The Copper-Catalyzed Decomposition of Some Dimethylphosphono-Substituted Diazoalkanes

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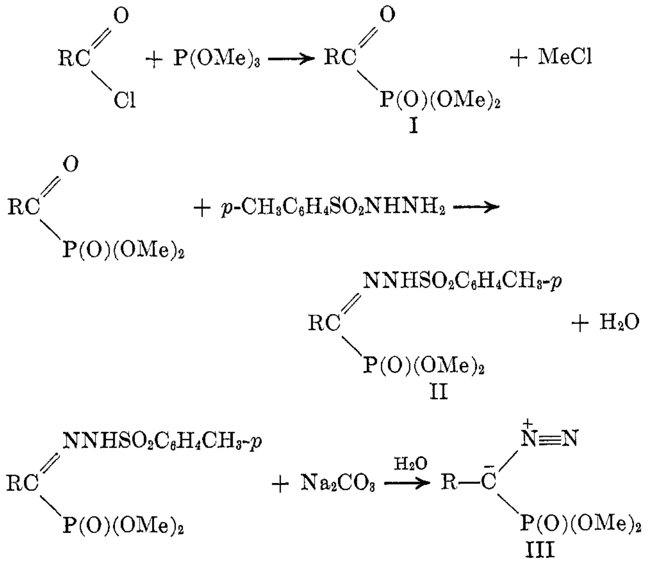
A number of dimethylphosphono-substituted diazoalkanes having the general formula $RC(N_2)P(O)(OMe)_2$ (R = alkyl, cycloalkyl, and substituted vinyl) have been prepared by the action of aqueous base on the corresponding *p*-toluenesulfonylhydrazone precursor. Copper powder catalyzed the decomposition of these diazo compounds to give a carbenoid which then underwent intramolecular rearrangement, the course of which varied depending on the nature of "R." The dimethylphosphono group was unaffected during these reactions.

There has been much interest recently in phosphorus-substituted diazoalkanes. Horner and coworkers[1] prepared the first such compound, $PhC(N_2)P(O)Ph_2$, in 1961. Kreutzkamp, *et al.*,[2] prepared $N_2CHP(O)Ph_2$ in 1965 by the direct diazotization of the amine $H_2NCH_2P(O)Ph_2$ and in 1967 we reported on the synthesis of dimethylphosphono-substituted diazo compounds *via* the base-induced decomposition of the *p*-toluenesulfonylhydrazone derivatives of α-ketophosphonates (see Scheme I) and on the copper-catalyzed addition of $PhCP(O)(OMe)_2$ to olefins using the diazoalkane precursor.[3] Petzold and Henning[4] have described the synthesis of a variety of phosphorus-substituted diazoalkanes by transdiazotization with *p*-toluenesulfonyl azide, a procedure also used by Regitz, *et al.*,[5,6] in the preparation of such phosphorus compounds. Notable were the photolyses of $Ph_2P(O)C(N_2)R$ compounds carried out by the latter workers, in which migrations of a phenyl group from phosphorus to the carbenic carbon atom were observed.[7,8] Very recently Regitz and Anschütz prepared the parent compound $N_2CHP(O)(OEt)_2$ in low yield.[9,10]

SCHEME I

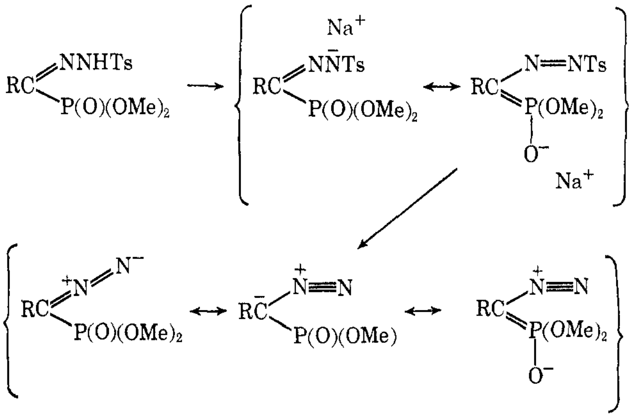


In the present paper we extend the scope of the chemistry of phosphorus-substituted diazoalkanes and carbenoids with a report concerning the synthesis and copper-catalyzed decomposition of a number of dimethylphosphono-substituted diazoalkanes of type $(MeO)_2(O)PC(N_2)R$, where R = alkyl, cycloalkyl, and substituted vinyl. Compounds of this type have not been reported previously.

Results and Discussion

Trimethyl phosphite underwent the Michaelis-Arbuzov reaction smoothly with the appropriate acid chlorides to give the corresponding α-ketophosphonates in high yield.[11] The compounds of this class prepared during the course of this study are listed in Table I. These reactive ketones readily formed *p*-toluenesulfonylhydrazones (Table II).

The great facility of the latter reaction at room temperature is evidence of the contribution of the phosphoryl group to the stability of the anion and of the resulting diazo compound after expulsion of the *p*-toluenesulfinate anion, in much the same way as that reported for α-diazocycloalkanones.[12] The en-



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* To whom correspondence should be addressed.

[1] L. Horner, H. Hoffmann, H. Ertel, and G. Klahre, *Tetrahedron Lett.*, 9 (1961).

[2] N. Kreutzkamp, E. Schmidt-Samoa, and A. K. Herberg, *Angew. Chem.*, **77**, 1138 (1965).

[3] D. Seyferth, P. Hilbert, and R. S. Marmor, *J. Amer. Chem. Soc.*, **89**, 4811 (1967).

[4] G. Petzold and H. G. Henning, *Naturwissenschaften*, **54**, 469 (1967).

[5] M. Regitz, W. Anschütz, and A. Liedhegener, *Chem. Ber.*, **101**, 3734 (1968).

[6] M. Regitz and W. Anschütz, *ibid.*, **102**, 2216 (1969).

[7] M. Regitz, W. Anschütz, W. Bartz, and A. Liedhegener, *Tetrahedron Lett.*, 3171 (1968).

[8] M. Regitz, H. Scherer, and W. Anschütz, *ibid.*, 753 (1970).

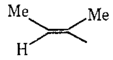
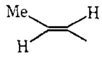
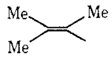
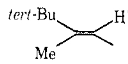
[9] M. Regitz and W. Anschütz, *Justus Liebigs Ann. Chem.*, **730**, 194 (1969).

[10] We have prepared the dimethyl ester, $N_2CHP(O)(OMe)_2$, in good yield by direct diazotization of dimethyl aminomethylphosphonate and have successfully generated the carbenoid by copper powder catalysis and added it to several olefins: D. Seyferth and R. S. Marmor, *Tetrahedron Lett.*, 2493 (1970).

[11] K. D. Berlin, D. M. Hellwege, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1265 (1965). These authors prepared a number of diethyl α-ketophosphonates in 73–88% yield, an improvement over previous reports.

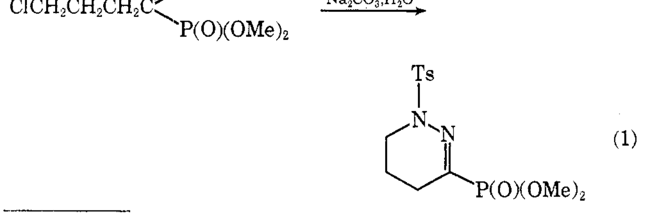
[12] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3159 (1961).

TABLE I
DIMETHYL ACYLPHOSPHONATES

$RC(O)P(O)(OMe)_2$ R =	Yield, %	Bp, °C (mm)	$n^{25}D$	ν (C═O), cm^{-1}	Nmr δ, ppm	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
Ia CH_3	90	82–86 (6.5)	1.4229			...[a]			
Ib n-C_5H_{11}	86	75.5 (0.12)–73.5 (0.07)	1.4339	1695	0.7–1.8 (m, 9), 2.75 (t, 2, J = 7 Hz), 3.78 (d, 6, J = 10.5 Hz)	46.15	46.11	8.23	8.46
Ic $(CH_3)_2CH$	97	53 (0.12)	1.4257	1690	1.13 (d, 6, J = 6.5 Hz), 3.05 (septuplet with fine splitting, 1, J = 6.5 Hz), 3.77 (d, 6, J = 11.5 Hz)	40.00	40.23	7.27	7.28
Id $(CH_3)_3C$	95	76 (2.1)–78 (2.0)	1.4280	1685	1.25 (s, 9), 3.80 (d, 6, J = 10.5 Hz)	43.30	42.92	7.79	7.82
Ie CH_3OCH_2	100 (crude)	Decomposes		1705		...[b]			
If $Cl(CH_2)_3$	88	110 (0.13)–120 (0.15)	1.4560	1695	2.05 (quintet, 2, J = 7 Hz), 2.92 (t, 2, J = 7 Hz), 3.56 [t (partially buried), 2, J = 7 Hz], 3.80 (d, 6, J = 10.5 Hz)	33.58	33.68	5.64[c]	5.70[c]
Ig c-C_3H_5	88	66–67 (0.02)	1.4543	1675	1.17 (d, 4, J = 6.5 Hz), 2.5–2.9 (m, 1), 3.80 (d, 6, J = 11 Hz)	40.45	40.36	6.23	6.22
Ih c-C_4H_7	84	82.5 (0.07)	1.4532	1690	1.5–2.5 (m, 7), 3.79 (d, 6, J = 11 Hz)	43.75	43.64	6.82	6.79
Ii c-C_5H_9	89	72–75 (0.05)	1.4588	1690	1.4–2.1 (m, 8), 3.1–3.6 (m, 1), 3.83 (d, 6, J = 11 Hz)	46.60	46.50	7.33	7.25
Ij c-C_6H_{11}	87	80–82 (0.05)	1.4680	1685	0.9–2.1 (m, 10), 2.5–3.0 (m, 1), 3.75 (d, 6, J = 11 Hz)	49.08	49.10	7.78	7.68
Ik 	82	79–84 (0.02)	1.4710	1645 (1625, C═C)	1.78 (s, 3), 2.02 (d, 3, J = 7 Hz), 3.79 (d, 6, J = 11.5 Hz), 7.65 (quintet with fine splitting, 1, J = 7 Hz)	43.75	43.63	6.82	6.84
Il 	79	86 (0.23)–100 (0.46)	1.4729	1660 (1600, C═C)	2.03 (s, 3), 2.20 (s, 3), 3.78 (d, 6, J = 11 Hz), 6.62 (finely split s, 1)	43.75	43.69	6.82	6.90
Im 	92	80–86 (0.22)	1.4678	1650 (1590, C═C)	1.7–2.0 (m, 9), 3.82 (d, 6, J = 11.5 Hz)	46.60	46.62	7.33	7.42
In 	91	99 (0.13)–102 (0.18)	1.4740	1655 (1585, C═C)	1.20 (s, 9), 2.18 (s, 3), 3.78 (d, 6, J = 10 Hz), 6.63 (s, 1)	51.27	51.12	8.18	8.21

[a] M. I. Kabachnik and P. A. Rossitskaya, *Bull. Acad. Sci. USSR*, 364 (1945); *Chem. Abstr.*, **40**, 4688 (1946). [b] Attempted purification gave decomposition, so the product was converted directly to the p-toluenesulfonylhydrazone. [c] Calcd for Cl: 16.52. Found: 16.68. [d] See Experimental Section for preparation of the acid chloride.

hanced stabilization of the diazoalkane imparted by the phosphoryl group can be explained on the basis of resonance forms of the type shown, where the P═C bond is of the (p → d) π type. Evidence for such P–C π bonding had been reported previously by Berlin and Burpo[13] for acylphosphonates. It was possible to fractionally crystallize compounds IIi and IIj to give both syn and anti isomers. Our assignments are based solely on their differing solubility in diethyl ether, as demonstrated quite generally by Regitz.[5] On treatment with aqueous sodium carbonate at room temperature these p-toluenesulfonylhydrazones underwent a remarkably facile Bamford–Stevens type of elimination[14] to give the diazoalkane, with the exception of IIf which underwent cyclization (eq 1).



(1)

The diazoalkanes prepared in this manner are listed in Table III. Their thermal stability varied considerably. Some could be distilled at reduced pressure and isolated in analytical purity, *e.g.*, dimethyl α-diazo-*n*-hexylphosphonate, bp 82° (44 mm), and dimethyl α-diazocyclohexylmethylphosphonate, bp 89° (0.15 mm). Others, such as dimethyl α-diazocyclopropylmethylphosphonate underwent spontaneous decomposition, while dimethyl α-diazocyclobutylmethylphosphonate decomposed partially under the reaction conditions and could not be obtained in analytical purity. All were yellow to orange colored liquids.

Although our major interest was in the copper-catalyzed decomposition of these diazoalkanes, a few other reactions of $MeC(N_2)P(O)(OMe)_2$ were examined. This compound reacted with acetic acid to give the expected ester, with triphenylphosphine to give the phosphazine, and with $PhHgCCl_2Br$-derived dichlorocarbene to give the dichloroolefin[15] (Scheme II).

Alkyl-Substituted Diazomethylphosphonates.—Five alkyl-substituted diazomethylphosphonates were prepared (IIIa–e in Table III), and their decomposition in benzene solution in the presence of copper powder was

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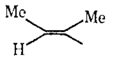
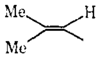
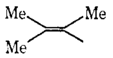
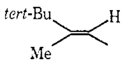
[13] K. D. Berlin and D. H. Burpo, *J. Org. Chem.*, **31**, 1304 (1966).
[14] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).
[15] D. Seyferth, J. D. H. Paetsch, and R. S. Marmor, *J. Organometal. Chem.*, **16**, 185 (1969).

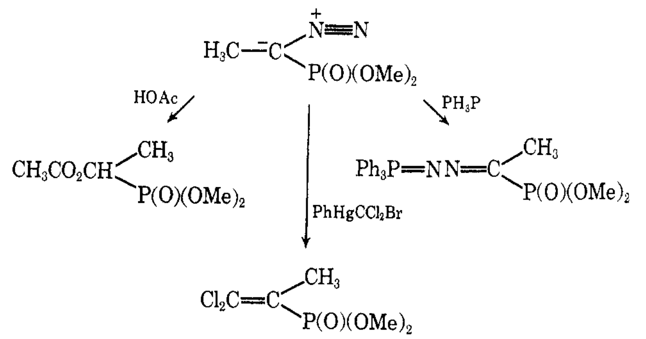
TABLE II

p-TOLUENESULFONYLHYDRAZONES

R in $\text{R}\overset{\overset{\text{NNHTs}}{\|}}{\text{C}}\text{P(O)(OMe)}_2$	Yield, %	Mp, °C	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd	Found	Calcd	Found	Calcd	Found
IIa CH_3	91[a]	183 dec	41.25	41.12	5.35	5.19		
IIb n-C_5H_{11}	73[a] 67[b]	106–107	47.86	48.05	6.69	6.82	7.44	7.40
IIc $(CH_3)_2CH$	86[b]	181–182 dec	44.82	44.93	6.08	5.83	8.04	8.32
IId $(CH_3)_3C$	66[b]	88.5–89.5	46.40	46.57	6.40	6.67	7.73	7.41
IIe CH_3OCH_2	46[b]	157.0–157.5 dec	41.14	41.30	5.47	5.68	8.00	8.10
IIf $Cl(CH_2)_3$	81[a]	140–141	40.79	40.79	5.27	5.33		
IIg c-C_3H_5	87[a]	201–202 dec	45.08	45.41	5.53	5.47	8.09	8.09
IIh c-C_4H_7	64[a]	169.5–171.0 dec	46.66	46.71	5.87	5.61	7.78	7.68
IIi c-C_5H_9 (syn)	72[c]	67–68	48.12	48.10	6.19	6.06	7.48	7.52
(anti)		145–146	48.12	48.11	6.19	6.12	7.48	7.31
IIj c-C_6H_{11} (syn)	92[c]	82.5–83.0	49.47	49.48	6.49	6.49	7.21	7.23
(anti)		167–168 dec	49.47	49.50	6.49	6.51	7.21	7.32
IIk 	85[b]	155–156 dec	46.66	46.60	5.87	5.89		
IIl 	57[b]	115.0–115.5	46.66	46.55	5.87	5.80	7.78	7.79
IIm 	58[b]	84–85	48.12	48.40	6.19	6.34	7.48	7.58
IIn 	65[b]	118.0–118.5	50.73	51.05	6.76	6.83	6.96	7.19

[a] Prepared in methanol. [b] Prepared in tetrahydrofuran with hydrochloric acid. [c] Prepared in methanol with hydrochloric acid.

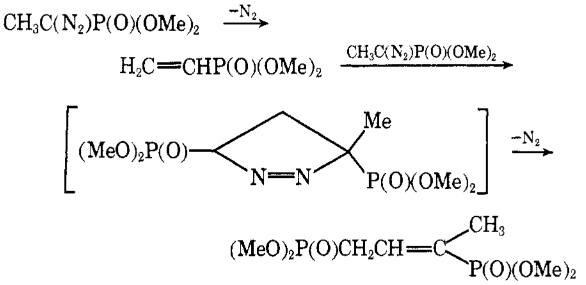
SCHEME II



studied. When the diazo compounds had available α hydrogens (IIIa–c,e), hydride migration occurred and the expected α,β-unsaturated phosphonate ester was produced (eq 2). Thus n-$C_5H_{11}C(N_2)P(O)(OMe)_2$ gave

$$XCH_2C(N_2)P(O)(OMe)_2 \longrightarrow XCH_2\dot{C}P(O)(OMe)_2 \longrightarrow XCH{=}CHP(O)(OMe)_2 \quad (2)$$

n-$C_4H_9CH{=}CHP(O)(OMe)_2$ in 79% yield, $Me_2CHC(N_2)P(O)(OMe)_2$ gave $Me_2C{=}CHP(O)(OMe)_2$ in 87% yield, and *trans*-$MeOCH{=}CHP(O)(OMe)_2$ was produced in 87% yield from $MeOCH_2C(N_2)P(O)(OMe)_2$. Such rearrangements are typical of alkyl carbenes containing an α-H substituent.[16] In the case of $CH_3C(N_2)P(O)(OMe)_2$, however, the expected product, dimethyl vinylphosphonate, was isolated in only trace amounts, the major product being a high-boiling oil derived from the 1,3-dipolar addition of as yet undecomposed diazo compound with the dimethyl vinylphosphonate produced (eq 3). The structure of the product


(3)

is based on the pmr spectrum which shows one vinyl proton and on the observed uptake of 1 mol of hydrogen on hydrogenation. The other diazo compounds (IIIb,d,e) did not undergo 1,3-dipolar addition side reactions during their decomposition to any appreciable extent, although high-boiling oils were found in small amounts in all cases. Presumably, dimethyl vinylphosphonate, having no β-alkyl substituents, undergoes 1,3-dipolar addition more readily. Vinylphosphonate esters have been reported to undergo 1,3-dipolar addition reactions.[17] We have found that all of the stable dimethylphosphono-substituted diazoalkanes react with ethyl acrylate to give Δ^2-pyrazolines, but these tended to decompose rather readily to give mixtures of cyclopropyl compounds and olefins which could be resolved only with difficulty.

Several attempts to capture an intermediate carbene or carbenoid from $CH_3C(N_2)P(O)(OMe)_2$ with cyclohexene were unsuccessful. It would appear that here also the intramolecular rearrangement of the carbene or carbenoid is faster than any possible intermolecular reaction with an olefin.

In the case of the copper-catalyzed decomposition of $Me_3CC(N_2)P(O)(OMe)_2$, a compound with no α-

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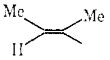
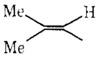
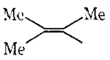
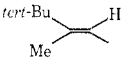
(16) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 3.

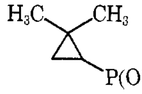
(17) A. N. Pudovik and R. D. Gareev, *Zh. Obshch. Khim.*, **34**, 3942 (1964); **38**, 1291 (1968).

TABLE III
DIMETHYLPHOSPHONO-SUBSTITUTED DIAZOALKANES

R in $RC(N_2)P(O)(OMe)_2$	Yield, %	Bp, °C (mm)	$n^{25}D$	ν (C=N=N)	Nmr (δ) ppm (in CCl_4)	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
IIIa CH_3[a]	44	50–52 (0.20)	1.4583	2080	1.83 (d, 3, J = 10 Hz), 3.73 (d, 6, J = 11.5 Hz)	29.27	29.57	5.53	5.55
IIIb n-C_5H_{11}	85	82 (0.44)	1.4555	2080	0.7–1.1, 1.1–1.6, 1.9–2.5 (m, 11), 3.75 (d, 6, J = 12 Hz)	43.63	43.86	7.78	7.91
IIIc $(CH_3)_2CH$	72	50 (0.11)	1.4545	2075	1.14 (d, 6, J = 6.5 Hz), 2.0–2.6 (m, 1), 3.65 (d, 6, J = 11.5 Hz)	37.50	38.09	6.82	6.87
IIId $(CH_3)_3C$	64	41.5 (0.10)	1.4562	2070	1.20 (s, 9), 3.69 (d, 6, J = 11.7 Hz)	40.77	40.97	7.73	7.51
IIIe CH_3OCH_2	71	56–58 (0.10)	1.4610	2085	3.27 (s, 3), 3.68 (d, 6, J = 11 Hz), 4.03 (d, 2, J = 12 Hz)	30.93	30.99	5.71	5.74
IIIh c-C_4H_7	80 (undistilled)	Decomposes[b]		2070	1.7–2.5 (m, 7), 3.63 (d, 6, J = 11.5 Hz)	41.18	42.88	6.42	6.72
IIIi c-C_5H_9	80	84 (0.20)	1.4800	2070	1.1–2.7 (m, 9), 3.62 (d, 6, J = 12 Hz)	44.03	44.49	6.93	6.91
IIIj c-C_6H_{11}	82	85 (0.10)–89 (0.15)	1.4841	2070	0.9–2.1 (m, 11), 3.66 (d, 6, J = 11.5 Hz)	46.54	46.70	7.38	7.34
IIIk 	12 (crude)	Undergoes ring closure		2070					
IIIl 	37 (crude)	Decomposes		2070					
IIIm 	4 (crude)	Decomposes		2075					
IIIn 	100 (crude)	Decomposes		2070					

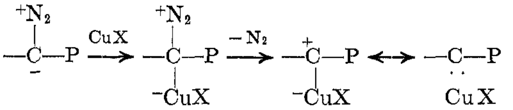
[a] Also prepared in 32% yield was $CH_3C(N_2)P(O)(OEt)_2$, an orange oil, bp 49° (0.14 mm), $n^{25}D$ 1.4503. *Anal.* Calcd for $C_6H_{13}N_2O_3P$: C, 37.50; H, 6.82. Found: C, 37.43; H, 6.93. Nmr (CCl_4) 1.32 (t, 6, J = 7.0 Hz, CH_3 of OEt), 1.82 [d, 3, J = 9.8 Hz, $CH_3C(N_2)$], 3.97 and 4.11 ppm [2 quartets, 4, J (HCCH) = 7.0 Hz, J (HCOP) = 8.5 Hz, CH_2 of OEt]. [b] Violent decomposition occurred on one attempted distillation.

hydrogen substituents, two products were formed. One, $Me_2C{=}C(Me)P(O)(OMe)_2$ (obtained in 81% yield), resulted from methyl migration in $Me_3C\ddot{C}P(O)(OMe)_2$ to the carbenic carbon atom; the other, a cyclopropane (IV, obtained in 9% yield), resulted from



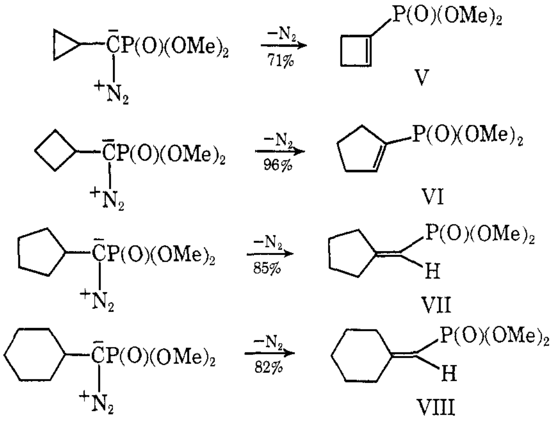
IV

intramolecular insertion of the carbene into a β-CH bond. The relative amounts of these products changed significantly when the diazoalkane was decomposed by photolysis in ether solution, and a third product was formed. In this reaction the olefin was formed in 49% yield, the cyclopropane in 21% yield, and dimethyl neopentylphosphonate in 13% yield. This change in product ratio, especially the increase in the amount of cyclopropane formed, suggests to us that the copper-catalyzed decomposition involves a complexed carbene in which there is less carbene character and some carbonium ion character at the α-carbon atom.[18]



Cycloalkyl-Substituted Diazomethylphosphonates.—The precursors for the dimethyl esters of cyclopropyl-, cyclobutyl-, cyclopentyl-, and cyclohexyldiazomethylphosphonates were prepared. The last two diazoalkanes could be isolated as pure compounds, the cyclobutyl derivative only in impure form; the cyclopropyl compound decomposed during the course of its preparation.

The cycloalkyl-substituted compounds with the three- and four-membered rings underwent ring enlargement, *i.e.*, alkyl migration, exclusively, even though an α-hydrogen atom was available, while the cyclopentyl- and cyclohexyl-substituted compounds gave products with an exocyclic double bond and no products of ring enlargement. The fact that with the latter two diazo compounds hydrogen migration was observed (*vs.* ring enlargement in the case of the cyclopropyl and cyclobutyl compounds) very likely is due to ring strain effects in the derivatives containing the three- and four-membered rings.



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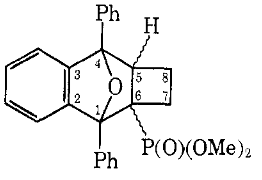
[18] The "copper metal catalyzed" decomposition of diazoalkanes is generally believed to be induced by small amounts of copper(I) salts present at the copper metal surface. We have found CuCl and $Cu(acac)_2$ to be effective in catalyzing decomposition of $N_2CHP(O)(OMe)_2$ but cyclopropane yields were highest when copper powder was used.[10]

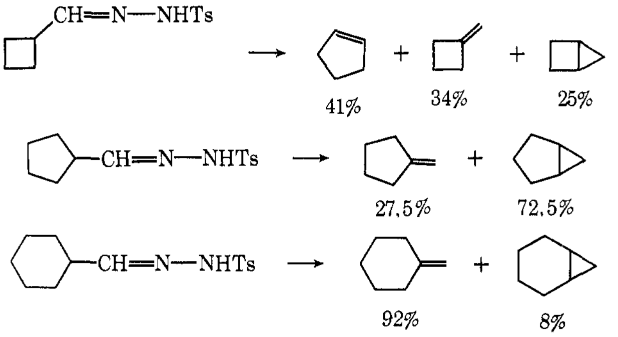
In the pmr spectrum of the hydrogenation product of V, the ring proton signals were found downfield from where they would be expected for a cyclopropyl compound. Cyclobutene V underwent a Diels–Alder reaction with 1,3-diphenylisobenzofuran to give IX. The formation of the cyclobutene V is an interesting result in view of the experiments of Wiberg and Lavanish[19] who observed two different modes of decomposition of cyclopropyldiazomethane depending on the solvent. In aprotic media cyclobutene was obtained; in protic solvents the product was bicyclobutane. In our case it is entirely possible that dimethyl bicyclobutylphosphonate was the initial product formed in the aqueous medium used, but that its strained ring system was destabilized by the dimethylphosphono group, resulting in rearrangement to V.



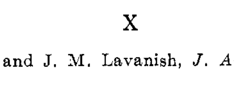
IX

The proof of structure of VI is based on comparison of the hydrogenated product, dimethyl cyclopentylphosphonate, and the acid resulting from its saponification with authentic samples. That ring enlargement had not occurred in the case of VII and VIII was demonstrated by direct comparison of the products of their hydrogenation followed by saponification with authentic samples of dimethyl cyclohexylphosphonate and cycloheptylphosphonate and their derived phosphonic acids. These were quite different in their physical and spectral properties.

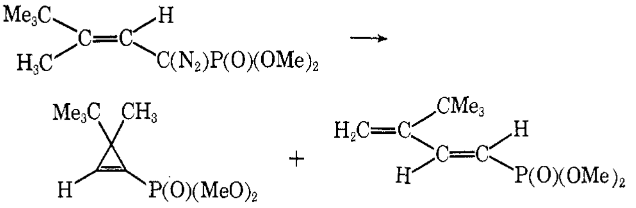
A comparison with the behavior of the unsubstituted cyclobutyl-, cyclopentyl-, and cyclohexylcarbenes is of interest.[20] It would appear that the introduction of the $P(O)(OMe)_2$ group has a profound effect on the course of the carbene chemistry observed. The major effect seems to involve steric hindrance to intramolecular C–H insertion in these cyclic systems.



Vinyl-Substituted Diazomethylphosphonates.—The vinyl-substituted diazo compound *cis*-$MeCH{=}C(Me)$-$C(N_2)P(O)(OMe)_2$ underwent slow cyclization at room temperature to give the pyrazole X. However, such ring closure could be prevented by the introduction of a second β-alkyl substituent on the C=C bond. The compounds $Me_2C{=}CHC(N_2)P(O)(OMe)_2$, $Me_2C{=}C$-$(Me)C(N_2)P(O)(OMe)_2$, and $Me_3C(Me)C{=}CHC(N_2)$-$P(O)(OMe)_2$ could be isolated, but they were too thermally unstable to survive distillation. The first underwent copper-catalyzed decomposition to give only tars and unidentified high-boiling oils, while the yield of the second was too low (4%) to permit its detailed study. The last compound was obtained in high yield and underwent smooth copper-catalyzed decomposition to a mixture of a cyclopropene (arising from intramolecular addition) and a *trans*-diene. No *cis*-diene was present, as indicated by pmr and glc.

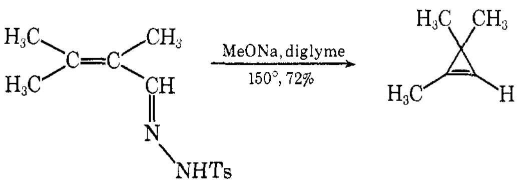


X



A 3-day reaction time gave an 86:14 mixture of the cyclopropene and diene in 64% yield; after 6 days the cyclopropene to diene ratio was changed to 40:60 and the total product yield had decreased to 34%. The diene was formed for the most part by decomposition of the cyclopropene under the reaction conditions. A control experiment with the cyclopropene showed its complete conversion to the diene after it had been stirred with copper powder in benzene for 1 week. Also, attempted resolution of the cyclopropene–diene mixture by glc resulted in thermal conversion to the diene, and, indeed, a pure sample of the diene was obtained by preparative glc of this mixture.

The possibility that the cyclopropene was formed by thermal decomposition of an intermediate Δ^1-pyrazole rather than by a direct intramolecular carbene addition to the C=C bond has not been ruled out. Also, it is possible that at least some of the diene arose by another pathway: migration of the α-vinylic hydrogen atom to form an allene which then rearranged to the 1,3-diene and/or polymerized. It should be noted that Closs and Closs[21] have observed the formation of a cyclopropene from an unsaturated diazoalkane.



Experimental Section

General Comments.—All reactions involving preparation or use of the dimethylphosphono-substituted diazoalkanes were carried out under an atmosphere of prepurified nitrogen. Infrared spectra were recorded using Perkin-Elmer Infracord 237B and 337 grating spectrophotometers, pmr spectra using Varian A60 or T60 spectrometers. Chemical shifts are given in ppm downfield from internal TMS (δ units). Melting points were measured using a Mel-Temp or Büchi melting point apparatus and are un-

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[19] K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 365 (1966).

[20] W. Kirmse, "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim, Germany, 1969, pp 146–147.

[21] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **83**, 2015 (1961).

corrected. All gas–liquid partition chromatography (glc) was carried out using an F & M 700 gas chromatograph.

Preparation of Dimethyl α-Ketoalkylphosphonates.—A solution of the appropriate acyl halide (X mmol) in $2.5X$ ml of diethyl ether was stirred under nitrogen in a flask equipped with a condenser, a dropping funnel, and a magnetic stirring assembly at *ca.* 0°. Trimethyl phosphite ($1.05X$ mmol, distilled before use) was added dropwise over a 20–60-min period, depending on the reaction scale. The reaction mixture was stirred overnight at room temperature and subsequently the solvent was removed on the steam bath under a stream of dry nitrogen. The residual oil was distilled using a Vigreux column. The product obtained in general was analytically pure. The compounds prepared are listed in Table I.

Preparation of α-Ketoalkylphosphonate *p*-Toluenesulfonylhydrazones.—A solution of equimolar amounts of the appropriate dimethyl α-ketoalkylphosphonate and *p*-toluenesulfonylhydrazine was set aside at room temperature for 24 hr and then concentrated and the residue was allowed to crystallize. In some cases, as indicated in Table II, better yields were obtained when hydrochloric acid was added and the reactants were mixed at 0°. Tetrahydrofuran was the preferred solvent for other acid-catalyzed reactions, as indicated in Table II. The compounds prepared are listed in Table II. Recrystallization from methanol or aqueous methanol gave pure samples for microanalysis.

Preparation of α-Diazoalkylphosphonates.—To a solution of sodium carbonate ($1.2X$ mmol) in $2X$ ml of water was added the appropriate dimethyl α-ketoalkylphosphonate *p*-toluenesulfonylhydrazone (X mmol). The resulting solution was stirred until no more diazo compound was forming, as indicated by the intensity of the yellow color of the reaction mixture. For compounds IIIa and b (*cf.* Table III), ether was present in a two-phase system and was replaced every few hours with fresh solvent. For compounds IIIc, i, j, l, m, and n, hexane was used in this manner. The reaction varied from *ca.* 24 to 72 hr. The aqueous layer then was extracted with dichloromethane until it was colorless and the combined organic layers were dried ($MgSO_4$) and evaporated using a rotary evaporator to give the crude diazoalkane. The product was dissolved in a small amount of diethyl ether and eluted through a short column containing neutral alumina, and then was concentrated and distilled (short path). If the chromatography was omitted, the diazo compounds decomposed partially on attempted distillation. In some cases, the microanalyses were not inside the acceptable range because of the relative instability of some of these compounds. However, the pmr spectra even in those cases indicated an acceptable degree of purity.

1-*p*-Toluenesulfonyl-3-dimethylphosphono-Δ²-tetrahydropyridazine.—Attempted conversion of the *p*-toluenesulfonylhydrazone derivative $ClCH_2CH_2CH_2C(=NNHTs)P(O)(OMe)_2$ to a diazo compound by the above method resulted in separation of a heavy, colorless oil after 5 min. The reaction mixture was stirred for 8 hr, and then extracted with a 100-ml and then two 50-ml portions of chloroform. The combined, dried organic layers were evaporated to leave an oil which solidified to a white solid after being kept overnight in high vacuum. A 97% yield (13.24 g) of the cyclic product was obtained, mp 82–83°. Slow recrystallization from ethyl acetate gave an analytical sample: mp 82.0–82.5°; ir (Nujol) 1360, 1350, 1260, 1165, 1130, 1045, 1020, 790, 730 cm⁻¹; nmr ($CDCl_3$) δ 1.8–2.5 (m, 4), 2.42 (s, 3), 3.44 (t, 2, J = 5.5 Hz), 3.77 (d, 6, J = 11.5 Hz), 7.35 and 7.78 ppm [two d, 4, J (both) = 8.5 Hz].

Anal. Calcd for $C_{13}H_{19}N_2O_5PS$: C, 45.08; H, 5.53; N, 8.09. Found: C, 44.89; H, 5.72; N, 8.09.

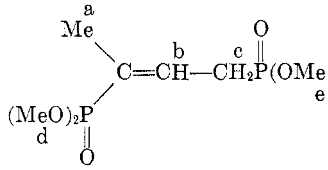
Copper-Catalyzed Decomposition of Dimethyl α-Diazoalkylphosphonates.—A mixture of dimethyl α-diazoalkylphosphonate (50 mmol), copper powder (2.5 g from J. T. Baker Co., "purified grade"), and 120 ml of benzene was stirred under nitrogen at room temperature for 24 hr and then refluxed until colorless or nearly so. The solution was filtered through Celite, evaporated using a rotary evaporator, and short-path distilled. Redistillation in most cases gave pure product.

Hydrogenation of the Products of the Decomposition of the Dimethyl α-Diazoalkylphosphonates.—To a solution of the olefinic decomposition product (10 mmol) in 10 ml of absolute ethanol under nitrogen was added 200 mg of 10% palladium on charcoal. The flask was swept with hydrogen and stirred very vigorously for 24–48 hr under hydrogen balloon pressure at room temperature. The flask then was swept with nitrogen and the reaction mixture was filtered through Celite. The filtrate was evaporated at reduced pressure and the residual oil short-path distilled to give pure product. Hydrogenation went to completion in all cases, as indicated by ir and nmr spectra.

Saponification of Dimethyl Alkylphosphonates.—A solution of the dimethyl alkylphosphonate (4.0 mmol) in 25 ml of concentrated HCl was heated at reflux for 5–7 hr and then placed in the refrigerator. If the product separated, the mixture was filtered and the product dried. When the product did not separate, the acid mixture was concentrated to a small volume and dried *in vacuo* in a desiccator over KOH flakes.

The monoaniline salt of these alkylphosphonic acids was prepared by adding an excess of aniline to an ether solution of the acid, filtering the voluminous precipitate, washing with ether, and recrystallizing from ethanol.

Tetramethyl 2-Butylene-1,3-diphosphonate.—Decomposition of $CH_3C(N_2)P(O)(OMe)_2$ by the general procedure gave the title compound, bp 124° (0.11 mm)–137° (0.25 mm), as a pale yellow oil in 51% yield. Redistillation gave very pale yellow liquid: bp 111–113° (0.03 mm); $n^{25}D$ 1.4642; ir (liquid film) 1615 (w), 1250 (s, P=O), 1180 (m), 1030 cm⁻¹ (s, POC); nmr (CCl_4) δ 1.30 (d of d, J (b,c) = 7 Hz, J_P = 18 Hz, c of major isomer), 1.1–3.2 (m, 5, a and c), 3.7 (m of d, 12, d and e), 5.8–6.8 ppm (m, 1, b).



Anal. Calcd for $C_8H_{18}O_6P_2$: C, 35.30; H, 6.67. Found: C, 35.36; H, 6.61.

Hydrogenation of this product gave tetramethyl 1-methyltrimethylenediphosphonate in 76% yield as a pale yellow oil: bp 113–115° (0.05 mm); $n^{25}D$ 1.4560; ir (liquid film) 1240, 1030, 820, 790 cm⁻¹; nmr (CCl_4) δ 0.9–2.6 (m with maximum peaks at 1.08, 1.27, 1.38, and 2.20, 8), 3.7 ppm (m of d with maximum d at 3.68, J = 10.5 Hz, 12).

Anal. Calcd for $C_8H_{20}O_6P_2$: C, 35.04; H, 7.35. Found: C, 35.18; H, 7.21.

Saponification of the hydrogenation product afforded a glassy free acid which formed a crystalline dianiline salt, mp ~167° (with sharp softening at 160°). The analysis suggested that the product was the dihydrate.

Anal. Calcd for $C_{16}H_{30}N_2O_8P_2$: C, 43.64; H, 6.87; N, 6.36. Found: C, 43.53; H, 6.22; N, 6.45.

An authentic sample was prepared by saponification (and conversion of the acid to the dianiline salt) of tetraethyl 1-methyltrimethylenediphosphonate. The latter was obtained by the Michaelis–Arbuzov reaction between triethyl phosphite and 1,3-dibromobutane; bp 139° (0.03 mm), $n^{25}D$ 1.4450.

Anal. Calcd for $C_{12}H_{28}O_6P_2$: C, 43.63; H, 8.54. Found: C, 43.44; H, 8.43.

The dianiline salt obtained in this manner showed the same melting behavior, and a mixture melting point with the dianiline salt from the sequence described above was not depressed.

Dimethyl 1-Hexenylphosphonate.—Decomposition of n-$C_5H_{11}C(N_2)P(O)(OMe)_2$ gave this compound in 79% yield as a colorless liquid, bp 63° (0.11)–61° (0.07 mm). Redistillation gave pure material: bp 57° (0.07 mm), 61° (0.03 mm); $n^{25}D$ 1.4450; ir (liquid film) 1635 (m, C=C), 1250 (s, P=O), 1030 cm⁻¹ (s, POC); nmr (neat) δ 0.7–1.1, 1.1–1.6 (m, 7), 2.0–2.4 (m, 2), 3.63 (d, 6, J = 11.0 Hz), 5.3–6.1, 6.3–7.2 ppm (m, 2).

Anal. Calcd for $C_8H_{17}O_3P$: C, 49.99; H, 8.92. Found: C, 50.13; H, 8.90.

Hydrogenation of this product gave dimethyl n-hexylphosphonate in 94% yield: bp 56–57° (0.10 mm); $n^{25}D$ 1.4292 (lit.[22] bp 121–123°; $n^{20}D$ 1.4276); ir (liquid film) 1245 (s, P=O), 1205 (m), 1180 (m), 1055 (s), 1030 (s, POC), 825 (s), 810 cm⁻¹ (s); nmr (CCl_4) δ 0.7–1.9 (m with maximum signals at 0.84 and 1.34, 13), 3.62 ppm (d, 6, J = 11 Hz). Saponification of the hydrogenation product afforded a 97% yield of n-hexylphosphonic acid, mp 104.5–106° (lit.[23] mp 104.5–106°).

Dimethyl β,β-Dimethylvinylphosphonate.—Decomposition of $Me_2CHC(N_2)P(O)(OMe)_2$ by the general procedure gave this

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[22] A. E. Canavan, B. F. Dowden, and C. Eaborn, *J. Chem. Soc.*, 331 (1962).

[23] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **67**, 1180 (1945).

compound as a colorless liquid, bp 75–76° (2.6 mm), $n^{25}\mathrm{D}$ 1.4502, in 87% yield. Prolonged exposure to air gave rise to unknown impurities.

Ir (liquid film) 1645 (s, C=C), 1250 (s, P=O), 1185 (m), 1060 (s), 1035 cm^{-1} (s, POC); nmr (CCl_4) δ 1.92 (s, 3), 2.05 (d, 3, J_P = 2.5 Hz), 3.60 (d, 6, J = 11.5 Hz), 5.32 ppm (d with fine splitting, 1, J = 18 Hz).

Anal. Calcd for $C_6H_{13}O_3P$: C, 43.90; H, 7.98. Found: C, 43.72; H, 8.33.

Hydrogenation of this ester gave dimethyl isobutylphosphonate in 78% yield: bp 66° (3.2 mm); $n^{25}\mathrm{D}$ 1.4206; ir (liquid film) 1260 (s, P=O), 1245 (s), 1185 (m), 1060 (s), 1035 cm^{-1} (s); nmr (CCl_4) δ 1.03 (d, 6, J = 7 Hz), 1.1–2.4 (m with maximum peaks at 1.38, 1.50 and 1.82, 3), 3.66 ppm (d, 6, J = 11.5 Hz).

Anal. Calcd for $C_6H_{15}O_3P$: C, 43.37; H, 9.10. Found: C, 43.20; H, 9.11.

Dimethyl Trimethylvinylphosphonate and Dimethyl 2,2-Dimethylcyclopropylphosphonate.—Copper-catalyzed decomposition of $Me_3CC(N_2)P(O)(OMe)_2$ gave a mixture of these compounds, bp 80° (3.6 mm), $n^{25}\mathrm{D}$ 1.4540, in 89% yield. Glc (4 ft Lac 728 at 125°) showed the ratio of the olefinic to the cyclopropyl product to be 9:1, with retention times of 13.0 and 9.6 min, respectively.

Anal. Calcd for $C_7H_{15}O_3P$: C, 47.19; H, 8.49. Found (for the mixture): C, 47.37; H, 8.54.

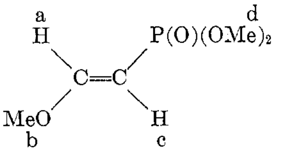
Photolysis of the diazoalkane (10 mmol) in 160 ml of dry ether under nitrogen with a Hanovia 140-W high-pressure mercury ultraviolet lamp in a quartz flask for 45 hr resulted in a colorless solution which on concentration and short-path distillation at 73.5° (2.3 mm)–78° (2.5 mm) afforded 1.44 g (81%) of product mixture, $n^{25}\mathrm{D}$ 1.4464. Glc analysis indicated the presence of three products in the (area) ratio of 13:26:61 with retention times (conditions as above) of 7.0, 10.2, and 13.8 min, respectively. The second and third products were the cyclopropane and the olefin, respectively.

Dimethyl 2,2-dimethylcyclopropylphosphonate was collected by glc and was identified by comparison with an authentic sample prepared by the copper-catalyzed addition of $HCP(O)(OMe)_2$ (*via* the diazoalkane) to isobutylene.[10]

Dimethyl trimethylvinylphosphonate showed the following principal bands in its ir spectrum (liquid film): 1630 (m, C=C), 1260 (s, P=O), 1225 (s), 1180 (m), 1025 (s, POC), 855 (s), 820 (s), 770 (s), 630 cm^{-1} (s); nmr (CCl_4) δ 1.63 (upfield peak of buried doublet, 1.5), 1.84 (s, 4.5), 2.13 (finely split s, 3), 3.61 (d, 6, J = 11 Hz). Hydrogenation of this phosphonate ester gave dimethyl α,β-dimethylpropylphosphonate, bp 65° (2.1 mm)–68° (2.5 mm), $n^{25}\mathrm{D}$ 1.4300, in 87% yield. This compound was saponified and the resulting acid was converted to the monoaniline salt in 91% overall yield. Recrystallization from ethanol gave pure material, mp 141–143° (with prior softening).

Anal. Calcd for $C_{11}H_{20}NO_3P$: C, 53.87; H, 8.22; N, 5.71. Found: C, 53.86; H, 8.27; N, 5.76.

***trans*-Dimethyl β-Methoxyvinylphosphonate.**—Decomposition of $MeOCH_2C(N_2)P(O)(OMe)_2$ gave this phosphonate ester: bp 52° (0.04 mm); $n^{25}\mathrm{D}$ 1.4506; 87% yield; ir (liq film) 1615 (s, C=C), 1250 (s, P=O), 1225 (s), 1185 (m), 1055 (s), 1030 (s), 830 cm^{-1} (s); nmr (CCl_4) δ 3.58 (d, 6, J = 12 Hz, d), 3.72 (s, 3, b, coincidental overlap with downfield peak of d doublet), 4.68 [d of d, 1; J (c,P) = 9 Hz, c], 7.09 ppm [d of d, 1, J (a,c) = 13.5 Hz, J (a,P) = 12 Hz, a].



Anal. Calcd for $C_5H_{11}O_4P$: C, 36.15; H, 6.68. Found: C, 36.21; H, 6.93.

Hydrogenation of this compound gave dimethyl β-methoxyethylphosphonate: bp 51° (0.23 mm); $n^{25}\mathrm{D}$ 1.4230; 70% yield; ir (liquid film) 1255 (s), 1230 (s, P=O), 1185 (s), 1115 (s), 1050 (s), 1030 (s), 830 cm^{-1} (s); nmr (CCl_4) δ 1.95 [d of t, 2, J (HCCH) = 7.5 Hz, J_P = 19 Hz], 3.27 (s, 3), 3.51 (t, partially buried beneath POMe doublet), 3.65 ppm [d, 8 (including 3.51 signal, J = 11 Hz)].

Anal. Calcd for $C_5H_{13}O_4P$: C, 35.72; H, 7.79. Found: C, 35.79; H, 8.05.

Dimethyl Δ^1-Cyclobutenylphosphonate.—Formation of this compound occurred spontaneously during the attempted conversion of *c*-$C_3H_5C(NNHTs)P(O)(OMe)_2$ to *c*-$C_3H_5C(N_2)P(O)(OMe)_2$ by the general procedure for preparing diazo compounds. Extraction of the aqueous carbonate solution with dichloromethane gave, after drying with sodium sulfate, evaporating at reduced pressure, and short-path distilling, a 71% yield of colorless liquid: bp 84° (2.8 mm); $n^{25}\mathrm{D}$ 1.4596; ir (liquid film) 1580 (m, C=C), 1260 (s, P=O), 1030 cm^{-1} (s, POC); nmr (neat) δ 2.70 (s, 4), 3.69 (d, 6, J = 11.5 Hz), 6.88 ppm (d, 1, J = 5 Hz).

Anal. Calcd for $C_6H_{11}O_3P$: C, 44.45; H, 6.84. Found: C, 44.56; H, 6.86.

Hydrogenation of this product gave dimethyl cyclobutylphosphonate in 86% yield: bp 67–70° (1.8 mm), $n^{25}\mathrm{D}$ 1.4442; ir (liquid film) 1240 (s, P=O), 1180 (s), 1030 (s, POC), 815 cm^{-1} (s); nmr (CCl_4) δ 1.8–2.6 (m with maximum peak at 2.13, 7), 3.64 ppm (d, 6, J = 10 Hz).

Anal. Calcd for $C_6H_{13}O_3P$: C, 43.90; H, 7.98. Found: C, 43.79; H, 8.06.

Saponification of this hydrogenation product afforded an oil which could not be crystallized. An aniline derivative could be prepared: mp 163–165° (methanol–ether); ir (Nujol) 3060 (sh, NH), 2610 (m, POH), 1185 (m), 1110 (s, P=O), 1025 cm^{-1} (s).

Anal. Calcd for $C_{10}H_{16}NO_3P$: C, 52.40; H, 7.03. Found: C, 52.12; H, 7.08.

Bromination of the cyclobutenylphosphonate in carbon tetrachloride gave on short-path distillation a 32% yield of dimethyl 1,2-dibromocyclobutylphosphonate, bp 94° (0.08 mm)–107° (0.16 mm), $n^{25}\mathrm{D}$ 1.5261. Redistillation gave pure material: bp 93° (0.05 mm), $n^{25}\mathrm{D}$ 1.5260; ir (liquid film) 1265 (s, P=O), 1185 (m), 1030 cm^{-1} (s, POC); nmr (CCl_4) δ 2.4–3.3 (m, 4), 3.85 and 3.87 (two d, 6, both J = 11 Hz), 4.5–5.2 ppm (m, 1).

Anal. Calcd for $C_6H_{11}Br_2O_3P$: C, 22.38; H, 3.44; Br, 49.64. Found: C, 22.30; H, 3.52; Br, 49.86.

Reaction of 5.6 mmol of the cyclobutenylphosphonate with 5.0 mmol of 1,3-diphenylisobenzofuran in 10 ml of xylene at reflux under nitrogen for 8.5 hr gave, after evaporation at reduced pressure, a solid residue which was extracted with hot hexane and diethyl ether to leave 0.15 g of white powder, mp 232–234°. Slow recrystallization from ethyl acetate gave white nuggets, mp 239–240°. The infrared spectrum of this material showed that the dimethylphosphono substitutent was not present, and its is believed that this solid was the dimer of 1,3-diphenylisobenzofuran. Evaporation of the hexane and ether extracts and recrystallization of the residue from ethyl acetate gave 0.35 g of white crystals of the desired adduct IX. Another recrystallization from ethyl acetate gave an analytical sample, mp 169–170°. The ir spectrum (Nujol) showed the P=O stretch at 1250 and the POC frequency at 1055 cm^{-1}: nmr ($CDCl_3$) δ 1.6–2.8 (m, cyclobutyl H, 5), 3.34 and 3.47 (two d, 6, both J = 11 Hz), 6.9–8.0 ppm (m, 14, aryl).

Anal. Calcd for $C_{26}H_{25}O_4P$: C, 72.21; H, 5.83. Found: C, 72.40; H, 6.19.

Dimethyl Δ^1-Cyclopentenylphosphonate.—Decomposition of *c*-$C_4H_7C(N_2)P(O)(OMe)_2$ by the general procedure gave this compound, bp 75–78° (0.70 mm), $n^{25}\mathrm{D}$ 1.4676, in 96% yield. Redistillation at 85–87° (1.7 mm) gave a center cut sample with $n^{25}\mathrm{D}$ 1.4669: ir (liquid film) 1605 (m, C=C), 1250 (s, P=O), 1175 (m), 1080 (s), 1050 (s), 1025 (s, POC), 815 cm^{-1} (s); nmr (CCl_4) δ 1.8–2.3 (m, 2), 2.3–2.8 (m with maximum peak at 2.50, 4), 3.63 (d, 6, J = 11.5 Hz), 6.60 ppm (d with fine splitting, 1, J = 11 Hz).

Anal. Calcd for $C_7H_{13}O_3P$: C, 47.73; H, 7.44. Found: C, 47.82; H, 7.93.

Hydrogenation of this product gave dimethyl cyclopentylphosphonate: bp 57° (0.35 mm); $n^{25}\mathrm{D}$ 1.4518; 88% yield; ir (liquid film) 1240 (s, P=O), 1185 (m), 1060 (s), 1030 (s, POC), 820 cm^{-1} (s); nmr (CCl_4) δ 1.4–2.1 (m with maximum peak at 1.60, 9), 3.67 ppm (d, 6, J = 11 Hz).

Anal. Calcd for $C_7H_{15}O_3P$: C, 47.19; H, 8.49. Found: C, 47.36; H, 8.55.

Saponification of the hydrogenation product gave a 93% yield of cyclopentylphosphonic acid, mp 122–122.5°. Several recrystallizations from benzene–heptane raised the melting point to a constant 123.0–123.5°.

Anal. Calcd for $C_5H_{11}O_3P$: C, 40.00; H, 7.39. Found: C, 39.92; H, 7.32.

Authentic dimethyl cyclopentylphosphonate and cyclopentylphosphonic acid were prepared from cyclopentylphosphonyl dichloride (available from the oxidative chlorophosphonation of cyclopentane).[24] The ester had identical ir and nmr spectra with the product described above and had $n^{25}D$ 1.4511. The authentic acid had mp 122–122.5° and was undepressed on admixture with the above acid.

Bromination of the dimethyl cyclopentenylphosphonate in carbon tetrachloride gave dimethyl 1,2-dibromocyclopentylphosphonate, bp 107° (0.15 mm)–124° (0.07 mm) (short-path distillation), which crystallized in the receiver to material with mp 62–68.5°. Recrystallization from petroleum ether gave silky white needles, mp 72.5–73.0°.

Anal. Calcd for $C_7H_{13}Br_2O_3P$: C, 25.02; H, 3.90; Br, 47.57. Found: C, 25.22; H, 4.11; Br, 47.80.

Dimethyl Cyclopentylidenemethylphosphonate.—Decomposition of $c\text{-}C_5H_9C(N_2)P(O)(OMe)_2$ by the general procedure gave this compound: bp 67° (0.08 mm); $n^{25}D$ 1.4750, 85% yield; ir (liquid film) 1640 (m, C=C), 1245 (s, P=O), 1180 (m), 1050 (s), 1030 (s), 875 (s,) 820 cm^{-1} (s); nmr (CCl_4) δ 1.5–2.0 (m with maximum peak at 1.68, 4), 2.2–2.9 (m, 4), 3.60 (d, 6, J = 10 Hz), 5.47 ppm (finely split d, 1, J_P = 17 Hz).

Anal. Calcd for $C_8H_{15}O_3P$: C, 50.52; H, 7.95. Found: C, 50.38; H, 7.89.

Hydrogenation of this product gave dimethyl cyclopentylmethylphosphonate: bp 74° (0.40 mm); $n^{25}D$ 1.4538; 88% yield; ir (liquid film) 1250 (s, P=O), 1185 (m), 1055 (s), 1030 (s), 840 cm^{-1} (s); nmr (CCl_4) δ 0.9–2.4 (m with maximum peaks at 1.58 and 1.88, 11), 3.63 ppm (d, 6, J = 11 Hz).

Anal. Calcd for $C_8H_{17}O_3P$: C, 49.99; H, 8.92. Found: C, 49.84; H, 8.82.

Saponification of the hydrogenated ester gave fluffy white crystals of cyclopentylmethylphosphonic acid, mp 169–170°.

Anal. Calcd for $C_6H_{13}O_3P$: C, 43.90; H, 7.98. Found: C, 43.61; H, 8.09.

Dimethyl cyclohexylphosphonate and cyclohexylphosphonic acid, the other possible products if the initial diazo compound decomposition had given dimethyl cyclohexenylphosphonate, were prepared for comparison from cyclohexylphosphonyl dichloride.[24] Dimethyl cyclohexylphosphonate had bp 66° (0.17 mm)–61° (0.12 mm), $n^{25}D$ 1.4533, but *different* ir and nmr spectra from dimethyl cyclopentylmethylphosphonate. Cyclohexylphosphonic acid melted at 164–165°, close to the melting point of cyclopentylmethylphosphonic acid, but a mixture melting point was depressed to 110–120°.

Dimethyl Cyclohexylidenemethylphosphonate.—Copper-catalyzed decomposition of $c\text{-}C_6H_{11}C(N_2)P(O)(OMe)_2$ gave the product: bp 76° (0.07 mm); $n^{25}D$ 1.4812; 82% yield; ir (liquid film) 1640 (s, C=C), 1245 (s, P=O), 1180 (m), 1050 (s), 1030 (s), 875 (s) and 820 cm^{-1} (s); nmr (CCl_4) δ 1.4–1.9 (m with maximum peak at 1.61, 6), 2.1–2.8 (m, 4), 3.60 (d, 6, J = 11 Hz), 5.22 ppm (broad d, 1, J_P = 19 Hz).

Anal. Calcd for $C_9H_{17}O_3P$: C, 52.93; H, 8.39. Found: C, 52.98; H, 8.39.

Hydrogenation of this compound gave dimethyl cyclohexylmethylphosphonate: bp 66° (0.09 mm); $n^{25}D$ 1.4598; 85% yield; ir (liquid film) 1250 (s, P=O), 1185 (m), 1055 (s), 1030 (s), 835 (s), 810 cm^{-1} (s); nmr (CCl_4) δ 0.7–2.2 (m with maximum peak at 1.68, 13), 3.63 ppm (d, 6, J = 11 Hz).

Anal. Calcd for $C_9H_{19}O_3P$: C, 52.41; H, 9.29. Found: C, 52.13; H, 9.20

Saponification of the hydrogenation product gave white crystals of cyclohexylmethylphosphonic acid, mp 199.5–200.5°, in 93% yield.

Anal. Calcd for $C_7H_{15}O_3P$: C, 47.19; H, 8.49. Found: C, 47.03; H, 8.41.

Authentic dimethyl cycloheptylphosphonate and cycloheptylphosphonic acid were prepared for comparison from cycloheptylphosphonyl dichloride (available from oxidative chlorophosphonation of cycloheptane[24]). Both of these compounds were different (spectral and physical properties) from the dimethyl cyclohexylmethylphosphonate and cyclohexylmethylphosphonic acid obtained above. These cycloheptylphosphorus derivatives are new compounds: dimethyl cycloheptylphosphonate, bp 72–73° (0.09 mm); $n^{25}D$ 1.4670; ir (liquid film) 1260 (s), 1230 (s), 1185 (m), 1030 (s), 815 (s), and 785 cm^{-1} (s); nmr (CCl_4) δ 1.1–2.4 (m with maximum peak at 1.57, 13), 3.64 ppm (d, J = 11 Hz).

Anal. Calcd for $C_9H_{19}O_3P$: C, 52.41; H, 9.29. Found: C, 52.60; H, 9.47.

Cycloheptylphosphonic acid melted at 106–107°.

Anal. Calcd for $C_7H_{15}O_3P$: C, 47.19; H, 8.49. Found: C, 46.98; H, 8.69.

A derivative, the monoaniline salt, was prepared as well, mp 166–168° (with prior softening).

Anal. Calcd for $C_{13}H_{22}NO_3P$: C, 57.55; H, 8.18; N, 5.16. Found: C, 57.74; H, 8.35; N, 5.06.

3,4-Dimethyl-5-(dimethylphosphono)pyrazole (X).—The formation of this compound occurred during the conversion of *cis*-MeCH=C(Me)C(NNHTs)P(O)(OMe)$_2$ to the diazoalkane by the general procedure for preparing diazo compounds. The crude diazoalkane, *cis*-MeCH=C(Me)C(N$_2$)P(O)(OMe)$_2$, changed on standing from an orange hexane-soluble oil to a white water-soluble solid, the pyrazole. The latter was isolated in 65% yield. Recrystallization from water gave white nuggets: mp 141–142° (with prior softening); ir (Nujol) 3170 (s, NH), 3120 (s, NH), 3050 (s), 1680 (broad, w), 1455 (s), 1355 (s), 1245 (s, P=O), 1230 (s), 1195 (s), 1040 (s), 1015 (s), 835 (s), 790 cm^{-1} (s); nmr (DMSO-d_6) δ 2.06 (s, 3), 2.18 (s, 3), 3.68 (d, 6, J = 12 Hz), and 10.94 ppm (broad s, 1).

Anal. Calcd for $C_7H_{13}N_2O_3P$: C, 41.18; H, 6.42; N, 13.72. Found: C, 40.97; H, 6.39; N, 13.70.

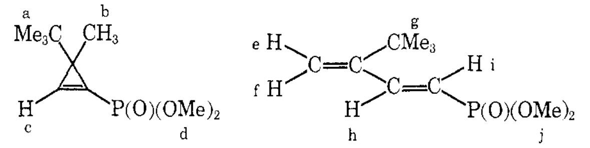
Dimethyl 3-Methyl-3-*tert*-butylcyclopropenylphosphonate and *trans*-Dimethyl 3-*tert*-Butyl-1,3-butadienylphosphonate.—Copper-catalyzed decomposition of Bu^t(Me)C=CHC(N$_2$)P(O)(OMe)$_2$ was carried out as usual except that the benzene solution of the diazo compound was stirred at room temperature for a longer time before being refluxed. When it had been stirred for 6 days, a product mixture was obtained at 61–63° (0.06 mm) as a pale yellow oil. A large amount of viscous oil was left behind. This residue began to distil at *ca.* 150° (0.7 mm) and then turned black and decomposed. Redistillation of the product (short-path) at 61–63° (0.04 mm) gave a 34% yield of product mixture, $n^{25}D$ 1.4610. The nmr spectrum suggested that a 60:40 mixture of the *trans*-diene and the cyclopropene (based on the relative areas of the dimethylphosphono and the *tert*-butyl signals) was present. The high $J_{h,i}$ coupling constant of 17.0 Hz suggests the *trans*-diene isomer, and the absence of other olefinic signals ruled out the presence of a significant amount of the cis isomer. Attempted glc purification (Lac 728 at 150°) of the distillate gave only a single peak at 14.7 min retention time. Collection of this product gave a liquid with the identical ir spectrum as the unpassed product mixture except for the complete absence of the 1690-cm^{-1} band.

Repetition of this experiment with a 3-day reaction time at room temperature gave a 64% yield of yellow product mixture at 61–65° (0.10 mm) which nmr analysis showed to be an 86:14 mixture of cyclopropene and *trans*-diene, respectively, $n^{25}D$ 1.4542.

A control experiment with this 86:14 product mixture showed that stirring in benzene solution at room temperature in the presence of copper powder for 7 days and 1 hr at reflux caused complete conversion of the cyclopropene to the diene and polymer. Distillation afforded a sample of the pure *trans*-diene.

Anal. Calcd for $C_{10}H_{19}O_3P$: C, 55.03; H, 8.78. Found for the 60:40 mixture of *trans*-diene and cyclopropene: C, 55.01; H, 8.74. Found for the pure diene: C, 54.80; H, 8.77.

Data for methyl 3-methyl-3-*tert*-butylcyclopropenylphosphonate are: ir (major band) (liquid film) 1690 cm^{-1} (s, C=C);[25] nmr ($CDCl_3$) (by subtraction of diene resonances from those of cyclopropene–diene mixture) δ 0.87 (s, 9, a), 1.23 (d, 3, J_P = 2.7 Hz, b), 3.78 (d, 6, J = 11.5 Hz, d), 8.27 ppm (d, 1, J_P = 4 Hz, c).[25]



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[24] A. F. Isbell and F. T. Wadsworth, *J. Amer. Chem. Soc.*, **78**, 6042 (1956).

[25] Long-range splitting has been observed in the nmr spectra of cyclopropenes. Also, there is a great variance in the C=C absorption frequency in the infrared spectra of reported cyclopropene compounds: G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *ibid.*, **90**, 173 (1968).

Data for *trans*-dimethyl 3-*tert*-butyl-1,3-butadienylphosphonate are: ir (liquid film) 1620 (w, C═C), 1600 (w, C═C), 1250 (s, P═O), 1215 (m, *tert*-Bu), 1180 (m), 1055 (s), 1030 (s, POC), 960 (w, diene), 920 cm^{-1} (sh, *tert*-Bu); nmr ($CDCl_3$) δ 1.13 (s, 9, g), 3.63 (d, 6, J = 11 Hz, j), 5.01 (s, 1, e or f), 5.24 (s, 1, e or f), 5.90 (d of d, 1, J_P = 19.5 Hz, $J_{h,i}$ = 17 Hz, i), 7.23 ppm (d of d, 1, J_P = 22.5 Hz, $J_{h,i}$ = 17 Hz, h).

Dimethyl α-Acetoxyethylphosphonate.—A solution of $MeC(N_2)P(O)(OMe)_2$ (10.5 mmol) and acetic acid (10.5 mmol) in 15 ml of diethyl ether was heated slowly on the steam bath. As the last of the ether solvent boiled off, a violent reaction occurred and a pale yellow, sweet-smelling oil remained behind. This was distilled (trap-to-trap) and the distillate was purified by glc (10% General Electric Co. SE-30 at 163°) to give as the major product $CH_3CH(OAc)P(O)(OMe)_2$: $n^{25}{}_D$ 1.4379; ir (liquid film) 1770 (s), 1750 (s), 1260 (s), 1220 (s), 1180 (s), 1025 (s), and 830 cm^{-1} (s).

Anal. Calcd for $C_6H_{13}O_5P$: C, 36.74; H, 6.68. Found: C, 36.94; H, 6.45.

Dimethyl α-Diazoethylphosphonate and Triphenylphosphine.—The diazo compound (7.8 mmol) and triphenylphosphine (7.8 mmol) were stirred in ether solution under nitrogen at room temperature for 69 hr. Removal of the ether at reduced pressure was followed by recrystallization of the residue from benzene–heptane to give 210 mg (15%) of short white needles of $Ph_3P{=}N{-}N{=}C(Me)P(O)(OMe)_2$. Another recrystallization gave an analytical sample, mp 136.5–137.5°. The compound decomposed slowly at room temperature: nmr ($CDCl_3$) δ 2.24 (d, 3, J = 10.7 Hz), 3.48 (d, 6, J = 10.5 Hz), 7.1–7.8 ppm (m, 15); ir (Nujol) 1245 (s, P═O), *1110* (s, P═N), *1035* cm^{-1} (s, POC).

Anal. Calcd for $C_{22}H_{24}N_2O_3P_2$: C, 61.97; H, 5.67. Found: C, 61.93; H, 5.85

***trans*-3,4,4-Trimethyl-2-pentenoyl Chloride.**—*trans*-Ethyl 3,4,4-trimethyl-2-pentenoate was prepared by the Wadsworth–Emmons modification[26] of the Wittig reaction between triethyl phosphonoacetate and pinacolone in refluxing toluene and saponified to the acid in 61% overall yield, mp 83.5–84.5° (lit.[27] mp 84–85°). The acid on reaction with thionyl chloride gave the desired acid chloride in 94% yield: bp 42–43° (1.0 mm); a colorless liquid; ν (C═O) 1775 cm^{-1}; ν (C═C) 1595 cm^{-1}.

Anal. Calcd for $C_8H_{13}ClO$: C, 59.81; H, 8.16. Found: C, 59.90; H, 8.20.

Registry No.—Ia, 17674-28-1; Ib, 26583-87-9; Ic, 6918-58-7; Id, 6918-59-8; Ie, 26583-90-4; If, 26583-92-5; Ig, 26583-92-6; Ih, 26583-93-7; Ii, 26583-94-8; Ij, 1490-12-6; Ik, 26583-96-0; Il, 26583-97-1; Im, 26583-98-2; In, 26583-99-3; IIa, 26584-00-9; IIb, 26584-01-0; IIc, 26584-02-1; IId, 26584-03-2; IIe, 26584-04-3; IIf, 26584-05-4; IIg, 26584-06-5; IIh, 26584-07-6; IIi (syn), 26584-08-7; IIi (anti), 26584-09-8; IIj (syn), 26584-10-1; IIj (anti), 26584-11-2; IIk, 26584-12-3; IIl, 26630-74-0; IIm, 26584-13-4; IIn, 26584-14-5; IIIa, 26584-15-6; IIIb, 26579-98-6; IIIc, 26579-99-7; IIId, 26580-00-7; IIIe, 26580-01-8; IIIh, 26580-02-9; IIIi, 26580-03-0; IIIj, 26580-04-1; IIIk, 26584-16-7; IIIl, 26580-05-2; IIIm, 26580-06-3; IIIn, 26630-75-1; 1-*p*-toluenesulfonyl-3-dimethylphosphono-Δ^2-tetrahydropyridazine, 26580-07-4; tetramethyl 2-butylene-1,3-diphosphonate, 26630-76-2; tetramethyl 1-methyltrimethylenediphosphonate, 26580-08-5; tetramethyl 2-butylene-1,3-diphosphonate (dianiline salt), 26580-09-6; tetraethyl 1-methyltrimethylene diphosphonate, 26580-10-9; dimethyl 1-hexenylphosphonate, 23897-48-5; dimethyl *n*-hexylphosphonate, 6172-92-5; dimethyl β,β-dimethylvinylphosphonate, 26580-13-2; dimethyl isobutylphosphonate, 26580-14-3; dimethyl trimethylvinylphosphonate, 26580-15-4; dimethyl 2,2-dimethylcyclopropylphosphonate, 26580-16-5; dimethyl α,β-dimethylpropylphosphonate, 6172-91-4; dimethyl α,β-dimethylpropylphosphonate (monoaniline salt), 26580-18-7; *trans*-dimethyl β-methoxyvinylphosphonate, 26584-17-8; dimethyl β-methoxyethylphosphonate, 26119-43-7; dimethyl Δ^1-cyclobutenylphosphonate, 26580-20-1; dimethyl cyclobutylphosphonate, 26580-21-2; dimethyl cyclobutylphosphonate (aniline salt), 26580-22-3; dimethyl 1,2-dibromocyclobutylphosphonate, 265-80-23-4; IX, 26630-77-3; dimethyl Δ^1-cyclopentenylphosphonate, 26580-24-5; dimethyl cyclopentylphosphonate, 26580-25-6; cyclopentylphosphonic acid, 6869-04-1; dimethyl 1,2-dibromocyclopentylphosphonate, 26580-27-8; dimethyl cyclopentylidenemethylphosphonate, 26580-28-9; dimethyl cyclopentylmethylphosphonate, 26580-29-0; cyclopentylmethylphosphonic acid, 26580-30-3; dimethyl cyclohexylidenemethylphosphonate, 26580-31-4; dimethyl cyclohexylmethylphosphonate, 26580-32-5; cyclohexylmethylphosphonic acid, 16016-55-0; dimethyl cycloheptylphosphonate, 26580-34-7; cycloheptylphosphonic acid, 26580-35-8; cycloheptylphosphonic acid (monoaniline salt), 26580-36-9; X, 26580-37-0; dimethyl 3-methyl-3-*tert*-butylcyclopropenylphosphonate, 26580-38-1; *trans*-dimethyl 3-*tert*-butyl-1,3-butadienylphosphonate, 26584-18-9; dimethyl α-acetoxyethylphosphonate, 17036-86-1; $Ph_3P{=}N{-}N{=}C(Me)P(O)(OMe)_2$, 16965-79-0; *trans*-3,4,4-trimethyl-2-pentenoyl chloride, 26584-19-0.

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