that obtained from **3**. Degradation of **7** afforded 7 mg of crude product which was similar but not identical with **8** or **9** on glpc analysis.

Registry No.—**2**, 19614-40-5; **5**, 19614-41-6.

Acknowledgment.—We are grateful to E. I. du Pont de Nemours and Co. for financial assistance in the form of a summer fellowship for D. L. F.

Tetramethyl Acetylenediphosphonate and Dimethyl Chloroacetylenephosphonate and Their Reactions with Cyclopentadiene, 1,3-Cyclohexadiene, and Diazomethane[1]

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Our previous work on Diels–Alder reactions of alkynyl derivatives of the group IVb elements, mainly of bis(trimethyltin)acetylene[1a–c] and bis(trimethylsilyl)acetylene,[1d] made an assessment of the Diels–Alder reactivity of acetylenes with group Vb organic substituents of interest to us. Especially noteworthy in our previous work was the formation of *m*-bis(trimethylsilyl)benzene as almost the sole product in the reaction of α-pyrone with bis(trimethylsilyl)acetylene,[1d] and it was especially of interest to investigate if a similar isomerization might occur in suitable Diels–alder reactions of phosphorus acetylenes of type $(RO)_2P(O)C{\equiv}CP(O)(OR)_2$.

The preparation of tetraethyl acetylenediphosphonate has been reported previously by Ionin and Petrov[3] (eq 1 and 2, R = Et). While some displacement re-

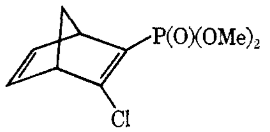
$$(RO)_3P + ClC{\equiv}CCl \xrightarrow[0^\circ]{Et_2O} \underset{\text{I}}{(RO)_2P(O)C{\equiv}CCl} + RCl \qquad (1)$$

$$(RO)_3P + (RO)_2P(O)C{\equiv}CCl \longrightarrow \underset{\text{II}}{(RO)_2P(O)C{\equiv}CP(O)(OR)_2} + RCl \qquad (2)$$

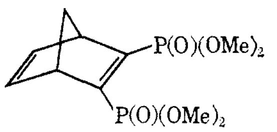
actions of the C—Cl bond of I (R = Et) were studied,[3,4] the reactivity of the C≡C bond in compounds such as I and II appears not to have been investigated. In the present study we have prepared tetramethyl acetylenediphosphonate by the Ionin–Petrov two-step procedure; in the first step $(MeO)_2P(O)C{\equiv}CCl$ was obtained in 88% yield and in the second step the $(MeO)_2P(O)C{\equiv}CP(O)(OMe)_2$ yield was 72%.

A brief study of the reactions of I and II (R = Me) showed that they readily undergo Diels–Alder reactions and 1,3 dipolar additions and thus organophosphorus-substituted acetylenes are potentially useful precursors for the introduction of organophosphorus substituents into diverse organic structures.

Reaction of cyclopentadiene with I and II (R = Me) gave the norbornadienephosphosphonates IIIa and IIIb

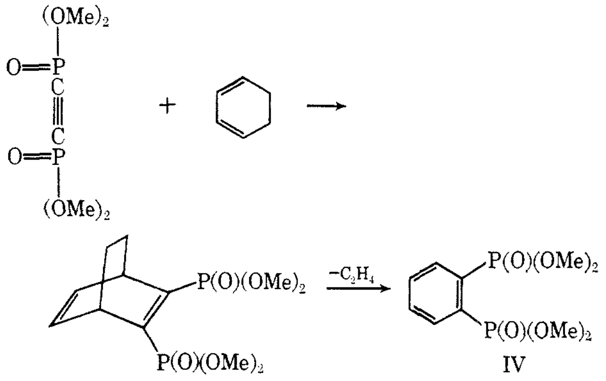


IIIa



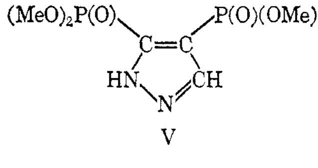
IIIb

in good yield. Tetramethyl acetylenediphosphonate also was allowed to react with 1,3-cyclohexadiene since in the case of this diene it was expected that the initial bicyclic Diels–Alder adduct would undergo thermolysis with loss of the dimethylene bridge to form a benzene derivative.[5,6] Such thermolysis would be analogous to the loss of carbon dioxide from an acetylene–α-pyrone Diels–Alder adduct, and the structure of the benzene derivative formed would provide further useful information concerning the factors which are important in determining whether or not isomerization occurs in Diels–Alder reactions of this type. The reaction of II (R = Me) with 1,3-cyclohexadiene at 150° gave a phenylenediphosphonate in 93% yield (eq 3), and the melting point and spectral properties of this product were in complete agreement with those of the known[7] tetramethyl *o*-phenylenediphosphonate (IV). The ethylene evolved in the thermolytic decomposition of the initial adduct was identified by means of its conversion into 1,2-dibromoethane. The reaction of I (R = Me) with 1,3-cyclohexadiene similarly gave dimethyl *o*-chlorobenzenephosphonate, which also has been prepared previously.[7] Although the reaction of II (R = Me) with α-pyrone remains to be studied, it would appear that this acetylene reacts normally in Diels–Alder reactions of this type and thus bis(trimethylsilyl)acetylene remains the only acetylene which we have examined thus far which reacts anomalously.



IV (3)

The addition of a solution of diazomethane to II (R = Me) resulted in formation of the 2-pyrazoline V.



V

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[1] Part V of a series of papers on "The Diels–Alder Reaction in Organometallic Chemistry." Parts I–IV are unnumbered and are listed below: (a) part I, D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organometal. Chem.*, **2**, 417 (1965); (b) part II, A. B. Evnin and D. Seyferth, *J. Amer. Chem. Soc.*, **89**, 952 (1967); (c) part III, D. Seyferth and A. B. Evnin, *ibid.*, **89**, 1468 (1967); (d) part IV, D. Seyferth, D. R. Blank, and A. B. Evnin, *ibid.*, **89**, 4793 (1967).

[2] Postdoctoral Research Associate, 1967–1968.

[3] B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **35**, 1917 (1965).

[4] B. I. Ionin and A. A. Petrov, *ibid.*, **35**, 2255 (1965).

[5] K. Alder and H. Rickert, *Ann. Chem.*, **524**, 180 (1937).

[6] K. Alder and H. Rickert, *Ber.*, **70**, 1354 (1937).

[7] R. Obrycki and C. E. Griffin, *Tetrahedron Lett.*, 5049 (1966).

Experimental Section

Preparation of Dimethyl Chloroacetylenephosphonate.—Dichloroacetylene diethyl ether azeotrope was prepared by the procedure described in detail by Wotiz, *et al.*,[8] from 0.5 mol each of trichloroethylene and diethyl ether and distilled [bp 32° (760 mm)] into a 250-ml three-necked flask cooled to −78° and equipped with a magnetic stirring assembly, a gas inlet tube, and an exit tube leading to a bubbler. To the flask then was added under nitrogen 0.1 mol of trimethyl phosphite. The reaction mixture was warmed slowly to 0° and, after 1 hr, to room temperature. The evolution of a gas (methyl chloride) was observed. The reaction mixture was kept at room temperature overnight. Subsequently the unconverted dichloroacetylene and the ether were evaporated in a stream of dry nitrogen, the flask being warmed to 30–35°. A brown liquid residue (17.19 g) remained. Distillation gave 14.7 g of colorless liquid: bp 55° (2.2 mm); n^{25}D 1.4569; nmr spectrum, 3.71 ppm (d, J = 12.4 cps);[9] ir spectrum (neat liquid), 3000 (w), 2975 (m), 2850 (m), 2250 (sh), 2180 (vs), 2130 (w), 2060 (w), 1460 (s), 1280 (vs), 1185 (s), 1040 (vs), 950 (s), 840 (s), 795 (sh), 775 (s) cm^{-1}.

Anal. Calcd for $C_4H_6O_3ClP$: C, 28.51; H, 3.51; Cl, 21.05. Found: C, 28.27; H, 3.61; Cl, 21.15.

Preparation of Tetramethyl Acetylenediphosphonate.—Dimethyl chloroacetylenephosphonate (25 mmol) and 30 mmol of trimethyl phosphite were mixed at 0° in a reaction assembly as described in the previous experiment. The mixture was warmed slowly to 10–15° and stirred at this temperature for 15 hr. Evolution of a gas was noticed. Finally, the reaction mixture was heated at 30° for 1 hr. (Rapid heating from 0° to room temperature can result in an exothermic, uncontrollable reaction.) The brown liquid mixture was then heated at 1 mm while the external oil-bath temperature was raised slowly to 100°; 0.55 g of trimethyl phosphite distilled into the cooled trap, leaving 6.1 g of brown liquid. The latter was distilled to give 4.35 g (72%) of colorless liquid: n^{25}D 1.4476; bp 155–156° (1.5 mm), solidifying at 13–15°; nmr spectrum, 3.83 ppm (d, J = 12.3 cps); ir spectrum (liquid film), 2995 (w), 2950 (m), 2895 (sh), 2845 (m), 2160 (vw), 2020 (vw), 1890 (w), 1455 (s), 1290 (vs), 1185 (s), 1040 (vs), 845 (vs), 805 (sh), 795 (sh), 755 (m) cm^{-1}.

Anal. Calcd for $C_6H_{12}O_6P_2$: C, 29.76; H, 4.99. Found: C, 29.54; H, 4.98.

Diels–Alder Reactions.—The acetylene and the diene in equimolar quantities either were heated together without solvent under nitrogen with stirring using an oil bath heated to *ca.* 140–150° for 2–4 hr or, in the case of the tetramethyl acetylenediphosphonate–cyclopentadiene reaction, were heated in benzene solution for 10.5 hr. Distillation or, in the case of IV, crystallization gave the product.

Dimethyl 2-chloronorbornadiene-3-phosphonate (IIIa) was obtained in 64% yield: bp 85° (0.02 mm); n^{25}D 1.4996; nmr spectrum, 3.63 ppm (d, J = 11.2 cps), 2.2, 3.7, and 6.93 ppm (m, 2 H each).

Anal. Calcd for $C_9H_{12}O_3ClP$: C, 46.07; H, 5.16; Cl, 15.11. Found: C, 46.30; H, 5.12; Cl, 15.26.

Tetramethyl norbornadiene-2,3-diphosphonate (IIIb) was obtained in 72% yield: bp 137° (0.01 mm); n^{25}D 1.4947; nmr spectrum, 3.66 ppm (d, J = 11 cps), 2.0, 4.03, and 6.78 ppm (m, 2 H each).

Anal. Calcd for $C_{11}H_{18}O_6P_2$: C, 42.87; H, 5.88. Found: C, 42.65; H, 6.07.

Dimethyl *o*-chlorobenzenephosphonate was obtained in 22% yield: bp 87–88° (0.01 mm); n^{25}D 1.5209; nmr spectrum, 3.75 ppm (d, J = 12 cps), 7.22 (m), and 8.0 ppm (m).

Anal. Calcd for $C_8H_{10}O_3ClP$: C, 43.55; H, 4.57; Cl, 16.07. Found: C, 43.67; H, 4.86; Cl, 16.23.

Tetramethyl *o*-phenylenediphosphonate was obtained in 93.5% yield: mp 82–84° (from benzene–heptane) (lit.[7] mp 80–81° (the *meta* isomer was a high-boiling liquid; the *para* isomer melted at 100–101°);[7] nmr spectrum, 3.80 ppm (d, J = 11.8 cps), 7.62 (m), and 8.1 ppm (m).

Anal. Calcd for $C_{10}H_{16}O_6P_2$: C, 38.99; H, 5.48. Found: C, 39.15; H, 5.48.

Reaction of Tetramethyl Acetylenediphosphonate with Diazomethane.—To a stirred and cooled solution of the acetylene (10 mmol) in 20 ml of diethyl ether was added dropwise a solution of diazomethane in ether until the yellow color of the diazomethane no longer was discharged. A white crystalline solid formed immediately upon addition of the first drops of diazomethane solution. Filtration gave 2.80 g (95% yield) of white crystals, mp 130°. These were insoluble in ether, carbon tetrachloride, benzene, and hexane and soluble in chloroform, ethanol, and water. Recrystallization from chloroform–hexane gave pure material: mp 131.5°; white needles; nmr spectrum (in $CDCl_3$), 3.76 and 3.82 ppm (d, J = 11.8 cps), 8.25 ppm (s), and 11.9 ppm (s, broad); ir spectrum (Nujol), 3115 (s, broad), 2978 (m), 2940 (s), 2845 (m), 1560 (w), 1455 (s), 1374 (w), 1326 (w), 1240 (vs), 1040 (vs), 944 (m), 895 (w), 840 (s), cm^{-1}.

Anal. Calcd for $C_7H_{14}O_6N_2P_2$: C, 29.45; H, 4.97; N, 9.85. Found: C, 29.21; H, 5.00; N, 9.75.

Registry No.—I (R = Me), 19519-59-6; II (R = Me), 19519-58-5; IIIa, 19581-55-6; IIIb, 19519-61-0; V, 19519-63-2; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; diazomethane, 334-88-3; dimethyl *o*-chlorobenzenephosphonate, 15104-43-5.

Acknowledgments.—The authors are grateful to the National Science Foundation (Grant GP 6466X) and the National Cancer Institute, U. S. Public Health Service (Research Grant CA 08278-03), for generous support of this work. We thank Professor C. E. Griffin for providing ir spectra of authentic IV and dimethyl *o*-chlorobenzenephosphonate.

Nitrogen Inversion in N-Benzoylaziridines

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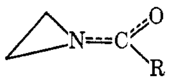
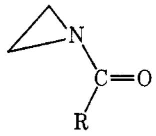
Received September 9, 1968

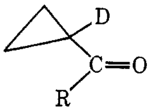
The molecular architecture of an N-acylaziridine is expected to be intermediate between two possible structures I and II. In form I, delocalization of the nitrogen lone-pair electrons is significant and the atoms of the aziridine ring and the carbonyl group tend to lie in a common plane. This delocalization is minimal in structure II and the aziridine nitrogen is in a trihedral state. A competition between the tendency toward electron delocalization and the unfavorable effects of incorporation of an sp^2 nitrogen atom into a three-membered ring leads to a compromise structure between these two extremes.



I



II



III

a, R = CH_3O
b, R = $(CH_3)_2N$
c, R = CH_3
d, R = C_6H_5

Each of these limiting forms for an N-acylaziridine has distinctive kinetic features as regards either rotational isomerism about the nitrogen–acyl carbon bond or lone-pair inversion at the nitrogen atom. Structure I should exhibit a high barrier to rotation but, because

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(8) J. H. Wotiz, F. Huba and R. Vendley, *J. Org. Chem.*, **26**, 1626 (1961).

(9) Nmr spectra were measured using a Varian Associates T-60 nmr spectrometer in carbon tetrachloride solution. Chemical shifts are given in parts per million downfield from internal tetramethylsilane.

[1] Abstracted from the M.A. Thesis of G. R. B., University of California at Santa Barbara, Santa Barbara, Calif., Aug 1968.