lithium compounds or, preferably, by organomagnesium compounds. The addition of 228 g. of degassed monomer to 0.04 mole of phenylmagnesium bromide in 744 ml. of anhydrous toluene maintained at −65°, and then after eighteen hours precipitation of the reaction mixture in petroleum ether, produces a 91% conversion to polymer, $\overline{M}v$ 205,000. This polymer crystallizes readily and is difficult to obtain in the amorphous state. Dilatometric measurements indicate a glass transition of −11° and a crystal melting point of 162°. Powder diffraction patterns exhibit strong scattering from spacings at 8.4 (vs); 5.15 (s); 4.85 (s); and 4.20 (s) Å. Figure 1 illustrates the diffraction

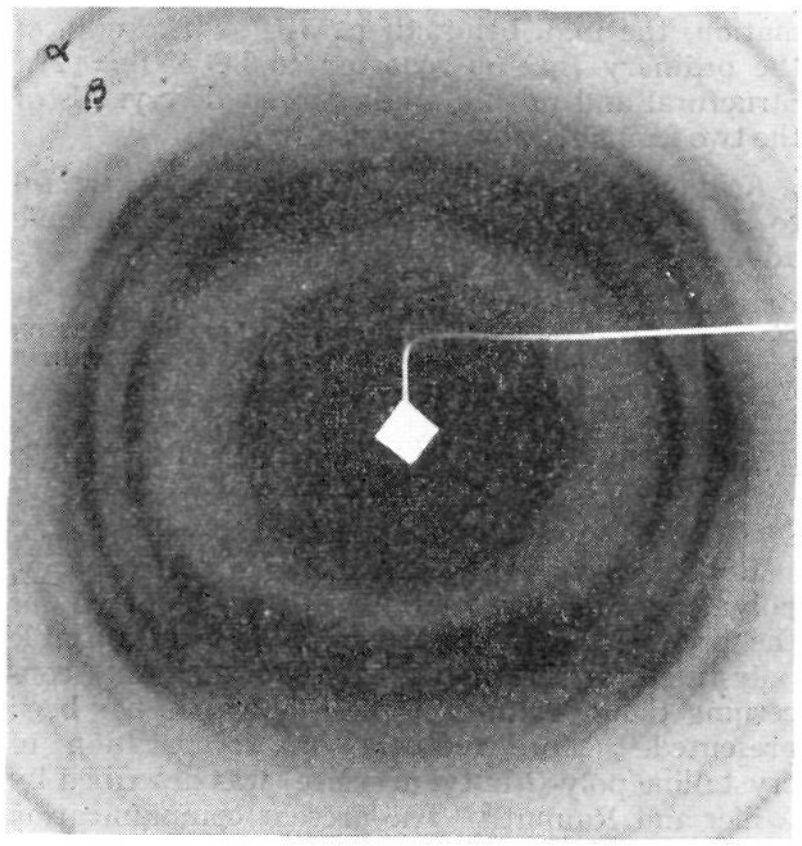

Fig. 1.—X-Ray fiber diffraction pattern of crystalline type II PiPA; stretch orientation vertical; Ni filtered Cu radiation; flat plate camera. Exposure geometry calibrated by superposed, unfiltered 2.81 Å. NaCl data.

characteristics of crystalline type II fibers. Fiber data also have been obtained for type I poly-(isopropyl acrylate); preliminary crystal structure analyses[6] suggest the syndiotactic arrangement for type I and the isotactic for type II.

By similar methods, two different crystallizable forms (I and II) of poly-(cyclohexyl acrylate) have been prepared. Polymers of *sec*-butyl and *tert*-butyl acrylates resulting from Grignard initiated polymerizations crystallize readily. The X-ray and infrared characteristics of crystalline poly-(*t*-butyl acrylate) prepared by the Grignard technique agree closely with those described[5] for polymer prepared with a lithium dispersion. However, the Grignard polymers remain crystalline at temperatures well above the 72° transition temperature reported earlier.[7]

Polymers of isopropyl, *sec*-butyl, and *tert*-butyl acrylates prepared by the Grignard method undergo rapid, spontaneous crystallization accompanied by marked changes in the infrared spectra. In contrast, polymers of cyclohexyl and isobornyl acrylates prepared by the same method usually require treatment with borderline solvents. Polymers of methyl, ethyl, and the higher *n*-alkyl acrylates prepared by the same techniques do not appear to be crystalline. These observations suggest the significance of branching at the α-carbon atom of the alkyl group in determining either the stereospecificity of the polymerizations or the crystallizability of the products. Study of the mechanism of this effect is in progress.

(6) Paper in preparation

(7) No first-order transition is observed dilatometrically below 120°; decomposition of the sample at higher temperatures prevented accurate determination of the melting point.

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DIPHENYLMETHYLENE, $(C_6H_5)_2C$, A DIRADICAL SPECIES

Sir:

The chemical properties of carbenes (CH_2,[1] CBr_2,[2] CCl_2,[3] $CHCOOC_2H_5$,[1,4] CHCOR[5]) which lead to assignment of a non-radical singlet structure are: (a) stereospecific *cis* addition to *cis*- and *trans*-2-butene, (b) reactivity characteristic of electrophilic reagents, (c) failure to correlate reactivity in addition to olefins with that anticipated for radical reagents, and (d) low reaction probability for $CH_2 + O_2$.[6]

The assignment of a non-radical singlet structure was predicted on the unsupported assumption that a triplet methylene would have the properties of a radical reagent.

It is now apparent that diphenylmethylene (obtained by photolysis of diphenyldiazomethane) does indeed have the properties anticipated for a diradical species, thus providing strong support for the singlet states assigned to previously studied carbenes and a triplet state for diphenylmethylene.

We wish to report that diphenylmethylene reacts[7] with *cis*- and *trans*-2-butene to produce cyclopropanes (product ratios from *cis*-2-butene 1:15 and from *trans*-2-butene 1:2.3) and olefins by nonstereospecific reaction paths. Diphenylmethylene also reacts with 1,3-butadiene and 1,1-diphenylethylene > 100 times more rapidly than with isobutylene, 1-hexene, or cyclohexene, a radical re-

(1) P. S. Skell and R. C. Woodworth, THIS JOURNAL, **78**, 4496 (1956).

(2) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(3) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(4) P. S. Skell and R. M. Etter, *Chem. and Ind.*, 624 (1958).

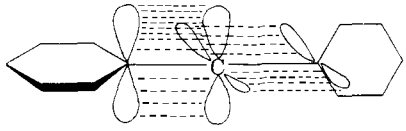
(5) P. S. Skell, A. Y. Garner and R. C. Woodworth, "Bivalent Carbon Reaction Intermediates, Carbenes," Abst. page 174 (presented at 16th Intern. Congr. Chem., Organic Section, Paris, France, 1957).

(6) A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 3258 (1954); R. A. Holroyd and W. A. Noyes, Jr., *ibid.*, **78**, 4831 (1956); R. A. Holroyd and F. E. Blacet, *ibid.*, **79**, 4830 (1957); H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

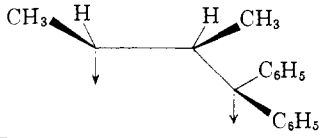
(7) Photolyses in the presence of olefins produce cyclopropanes and olefins. Pure products were separated by conventional methods. Competitions were carried out similarly, using a mixture of olefins, analyses being performed by chromatography to eliminate uncertainties about product identities. In the experiments with the *cis*- and *trans*-2-butenes the recovered olefins were not isomerized.

activity sequence. Also it has been reported that diphenylmethylene reacts with oxygen to produce benzophenone, and tetraethyl-*p*-phenylenediamine to give a blue Wurster's salt.[8]

These radical properties lead us to the assignment of a diradical (two electrons with parallel spins) structure to diphenylmethylene. Application of Hund's stabilization rule leads to the placement of these electrons in different orbitals which are nearly equivalent in stabilization. A rationalization consistent with these requirements involves a central sp carbon (orthogonal p-orbitals) and orthogonal aromatic nuclei. This rationalization has the virtue of permitting each benzene ring to interact with a different electron, the two benzene nuclei being insulated from one another, thus leading to a structure which might be described as two resonance stabilized benzyl radicals.



The spin conservation rules lead one to anticipate in the olefin addition reaction an open chain diradical intermediate of appreciable lifetime, permitting rotation about the single bond to compete with ring closure, and thus accounting for the nonstereospecific addition to *cis*- and *trans*-2-butene.[9]



(8) W. Kirmse, L. Horner and H. Hoffmann, *Ann.*, **614**, 19 (1958).

(9) Although it is not desirable to assign different names to the different spectroscopic states of a molecule, there might be sufficient reason for doing so with the triplet and singlet states of bivalent carbon. For the benefit of the chemist it is here suggested that all triplet states be given the traditional names of methylene derivatives and the name carbene be reserved for singlet states. Thus the name would convey the implication of radical or non-radical chemical properties. The authors welcome comments regarding this proposal.

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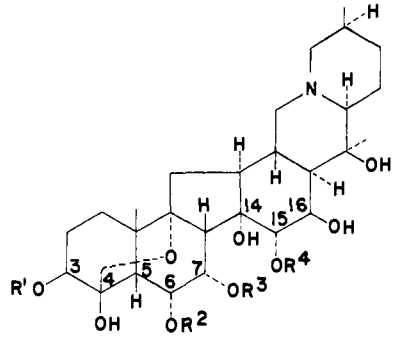
VERATRUM ALKALOIDS. XXVII. THE STRUCTURE OF PROTOVERATRINE A[1]

Sir:

Protoveratrine A[2] is a clinically useful hypotensive ester alkaloid.[3] Evidence is advanced herewith for assignment of structure I to protoveratrine A.

Alkaline hydrolysis[2c,d] of protoveratrine A has afforded the known alkamine protoverine[4] (II),[1] two mol. eq. of acetic acid, one mol. eq. of (*l*)-2-methylbutyric acid and one mol. eq. of (*d*)-2-hydroxy-2-methylbutyric acid. Protoveratrine A consumed 0.9 mol. eq. of chromic acid, an indication that the C_4 hydroxyl group is not acylated in the tetraester. The oxidation product, protoveratrone A, m.p. 221–223° dec., $[\alpha]^{25}D$ −97° (*c* 1.18, py.), on alkaline hydrolysis afforded an amorphous diosphenol with spectral properties identical with those of the diosphenol obtained from alkaline hydrolysis of 16-dehydroprotoverine 3,4,6,7,15-pentaacetate.[1] Thus, the C_{16} hydroxyl group is not acylated in protoveratrine A. Protoveratrine A readily formed a monoacetate, m.p. 249–250° dec., $[\alpha]^{22}D$ −52° (*c* 1.07, py.), and a mono-isobutyrate, m.p. 245–246° dec., $[\alpha]^{21}D$ −41° (*c* 1.36, py.). Protoveratrine A was obtained by methanolysis of the isobutyrate; this fact provides supporting evidence for a free C_{16} hydroxyl group in the naturally occurring tetraester (*cf.* ref. 1).



I, R^1 = HMB; R^2 = R^3 = Ac; R^4 = MB
II, R^1 = R^2 = R^3 = R^4 = H
III, R^1 = R^2 = R^3 = H; R^4 = MB
IV, R^1 = HMB; R^2 = R^3 = H; R^4 = MB
MB = (*l*)-2-methylbutyryl
HMB = (*d*)-2-hydroxy-2-methylbutyryl

Vigorous methanolysis of protoveratrine A resulted in loss of two acetyl groups. The resulting diester, protoverine mono-(*l*)-2-methylbutyrate mono-(*d*)-2-hydroxy-2-methylbutyrate, m.p. 203–205° dec., $[\alpha]^{23}D$ −19° (*c* 1.07, py.), consumed 0.9 mol. eq. of sodium periodate. The infrared spectrum of the amorphous oxidation product did *not* show absorption characteristic of the γ-lactone formed by periodate cleavage in Ring A of protoverine derivatives.[1] Furthermore, cyanometric titration[5] of the oxidation product indicated the presence of two aldehyde groups (from scission between C_6 and C_7). Thus the diester is a protoverine 3,15-diester and protoveratrine A has acetate groups at C_6 and C_7. Acetylation of the diester yielded protoveratrine A monoacetate.

A protoverine mono-(*l*)-2-methylbutyrate, m.p. 218–220° dec., $[\alpha]^{23}D$ −18° (*c* 0.97, py.), also was isolated from the methanolysis of protoveratrine A. This compound consumed 1.9 mol. eq. of sodium periodate, an indication that the (*l*)-2-methylbutyryl residue was attached to the C_{15} hydroxyl group. This was confirmed by acetylation to a tetraacetate, m.p. 262–263° dec., $[\alpha]^{23}D$ −46° (*c* 1.10, py.), shown to be protoverine 15-mono-(*l*)-2-methylbutyrate 3,6,7,16-tetraacetate as

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(2) (a) W. L. Glen, G. S. Myers, R. Barber, P. Morozovitch and G. A. Grant, *Nature*, **170**, 932 (1952); (b) M. W. Klohs, R. Arons, M. D. Draper, F. Keller, S. Koster, W. Malesh and F. J. Petracek, THIS JOURNAL, **74**, 5107 (1952); (c) H. A. Nash and R. M. Brooker, *ibid.*, **75**, 1942 (1953); (d) A. Stoll and E. Seebeck, *Helv. Chim Acta*, **36**, 718 (1953).

(3) O. Krayer in V. A. Drill, "Pharmacology in Medicine," McGraw-Hill Book Co., Inc., New York, N. Y., Second Edition, 1958, pp. 515–524.

(4) L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **149**, 271 (1943).

(5) J. R. Dyer in David Glick "Methods of Biochemical Analysis," Interscience Publishers, Inc., New York, N. Y., Volume III, 1956, p. 132.