basis of the recent report on the enzymatic conversion of phenylalanine to phenylserine followed by cleavage with threonine aldolase to give benzaldehyde and glycine.[15] If a similar enzyme were functioning in *N. incomparabilis*, it may be possible for phenylalanine → phenylserine → protocatechuic aldehyde without going through tyrosine. The protocatechuic aldehyde then would be the C_6–C_1 fragment. To test this possibility, H^3-protocatechuic aldehyde was injected into four plants, and 0.23% of the tritium was incorporated into the lycorine (recrystallized four times) (Table I). The exact location of the tritium is currently being determined. Protocatechuic acid-C^{14} is not incorporated.[16] On the basis of the above results, it appears that the two aromatic amino acids, phenylalanine and tyrosine, give rise to protocatechuic aldehyde and tyramine which serve as the C_6–C_1 and C_6–C_2 units, respectively, in the biosynthesis of lycorine. Tyrosine or tyramine can not replace phenylalanine as the C_6–C_1 fragment and phenylalanine can not replace tyrosine or tyramine as the C_6–C_2 unit.

(15) A. L. Jordan, W. J. Hartman, *Fed. Proc.*, **21**, 51 (1962).

(16) A. R. Battersby, Private Communication.

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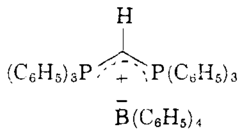
RECEIVED SEPTEMBER 20, 1962

PHOTOCHROMISM IN MESOMERIC PHOSPHONIUM SALTS[1]

Sir:

We wish to report preliminary results on the photochromism of mesomeric phosphonium salts. When white crystals of triphenylphosphonium methylenetriphenylphosphorane tetraphenylboron, Ia, are irradiated by sunlight or an ultraviolet lamp, an orange-red color rapidly develops. With a Hanovia Lamp (Model 30600), at a distance of four centimeters, the change occurs in four seconds. E.p.r. measurements show that unpaired electrons are present in the orange-red material, but not in the white crystals. The corresponding inner salt, triphenylphosphonium(triphenylboronyl)methylenetriphenylphosphorane, II, was synthesized and found also to be photochromic, white crystals becoming yellow on irradiation. Other salts of type I, including triphenylphosphonium methylenetriphenylphosphorane tetrafluoroborate, Ib, and iodide, Ic, change color more slowly than Ia. Colors resulting from ultraviolet irradiation are listed in Table I, together with analytical data. Color changes were observed in air or nitrogen at room temperature, and were not reversed by heating to 100°. When the source was removed, the intensity of the color slowly diminished to a pale yellow.


Ia

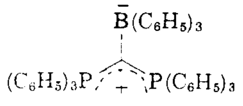

II

TABLE I

MESOMERIC PHOSPHONIUM SALTS

Compound	Empirical formula	M.p.,[a] °C.	Irradiated color	Elemental analyses, %[b] C	H	P	B	X[c]
Ia	$C_{61}H_{51}P_2B$	205–208	Orange-red	85.5	6.0	7.2	1.3	..
				85.3	6.1	7.4	1.0	..
Ib	$C_{37}H_{31}P_2BF_4$	259.5–260.5	Yellow	71.2	5.0	9.95	1.7	12.2
				71.5	5.55	10.0	1.5	12.0
Ic	$C_{37}H_{31}P_2I$	253–254	Yellow	66.9	4.7	9.3	..	19.1
				67.2	4.7	9.4	..	19.0
Id	$C_{37}H_{31}P_2Br$	274–275	White	72.0	5.0	10.0	..	13.0
				71.9	5.2	10.1	..	13.2
II	$C_{55}H_{45}P_2B$	253–255	Yellow	84.8	5.8	7.95	1.4	..
				85.1	5.9	7.7	1.5	..

[a] Melting points are corrected. [b] Calculated values are listed on the upper line; found values on the lower. [c] X values are for halogen as indicated in empirical formulas.

Infrared and ultraviolet spectra of the compounds were unchanged by irradiation. Characteristic infrared bands (KBr pellet) attributed to the mesomeric cation occur as a triplet of increasing intensity at 1027, 1010, and 988 cm.$^{-1}$. Ultraviolet λ_{max} (acetonitrile) occur at 267 mμ (ϵ = 7200–10,800). For Ia, continuous absorption with no peaks occurs in acetonitrile in the visible region (ϵ = 1, 7, and 51 at 600 ,500 and 400 mμ, respectively).

The mesomeric compounds were prepared from triphenylphosphonium methylenetriphenylphosphorane bromide,[2] Id, which is not photochromic. Id was obtained by treating methylenebis-(triphenylphosphonium bromide) with aqueous sodium carbonate[2] or lithium butyl in ether. Metathesis reactions of Id, in methanol or water, yielded triphenylphosphonium methylenetriphenylphosphorane tetraphenylboron, Ia, tetrafluoborate, Ib, and iodide, Ic. The inner salt II was synthesized by the addition of triphenylboron to hexaphenylcarbodiphosphorane,[2] obtainable from Id by reactions with potassium,[2] sodium hydride or lithium butyl. Proton and P^{31} n.m.r. spectra are consistent with the assigned mesomeric structures. For Ia, B^{11} resonance was observed at +25 p.p.m. relative to trimethyl borate in methylene chloride. For the inner salt II it was necessary to utilize

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(1) This work was supported in part by the Office of Naval Research.

(2) F. Ramirez, N. B. Desai, B. Hansen and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

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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RECEIVED OCTOBER 8, 1962

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]

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[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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RECEIVED SEPTEMBER 21, 1962

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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[1] Presented in part at the International Symposium on Organic Chemistry of Natural Products, Brussels, June 12–15, 1962. This work was supported by a grant, A-686, from the National Research Council of Canada.

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