratio of the two 1-chloro-*cis*-2,3-dimethylcyclopropanes resulting from the addition to *cis*-2-butene is 5.5)[6] suggests that in the α-eliminations a truly free carbene might be bypassed.[7]

(1) Supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(2) For a recent review see: W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

(3) Since a satisfactory method for assaying the chlorodiazomethane solutions has not yet been found, the ϵ value is based on an estimated yield of 50% and undoubtedly will be subject to revision.

(4) *Cf.* G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

(5) These compounds were isolated by v.p.c. and their infrared spectra were compared with those of authentic samples.

(6) G. L. Closs and G. M. Schwartz, *ibid.*, **82**, 5729 (1960).

(7) *Cf.* the similar observations for diphenylcarbene; G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(8) A. P. Sloan Foundation Fellow, 1962–1964.

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ON THE MECHANISM OF ERGOT ALKALOID BIOGENESIS[1]

Sir:

Although the biogenetic origin of the C–8 substituted N-methylergoline skeleton of the ergot alkaloids has been established as arising from tryptophan,[2] mevalonate[2] and the S-methyl of methionine,[2] the mechanism of the biosynthesis is still unknown.

The association of mevalonic acid (I) with tryptophan (III) involves the bond formation of C–5 of mevalonate (I) with the C–4 and α-carbon of tryptophan (III), and the C–3′ of mevalonate (I) with the α-amino group of tryptophan (III), respectively. In order to obtain information on the mechanism of the formation of the new C–C linkages and of the biosynthetic route by which the different substituents appear at C–8 of the ergot alkaloids, the changes in the oxidation state at C–5 and C–2 of mevalonate were examined during its conversion into ergot alkaloids.

During the over-all biosynthetic reaction the T,C^{14} ratio of DL-mevalonic acid-2-C^{14}-5-T compared to the same ratio of the ergot alkaloid (festuclavine and pyroclavine) has been changed to a degree which indicates the net loss of 1 atom of hydrogen. The T,C^{14} ratio of DL-mevalonic acid-2-C^{14}-2-T did not change during its conversion into agroclavine, indicating that there is no change in the oxidation level at C–2 of mevalonate during the biosynthesis (Table I).

The loss of one atom of hydrogen from DL-mevalonic acid-2-C^{14}-5-T may be associated with the oxidation of the primary alcoholic group of mevalonate (I) into an aldehyde group before its bond formation with tryptophan. Another possibility which may exist is that the first bond formation occurs without any change in the oxidation

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(2) K. Bentley, *Ann. Rev. Biochemistry*, **31**, 618 (1962).