Some Reactions of Dimethylphosphono-Substituted Diazoalkanes. $(MeO)_2P(O)CR$ Transfer to Olefins and 1,3-Dipolar Additions of $(MeO)_2P(O)C(N_2)R$[1]

DIETMAR SEYFERTH,* ROBERT S. MARMOR, AND PETER HILBERT

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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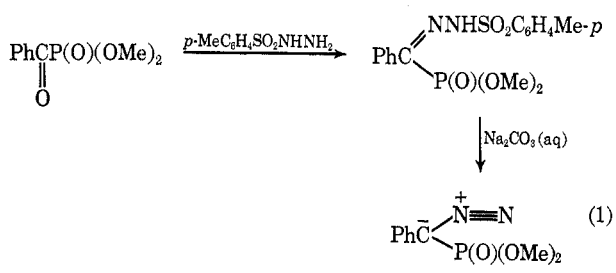
The dimethylphosphono-substituted diazoalkanes $PhC(N_2)P(O)(OMe)_2$ and $N_2CHP(O)(OMe)_2$ have been prepared, the first *via* the tosylhydrazone route, and the second by diazotization of the amine, and both could be isolated as the pure compounds. Their copper-catalyzed decomposition in the presence of olefins serves well in the preparation of dimethylphosphono-substituted cyclopropanes. Dimethyl α-diazobenzylphosphonate was found to react with triphenylphosphine to give the phosphazine and to methylenate mercuric chloride. 1,3-Dipolar addition to acrylonitrile, methyl vinyl ketone, and diethyl maleate gave stable Δ^2-pyrazolines, and 1,3-dipolar additions to two vinylphosphonate esters were carried out in such a manner that the pyrazolines were decomposed to the cyclopropanes. Protolysis reactions of both diazo compounds are described and dimethyl diazomethylphosphonate could be metalated with mercury(II) and silver(I) acetylacetonates.

We have reported recently concerning the preparation and copper-catalyzed decomposition of a number of substituted α-dimethylphosphonodiazoalkanes.[2,3] In all these examples the intermediate carbene, $(MeO)_2P(O)CR$ [or its Cu(I) complex], underwent rapid intramolecular rearrangements, and attempted trapping of the divalent carbon species with olefinic substrates was not successful. We report here concerning two such reagents which are useful divalent carbon transfer reagents, dimethyl α-diazomethylphosphonate, $(MeO)_2P(O)CHN_2$, and dimethyl α-diazobenzylphosphonate, $(MeO)_2P(O)C(N_2)C_6H_5$. Also described are some other types of reactions of these diazoalkanes and of dimethyl α-diazoethylphosphonate, $(MeO)_2P(O)C(N_2)CH_3$.

Results and Discussion

Preparation of the Diazoalkanes.—The preparation of dimethyl α-diazoethylphosphonate already has been described.[2] A very similar procedure, room-temperature decomposition of the *p*-toluenesulfonylhydrazone sodium salt, was used in the synthesis of the α-diazobenzylphosphonate ester (eq 1). This compound

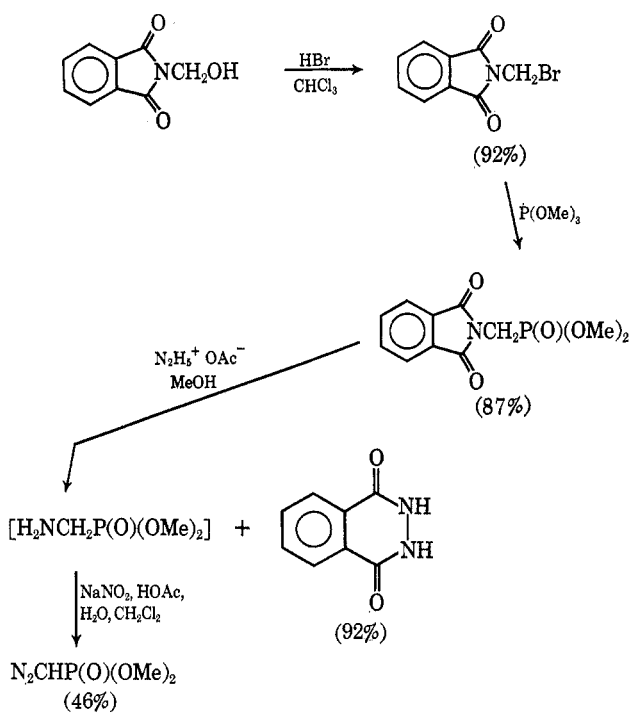


(1)

was isolated as an orange crystalline solid, mp 44.0–44.5°, which was unusually stable. It could be distilled at reduced pressure and was stable indefinitely at room temperature. It was recovered unchanged after its benzene solution had been heated at reflux for 48 hr but underwent complete decomposition when this treatment was carried out in the presence of copper powder. Pure $(MeO)_2P(O)C(N_2)Ph$ could be heated to 140° before evolution of a gas became apparent, and decomposition was not complete even at 190°.

A different synthetic sequence was employed in the preparation of dimethyl diazomethylphosphonate because of the nonexistence and presumed instability of the required carbonyl precursor [$HCOP(O)(OMe)_2 \rightarrow HP(O)(OMe)_2 + CO$] (Scheme I). The intermediate dimethyl aminomethylphosphonate was too unstable to be isolated in the free form but was stable as the unisolated acetate in solution. The presence of this amine in solution was demonstrated by the preparation of its *N*-tosyl derivative.

SCHEME I



Dimethyl diazomethylphosphonate was isolated as a distillable yellow liquid which was stable indefinitely when stored in a refrigerator.

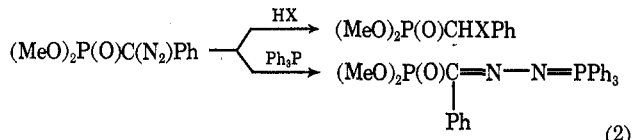
Both dimethylphosphono-substituted diazoalkanes reacted as expected with acids and with triphenylphos-

(1) Preliminary communications: (a) D. Seyferth, P. Hilbert, and R. S. Marmor, *J. Amer. Chem. Soc.*, **89**, 4811 (1967); (b) D. Seyferth and R. S. Marmor, *Tetrahedron Lett.*, 2493 (1970).

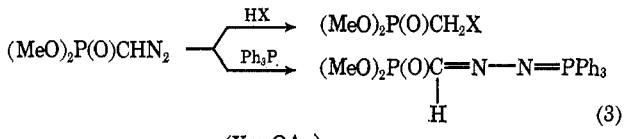
(2) D. Seyferth and R. S. Marmor, *J. Org. Chem.*, **36**, 128 (1971).

(3) A brief survey of the literature of phosphorus-substituted diazoalkanes is given in ref 2 and will not be repeated here.

phine (eq 2 and 3). Dimethyl diazomethylphosphonate could be metalated: with silver acetylacetonate to

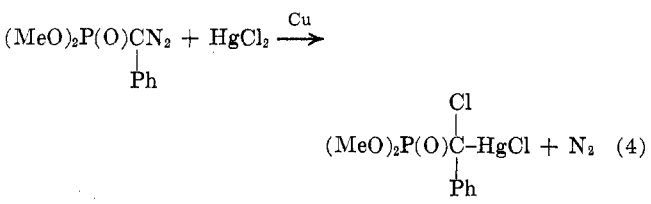


(X = Cl, OTs, OAc) (2)



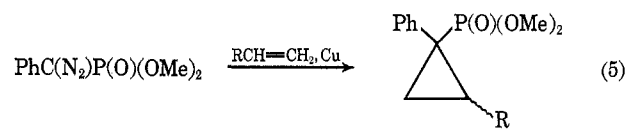
(X = OAc) (3)

give a surprisingly stable silver derivative as a yellow powder and with mercuric acetylacetonate to give the mercurial, $Hg[C(N_2)P(O)(OMe)_2]_2$. The well-known methylenation of mercuric halides by diazoalkanes[4,5] also could be effected using dimethyl α-diazobenzylphosphonate, but the yield of pure product was low (eq 4).

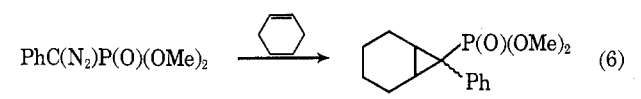


(4)

Preparation of Dimethylphosphono-Substituted Cyclopropanes.—Decomposition of $(MeO)_2P(O)C(N_2)Ph$ and $(MeO)_2P(O)CHN_2$ in the presence of copper powder and an excess of an olefin produced cyclopropanes.



(R = n-C5H11, Me3SiCH2) (5)



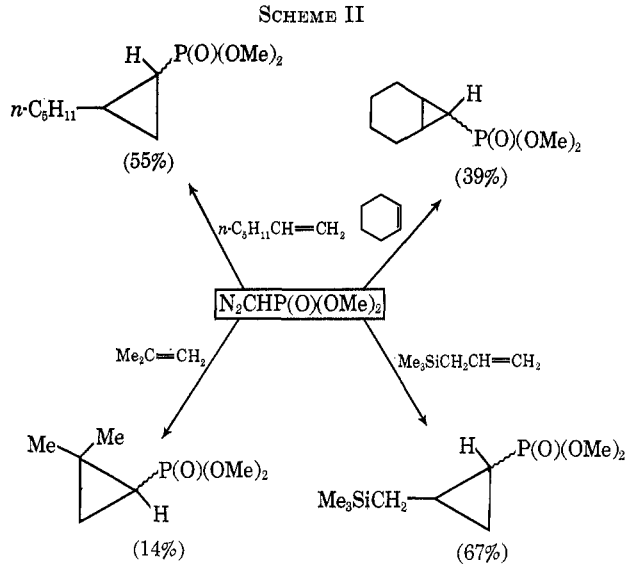
(6)

Dimethyl diazomethylphosphonate underwent divalent carbon transfer reactions with olefins when it was stirred at 0° with a large excess of the olefin, dichloromethane as a cosolvent, and copper powder. In the absence of dichloromethane the yields were markedly lower owing to the low solubility of the diazoalkane in the various olefins. In the reaction with cyclohexene, copper powder was found to be the most effective catalyst, giving higher yields and less tar than in reactions employing copper(I) chloride and copper(II) acetylacetonate. Scheme II summarizes these results.

The available evidence[6] suggests that copper-catalyzed diazoalkane reactions involve intermediate carbene–Cu(I) complexes, and that it is these which react with the olefin to form the cyclopropane. In the present examples the possibility of forming the olefins *via* a 1,3-dipolar addition of the diazoalkane to the olefin

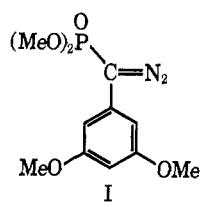
(4) L. Hellerman and M. D. Newman, *J. Amer. Chem. Soc.*, **54**, 2859 (1932).
(5) D. Seyferth, *Chem. Rev.*, **55**, 1155 (1955).
(6) W. Kirmse, "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim/Bergstr., 1969, Chapter 5.

SCHEME II



followed by decomposition of the resulting Δ1-pyrazoline to the cyclopropane also must be considered. The latter course is rather unlikely since we are dealing with unactivated (toward 1,3 dipoles) olefins. With activated olefins (see below), the latter course most certainly is operative. For the examples given above, however, a carbenoid process is the most likely.

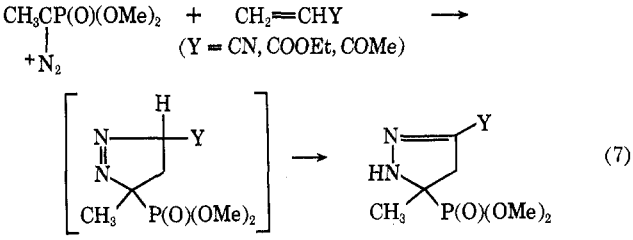
During the course of this study dimethyl α-diazo-3,5-dimethoxybenzylphosphonate (I) also was pre-



I

pared, but its chemistry was not investigated. Its copper-catalyzed decomposition gave a complex product mixture.

1,3-Dipolar Additions.—Dimethyl α-diazoethylphosphonate underwent 1,3-dipolar addition reactions with ethyl acrylate, acrylonitrile, and methyl vinyl ketone to give the corresponding dimethylphosphono-substituted Δ2-pyrazoline (eq 7). These adducts were not

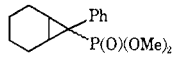
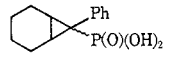
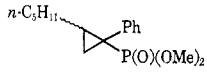
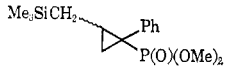
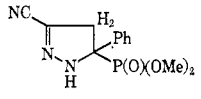
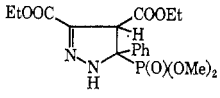
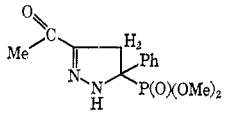
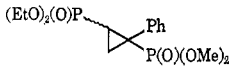
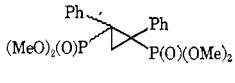
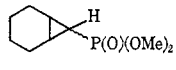
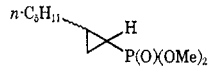
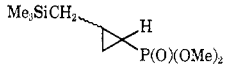
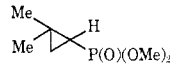
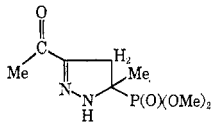
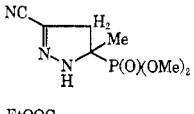
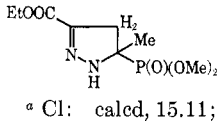


(7)

stable on storage at room temperature, presumably because of their ability to revert to the Δ1-pyrazoline and lose nitrogen to form a cyclopropane contaminated with olefin and polymer. Dimethyl α-diazobenzylphosphonate showed similar reactivity toward activated olefins such as acrylonitrile, methyl vinyl ketone, diethyl maleate, diethyl vinylphosphonate, and dimethyl α-styrylphosphonate. The pyrazolines derived from the two dialkylphosphono-substituted olefins

TABLE I

PRODUCTS DERIVED FROM DIMETHYLPHOSPHONO-SUBSTITUTED DIAZOALKANES

Compound	Registry no.	Obtained from reaction with (% yield)	Bp, °C (mm)	Mp, °C	$n^{25}D$	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
A. From $PhC(N_2)P(O)(OMe)_2$									
$PhCHClP(O)(OMe)_2$	16965-75-6	HCl (86)	105 (0.07)	...	1.5276	46.07	46.28	5.16	5.36[a]
$PhCH(OAc)P(O)(OMe)_2$	16965-84-7	HOAc (79)	74 (0.03)	...	1.5010	51.16	50.91	5.86	5.96
$PhCH(OTs)P(O)(OMe)_2$	28446-79-9	p-$CH_3C_6H_4SO_3H$ (71)	...	86–87	...	51.89	51.72	5.17	5.28
$Ph_3P{=}NN{=}C(Ph)P(O)(OMe)_2$	16965-77-8	Ph_3P (20)	...	132–133	...	66.39	66.50	5.37	5.69
$PhC(Cl)P(O)(OMe)_2$ | HgCl	16965-74-5	$HgCl_2$ (8)	...	151	...	23.01	23.32	2.36	2.51[b]
	16965-86-9	 (96) crude	...	187.5–188.0	...	54.55	54.29	5.60	5.67
	28446-82-4	(95)	...	274–275	...	61.89	62.16	6.79	6.92
	16965-85-8	n-$C_5H_{11}CH{=}CH_2$ (73)	108 (0.04)	...	1.5025	64.84	65.01	8.50	8.63
	28446-84-6	$Me_3SiCH_2CH{=}CH_2$ (76)	109–111 (0.02)	...	1.5050	57.66	57.43	8.07	8.01
	28446-85-7	$CH_2{=}CHCN$ (90)	...	137.5–138.5	...	51.61	51.97	5.05	5.00
	16965-78-9	HC—COOEt (46) ‖ HC—COOEt	...	148.5–149.0	...	51.25	51.48	5.82	5.88
	16965-76-7	O ‖ $CH_2{=}CHCMe$ (92)	...	70	...	52.69	52.88	5.79	5.79
	28446-88-0	$CH_2{=}CHP(O)(OEt)_2$ (90)	>100 (0.10)	...	1.5078	49.73	49.64	6.68	6.62
	28446-89-1	$CH_2{=}C(Ph)PO(OMe)_2$ (30)	190 (0.04)	100–125	...	55.61	55.39	5.90	6.31
B. From $HC(N_2)P(O)(OMe)_2$									
$AcOCH_2P(O)(OMe)_2$	24630-57-7	AcOH (78)	63 (0.08)	...	1.4295	32.97	32.88	6.09	6.38
$Ph_3P{=}NN{=}CHP(O)(OMe)_2$	27491-71-0	Ph_3P (12)	...	132–133	...	61.16	61.12	5.38	5.30
$Hg[C(N_2)P(O)(OMe)_2]_2$	27491-73-2	$Hg(acac)_2$ (80)	...	106.5–107.0	...	14.45	14.65	2.43	2.56
	28446-93-7	 (39)	61–63 (0.02)	...	1.4721	52.93	52.50	8.39	8.33
	28446-94-8	n-$C_5H_{11}CH{=}CH_2$ (55)	63–65 (0.03)	...	1.4439	54.33	54.14	9.61	9.59
	28446-95-9	$Me_3SiCH_2CH{=}CH_2$ (67)	55–57 (0.02)	...	1.4489	45.74	45.63	8.96	8.92
	26580-16-5	$Me_2C{=}CH_2$ (14)	52 (0.90)	...	1.4369	47.19	47.01	8.49	8.49
C. From $CH_3C(N_2)P(O)(OMe)_2$									
	16965-81-4	O ‖ $CH_2{=}CH{-}CMe$ (100)	...	111–112	...	41.04	41.35	6.45	6.72
	16965-83-6	$CH_2{=}CHCN$ (100)	...	89–92	...	38.71	38.80	5.57	5.76
	16965-82-5	$CH_2{=}CHCOOEt$ (98)	...	120–123	...	40.91	40.52	6.49	6.57

[a] Cl: calcd, 15.11; found, 14.76. [b] Cl: calcd, 15.10; found, 14.93.

TABLE II

SPECTROSCOPIC PROPERTIES OF PRODUCTS DERIVED FROM DIMETHYLPHOSPHONO-SUBSTITUTED DIAZOALKANES

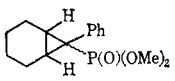
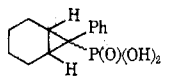
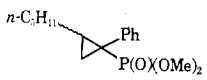
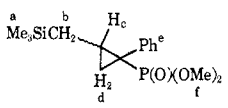
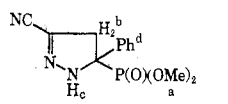
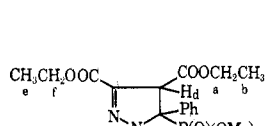
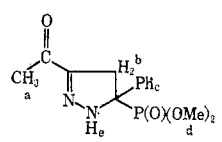
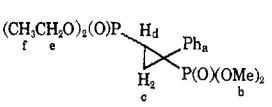
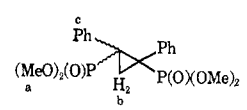
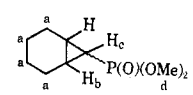
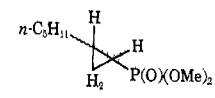
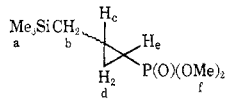
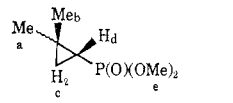
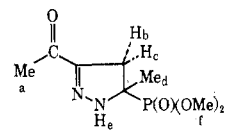
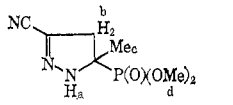
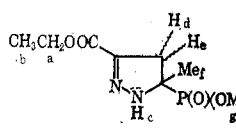
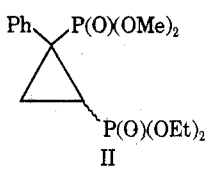
Compound	Nmr (solvent), δ (ppm)	Ir (medium), cm^{-1} (principal bands)
$PhCHClP(O)(OMe)_2$	(CCl_4) 3.50, 3.74 (two d, 6, J = 10.5 Hz), 4.97 (d, 1, J = 14 Hz), 7.17-7.65 (m, 5)	(Neat liq) 1265 (s, P=O), 1185 (m), 1030 (s, POC)
$PhCH(OAc)P(O)(OMe)_2$	(CCl_4) 2.02 (s, 3), 3.52, 3.58 (two d, 6, J = 10.5 Hz), 6.13 (d, 1, J = 13.5 Hz), 7.17-7.67 (m, 5).	(Neat liq) 1755 (s, C=O), 1265 (s, P=O), 1025 (s, POC).
$PhCH(OTs)P(O)(OMe)_2$	($CDCl_3$) 2.24 (s, 3), 3.47, 3.52 (two overlapping d, 6, J = 10.5 Hz), 5.62 (d, 1, J = 15.5 Hz), 6.9 7.6 (m, 9)	(Nujol) 1370 (s, SO_2), 1260 (s, P=O), 1175 (s, SO_2), 1030 (s, POC)
$Ph_3P{=}NN{=}C(Ph)P(O)(OMe)_2$	...	(Nujol) 1240 (s, P=O), 1110 (s, P=N), 1020 (s, POC)
$PhC(Cl)(HgCl)P(O)(OMe)_2$	...	(Nujol) 1225 (s, P=O), 1035 (s, POC)
	($CDCl_3$), 0.2-1.3, 1.5-2.2 (m, 10), 3.58 (d, 6, J = 10.5 Hz), 7.28 (s, 5)	(KBr) 1250 (s, P=O), 1030 (s, POC)
	...	(Nujol) 1210 (m), 1180 (m), 1135 (m), 1010 (s, POH), 705 (m)
	(CCl_4) 0.2-2.0 (m, 14), 3.51, 3.57 (two d, 6, J = 10.5 Hz), 7.25 (s, 5)	(Neat liq) 1260 (s, P=O), 1040 (s, POC)
	(CCl_4) 0.00 [s, a (major isomer)], 0.02 [s, a (minor isomer)], 9], 0.5-1.9 (m, 5, b, c, and d), 3.52 [d, 6, J = 11 Hz (major isomer; minor isomer seen as a doublet shoulder), f], 7.23 (s, 5, e)	Neat liq) 1250 (s, P=O and Me_3Si), 1030 (s, POC)
	($CDCl_3$) 2.8-3.9 [m with two d at 3.58 and 3.63 (J = 10 Hz, a), 8, a and b], 7.26 (s, 5, d), 8.64 (s, 1, c)	(Nujol) 3205 (m, NH), 2210 (m, C≡N), 1225 (s, P=O), 1020 (s, POC)
	($CDCl_3$) 0.81 (t, 3, J = 7 Hz, b or e), 1.29 (t, 3, J = 7 Hz, b or e), 3.68 (t, 6, J = 11 Hz, g, coincidental overlap of two d), 4.26 (quartet, 4, J = 11 Hz, a and f), 3.0-4.6 (underlying peaks distorting major peaks, 1, d), 4.90 (impurity, 0.5), 7.32, 7.58 (two broad s, 5, Ph), 8.51 (s, 1, c)	(Nujol) 3205 (m, NH), 1735 (s, $COOCH_2CH_3$), 1725 (s, $COOCH_2CH_3$), 1050 (s), 1020 (s)
	($CDCl_3$) 2.40 (s, 3, a), 3.62, 3.68 (two d, J = 10.2 Hz, d, 6), 2.9-4.2 (complex underlying pattern, 2, b), 7.2-7.6 (m, 5, c), 8.13 (broad s, 1, e)	(Nujol) 3220 (s, NH), 1660 (s, C=O), 1230 (s, P=O), 1030 (s, POC)
	(CCl_4) 0.75-1.95 (m with max peak at 1.32, 9, c, d, and f), 3.3-4.3 (m, 10, b and e), 6.9-7.5 (m with max peak at 7.15, 5, a)	(Neat liq) 1250 (s, P=O), 1025 (s, POC)
	($CDCl_3$) 2.33 (t with underlying peaks, J = 14.5 Hz, 2, b), 2.98, 3.20, 3.64 (three d with underlying peaks, J = 11 Hz, 12, a), 7.2-7.8 (m with max peak at 7.36, 10, c)	(Neat liq) 1250 (s, P=O), 1030 (s, POC)
$AcOCH_2P(O)(OMe)_2$	(CCl_4) 2.12 (s, 3), 3.78 (d, 6, J = 10.5 Hz), 4.37 (d, 2, J = 8.5 Hz)	(Neat liq) 1755 (s, C=O), 1220 (s, P=O), 1040 (s, POC)
$Ph_3P{=}NN{=}CHP(O)(OMe)_2$	($CDCl_3$) 3.54 (d, 6, J = 10.5 Hz, c), 7.1-7.7 (m, 16, a + b)	(Nujol) 1290 (s), 1240 (s), 1110 (s, P=N), 825 (s), 720 (s)
$Hg[C(N_2)P(O)(OMe)_2]_2$	($CDCl_3$) 3.80 (d, J = 11.5 Hz)	(Nujol) 2070 (s, C=N=N), 1245 (s, P=O), 1020 (s, POC)
	(CCl_4) 0.43 (quartet, 1, J_P = $J_{b,c}$ = 5 Hz, c), 1.1-2.2 (m with max peaks at 1.23 and 1.75, 10, a and b), 3.60 (d, 6, J = 11 Hz, d)	(Neat liq) 1250 (s, P=O), 1030 (s, POC)
	(CCl_4) 0.3-1.7 (m with max peaks at 0.90 and 1.36, 15), 3.65 (d, 6, J = 10.7 Hz)	(Neat liq) 3060 (w), 1245 (s, P=O), 1030 (s, POC)

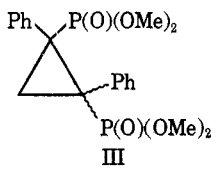
TABLE II (*Continued*)

Compound	Nmr (solvent), δ (ppm)	Ir (medium), cm⁻¹ (principal bands)
	(CCl_4) 0.06 (s, 9, a), 0.25–1.25 (m, 6, b, c, d, and e), 3.64 (d, J = 10.7 Hz, minor isomer), 3.65 [d, J = 10.7 Hz, major isomer), 6, f]	(Neat liq) 3060 (w), 1250 (s, P=O and Me_3Si), 1030 (s, POC)
	(CCl_4) 0.3–1.3 (m with max peaks at 0.70, 3, c and d), 1.14 (d, 3, J_P = 2.2 Hz, a or b), 1.29 (s, 3, a or b), 3.64 (d, 6, J = 10.7 Hz, e)	(Neat liq) 3060 (w), 1250 (s, P=O), 1030 (s, POC)
	($CDCl_3$) 1.46 (d, 3, J = 15 Hz, 3), 2.39 (s, 3, a), 2.88 (d, 1, J = 11.5 Hz, b), 3.20 (d, 1, J = 19 Hz, c), 3.83 and 3.86 (two d, 6, J = 10 Hz, f), 7.85 (broad s, 1, e)	(Nujol) 3225 (s, NH), 1655 (s, C=O), 1240 (m, P=O), 1025 (s, POC)
	($CDCl_3$) 1.48 (d, 3, J = 15 Hz, c), 2.77, 3.04, 3.41 (three s, 2, b), 3.82, 3.84 (two d, 6, J = 10 Hz, d), 7.66 broad s, 1, a)	(Nujol) 3215 (s, NH), 2220 (s, C≡N), 1220 (s, P=O), 1045 (s, POC)
	($CDCl_3$) 1.33 (t, 3, J = 7 Hz, b), 1.46 (d, 3, J = 14.5 Hz, f), 2.95 (d, 1, J = 13 Hz, d), 3.28 (d, 1, J = 20 Hz, e), 3.81, 3.85 (two d, 6, J = 10 Hz, g), 4.32 (quartet, 2, J = 7 Hz, a), 6.54 (broad s, 1, c)	(Nujol) 3220 (s, NH), 1725 (s, C=O), 1240 (s, P=O), 1050 (s, POC)

decomposed smoothly on distillation to give the cyclopropanes II and III, respectively, which contain two phosphorus substituents.



II



III

The results described here thus show $(MeO)_2P(O)C(N_2)R$ (R = H, Ph, and Me) to be useful reagents for organophosphorus syntheses, especially in the synthesis of phosphorus-substituted cyclopropanes. In view of the widely varied reactivity of their diazoalkane function, they should serve in the preparation of a wide variety of organophosphorus compounds.

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, nmr spectra using Varian A-60 or T-60 spectrometers. Chemical shifts are given in ppm downfield from internal TMS (δ units). Melting points are uncorrected. All gas–liquid partition chromatography (glc) was carried out using an F & M gas chromatograph.

All the products derived from the dimethylphosphono-substituted diazoalkanes, together with their physical properties and analytical data, are listed in Table I. Their spectroscopic properties are given in Table II.

Preparation of Dimethyl α-Diazobenzylphosphonate.—A solution of 186.2 g (1.0 mol) of *p*-toluenesulfonylhydrazine in 1 l. of THF in a 4-l. flask was chilled to 0°, and 37 ml of concentrated HCl (0.5 mol) was added. The resulting solution was stirred in an ice bath while 214.2 g (1.0 mol) of dimethyl benzoylphosphonate[7] ($n^{25}D$ 1.5248) was added over a 5-min period. The flask was stoppered and the mixture was allowed to warm to room temperature over a 6-hr period. The resulting heavy white precipitate was filtered and dried to give 304.9 g of solid, mp 168–169° (dec). The mother liquor was evaporated overnight at room temperature under an air stream to give a second crop, 47.6 g, mp 165–166° (dec); the total yield thus was 92%. Recrystallization from methanol gave an 84% recovery of pure product, mp 173–174°.

Anal. Calcd for $C_{16}H_{19}N_2O_5SP$: C, 50.25; H, 5.01. Found: C, 50.28; H, 5.04. Nmr ($CDCl_3$): δ 2.44 (s, 3, Ar CH_3), 3.73 (d, 6, J = 11 Hz, $POCH_3$), 7.1–7.9 (m, 9, aryl), and 8.4 ppm (broad s, 1, NH).

A suspension of dimethyl benzoylphosphonate *p*-toluenesulfonylhydrazone (21.35 g, 55.9 mmol) in a solution of sodium carbonate (6.05 g, 57.0 mmol) in 100 ml of distilled water was stirred at room temperature for 15 hr, during which time the hydrazone slowly dissolved and the solution became orange and opaque. The mixture was extracted with two 100-ml portions of diethyl ether, each portion being washed with 50 ml of water. The combined ether extracts were dried (Na_2SO_4) and evaporated to a volume of 50 ml. The concentrated ether solution was chilled slowly in a −78° bath with scratching of the flask sides. This procedure gave 9.14 g of orange crystals, mp 38–42°. The mother liquor was concentrated to 20 ml and 20 ml of pentane was added; on chilling, a second crop of 2.70 g, mp 38–40°, was obtained, giving a total yield of 94%. Recrystallization from diethyl ether at −78° gave pure product (93% recovery), mp 44.0–44.5°.

Anal. Calcd for $C_9H_{11}N_2O_3P$: C, 47.78; H, 4.91. Found: C, 47.84; H, 5.03. Nmr (CCl_4): δ 3.67 (d, 6, J = 11.7 Hz, $POCH_3$), 6.9–7.4 ppm (m, 5, aryl). Ir (liq film): 2950 (m), 2825 (m), 2975 (s, C=N=N), 1600 (m), 1500 (m), 1295 (s), 1265 (s, P=O), 1185 (s), 1025 (s, POC), 830 (s), 755 (s), and 685 (m) cm^{-1}.

Preparation of Dimethyl Diazomethylphosphonate. A. Bromomethylphthalimide.—An improved procedure is reported. A suspension of hydroxymethylphthalimide[8] in 3 l. of chloroform was stirred and refluxed gently in a 5-l. flask while gaseous hydrogen bromide (Matheson) was admitted through a submerged fritted glass gas inlet tube at a moderate rate for 2 hr. After 25 min the mixture became homogeneous, and after 70 min gas was no longer being absorbed rapidly. The solution was poured (while still warm) into a separatory funnel and the lower aqueous HBr layer was discarded. The organic layer was extracted with 500 ml of warm water (color change from orange to white). The organic layer then was dried (Na_2SO_4), filtered through Celite, and evaporated at reduced pressure. The crystalline residue was recrystallized from 2.1 l. of acetone to give 577 g of thick white needles, mp 150–152°. The mother liquor was concentrated to give a second crop of 82 g, mp 150–151°. The total yield was 659 g (92%), lit.[9] mp 148°. It must be emphasized that an adequate excess of HBr must be used in the above procedure; if this is not done, the yield is greatly reduced. Other routes to

(7) K. D. Berlin, D. M. Hellwege, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1265 (1965).

(8) S. R. Buc, *J. Amer. Chem. Soc.*, **69**, 254 (1947).

(9) G. W. Pucher and T. B. Johnson, *ibid.*, **44**, 817 (1922).

this product were tried (*via* HBr and H_2SO_4[9] and *via* PBr_3[10]), but the yields obtained were not so high.

B. Dimethyl Phthalimidomethylphosphonate.—A 2-l. flask equipped with a reflux condenser and a stirrer was charged with 240 g (1.0 mol) of bromomethylphthalimide, freshly distilled trimethyl phosphite (136.5 g, 1.1 mol), and 400 ml of xylene. The flask was swept with nitrogen and heated slowly to near reflux, at which time a vigorous but controllable reaction ensued. Heating was discontinued at this point and continued after the initial exothermic reaction had subsided. The reaction mixture was heated at reflux for 5 hr, then 300 ml of solvent was distilled away, and the remaining solution was allowed to cool overnight in a sealed flask. The crystalline product which had formed was collected, heated in 300 ml of dry ether for several hr, filtered again, and dried under vacuum to give 232.5 g of product (87%), mp 113–117° (prior softening). Several recrystallizations from ether and a final recrystallization from $CHCl_3$–CCl_4 afforded an analytical sample, mp 117.5–119°.

Anal. Calcd for $C_{11}H_{12}NO_5P$: C, 49.08; H, 4.49. Found: C, 48.98; H, 4.45. Nmr ($CDCl_3$): δ 3.85 (d, 6, J = 10.7 Hz, $POCH_3$), 4.14 (d, 2, J = 11.5 Hz, NCH_2P), 7.8 ppm (broad s, 4, aryl). Ir (Nujol mull, principal bands): 1720 (C=O), 1465, 1405, 1385, 1310, 1250 (P=O), 1190, 1070, 1050, 1020 (POC), 910, 840, and 715 cm^{-1}.

C. Dimethyl Diazomethylphosphonate.—A solution of 53.8 g (0.20 mol) of dimethyl phthalimidomethylphosphonate and 95% anhydrous hydrazine (0.21 mol) in 400 ml of methanol was stirred at room temperature under nitrogen for 45 hr. Then 20 ml of acetic acid was added and the mixture was stirred 5 min longer and filtered. The precipitated phthalhydrazide was dried, 29.7 g (92%). The filtrate was evaporated at reduced pressure and the residue was dissolved in 50 ml of acetic acid. A solution of sodium nitrite (21.7 g, 0.30 mol, in 50 ml of water) was added dropwise over 5 min while the flask was being swirled in an ice bath. The flask was kept in the ice bath, with occasional swirling, for another 5 min, and then 53 g of sodium carbonate was added slowly in portions, followed by 200 ml of ice water. The reaction mixture was extracted with three 100-ml portions of dichloromethane. The combined organic layers were extracted with 100 ml of saturated $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated at reduced pressure. The orange liquid residue was short-path distilled to give 13.77 g (46%) of the diazo compound, bp 59° (0.42 mm), as a yellow liquid, $n^{25}D$ 1.4585.

Anal. Calcd for $C_3H_7N_2O_3P$: C, 24.01; H, 4.70. Found: C, 23.73; H, 4.85. Nmr (neat): δ 3.73 (d, 6, J = 11.5 Hz, $POCH_3$), 4.49 ppm (d, 1, J = 10.7 Hz, PCH). Ir (liq film): 3075 (w), 3020 (w), 2960 (m), 2860 (m), 2110 (s, C=N=N), 1760 (s), 1660 (w), 1465 (m), 1300 (s), 1250 (s, P=O), 1185 (m), 1160 (sh), 1030 (POC), 915 (w), 830 (s), 770 (w), 735 (w), and 710 (w) cm^{-1}.

The intermediacy of **dimethyl aminomethylphosphonate** was demonstrated in the following manner. A solution of dimethyl phthalimidomethyl phosphonate (8.7 mmol) and a slight excess of 95% anhydrous hydrazine in 15 ml of methanol was stirred at room temperature for 15 hr, as in the preparation above. The precipitated phthalhydrazide was filtered and the filtrate evaporated (near room temperature) to leave a yellow oil. Since acetic acid was not added as it had been in the diazo compound preparation, the free amine was present after evaporation of the solvent, and it was necessary to not allow the temperature to rise much above room temperature to prevent exothermic decomposition of the amine. Benzene (10 ml) was added and the mixture cooled to 0°. An ice-cold solution of 1.66 g of *p*-toluenesulfonyl chloride in 5 ml of pyridine was added and the mixture poured into 50 ml of water containing 10 ml of concentrated HCl after a 10-min reaction time. Extraction with chloroform, evaporation of the organic layer, and trituration of the residual oil with hexane followed. The resulting solid was recrystallized from benzene to give yellow needles, mp 117–118° (1.0 g, 38%). An analytical sample (from benzene), long thick white needles, had mp 118–119° and was shown to be **dimethyl *p*-toluenesulfonylaminomethylphosphonate**, p-$CH_3C_6H_4SO_2NHCH_2P(O)(OMe)_2$.

Anal. Calcd for $C_{10}H_{16}NO_5SP$: C, 40.95; H, 5.50; N, 4.78. Found: C, 41.23; H, 5.47; N, 4.69. Nmr ($CDCl_3$): δ 2.43 (s, 3, Ar-CH_3), 3.27 (d of d, 2, J_{HCNH} = 6.5 Hz, J_{HCP} = 13.5 Hz, PCH_2N), 3.78 (d, 6, J = 10.5 Hz, $POCH_3$), 6.6 (broad s, 1, NH), 7.32 and 7.80 [two d, 4, J (both) = 8 Hz, aryl].

(10) O. Mancera and O. Lemberger, *J. Org. Chem.*, **15**, 1253 (1950).

Preparation of Dimethyl α-Diazo-3,5-dimethoxybenzylphosphonate.—Dimethyl 3,5-dimethoxybenzoylphosphonate was prepared[7] on a 0.113-mol scale in 92% yield. The product was isolated as a viscous, yellow liquid, $n^{25}D$ 1.5337, bp *ca.* 153° (0.02 mm).

Anal. Calcd for $C_{11}H_{15}O_6P$: C, 48.18; H, 5.51. Found: C, 48.49; H, 5.45.

This compound (102.8 mmol) was converted to the *p*-toluenesulfonylhydrazone by the procedure described above for dimethyl benzoylphosphonate. The crude product was obtained as a yellow oil. This was washed with water and extracted with boiling ether to leave 30.16 g of presumed anti isomer, mp 158° (dec). The ether extracts were evaporated; the residual oil crystallized and was triturated with ether to give 10.40 g of presumed syn isomer, mp 107–108°. The total yield, 40.56 g, was 89%.

An analytical sample (from methanol) of the anti isomer had mp 164.5–165.5° (dec); the syn isomer (from methanol) had mp 113–114°.

Anal. Calcd for $C_{18}H_{23}N_2O_7SP$: C, 48.86; H, 5.24; N, 6.33. Found (anti isomer): C, 48.84; H, 5.23; N, 6.36. Found (syn isomer): C, 49.03; H, 5.30; N, 6.32.

To a solution of sodium carbonate (23.3 mmol) in 39 ml of water was added 8.57 g (19.4 mmol) of *syn*-dimethyl 3,5-dimethoxybenzoylphosphonate *p*-toluenesulfonylhydrazone. The reaction mixture was stirred under nitrogen for 24.5 hr, then was extracted with dichloromethane. Work-up of the organic layer gave 4.96 g of bright yellow powder (90%), mp 55–56° (from diethyl ether at −78°).

When the anti isomer was used, the reaction was noticeably slower in forming the yellow color, but work-up after 31 hr gave the diazo compound in 91% yield.

Anal. Calcd for $C_{11}H_{15}N_2O_5P$: C, 46.16; H, 5.28; N, 9.79. Found: C, 46.22; H, 5.43; N, 9.75. Nmr (CCl_4): δ 3.72 (s, 6, Ar OCH_3), 3.73 (d, 6, J = 12 Hz, $POCH_3$), 6.1–6.3 (m, 3, aryl). The ir spectrum (Nujol mull) showed the bands due to C=N=N at 2090, to P=O at 1255, and to POC at 1020 cm^{-1}.

Reactions of the Diazoalkanes with Acids.—Physical properties and analytical data for the products are given in Table I.

A. Dimethyl α-Diazobenzylphosphonate.—Diethyl ether, 100 ml, in a three-necked flask equipped with a dropping funnel, a stirring unit, a gas inlet tube whose tip was submerged below the liquid level, and a drying tube, was saturated with anhydrous hydrogen chloride at −78°. While the HCl stream was continued, 1.40 g of the diazo compound in 50 ml of ether was added dropwise over 15 min, its orange color being discharged instantaneously. Evaporation of solvent, treatment of the residual oil with sodium bicarbonate solution, and ether extraction followed. Distillation of the ether extracts gave 1.25 g (86%) of **dimethyl α-chlorobenzylphosphonate.**

A solution of 10.0 mmol of the diazo compound and 20.0 mmol of glacial acetic acid in 20 ml of diethyl ether was heated at reflux for 15 hr, at which time nitrogen evolution was complete. Distillation of the reaction mixture gave 2.0 g (79%) of **dimethyl α-acetoxybenzylphosphonate.**

A warm solution of anhydrous *p*-toluenesulfonic acid in benzene (prepared by distilling 25 ml of benzene and water from a solution of 10 mmol of *p*-toluenesulfonic acid monohydrate in 50 ml of benzene) was added in portions to a solution of the diazo compound until the orange color was discharged. Evaporation of the reaction mixture was followed by extraction of the residual yellow oil with ether and washing of the ether solution with saturated sodium bicarbonate. Evaporation of the dried ether solution gave a solid which was recrystallized from methanol–water to give 1.32 g (71%) of **dimethyl α-(*p*-toluenesulfonyloxy)-benzylphosphonate,** mp 84–86°. An analytical sample (from CCl_4) had mp 86–87°.

B. Dimethyl Diazomethylphosphonate.—A solution of 4.36 mmol of the diazo compound in 15 ml of glacial acetic acid was heated on the steam bath with exclusion of moisture for 1.5 hr. Evaporation of the excess acid, treatment of the residue with saturated sodium bicarbonate solution, and extraction with chloroform followed. Distillation (short path) of the chloroform solutions gave 617 mg (78%) of the product, **dimethyl acetoxymethylphosphonate.**

Miscellaneous Reactions of the Diazoalkanes. A. With Triphenylphosphine.—A solution containing 5 mmol each of dimethyl α-diazobenzylphosphonate and triphenylphosphine in 10 ml of benzene was kept at room temperature under nitrogen for 56 hr. It then was warmed on the steam bath for 5 min and

diluted with heptane. The product separated out as an oil. The solution was decanted and the oil was triturated with pentane. The resulting powder was recrystallized twice from benzene–heptane to give the phosphazine $Ph_3P{=}NNC(Ph)P(O)(OMe)_2$.

When 2.41 mmol each of triphenylphosphine and dimethyl diazomethylphosphonate in 10 ml of benzene were stirred at room temperature under nitrogen for 12 hr, a white precipitate resulted. Recrystallization gave the phosphazine $Ph_3P{=}NN{=}CHP(O)(OMe)_2$ as long white silky needles in 12% yield.

B. Reaction of Dimethyl α-Diazobenzylphosphonate with Mercuric Chloride.—A THF solution (10 ml) of the diazo compound (9.08 mmol) and an equimolar quantity of mercuric chloride was heated at reflux for 30 min. No perceptible color change or gas evolution was apparent, but nitrogen evolution began after a trace of copper powder was added. The reaction mixture was heated at reflux for another hour. Removal of solvent at reduced pressure left a yellow oil. This was taken up in 150 ml of benzene, treated with activated charcoal, and filtered through Celite. Evaporation to 80 ml was followed by addition of 670 ml of hexane. The resulting solution was left to stand overnight; 0.35 g (8%) of light yellow crystals was deposited. An analytical sample was recrystallized once from benzene–cyclohexane and twice from benzene–heptane.

C. Reaction of Dimethyl Diazomethylphosphonate with Mercury(II) and Silver(I) Acetylacetonates.—To a solution of 10.0 mmol of the diazo compound in 10 ml of dichloromethane was added 2.19 g (5.5 mmol) of mercury(II) acetylacetonate. The reaction mixture was stirred in a sealed flask for 40 min and filtered through Celite; the filtrate was evaporated to *ca.* 5 ml. Diethyl ether (50 ml) was added slowly; 2.0 g (80%) of yellow needles formed. These were characterized as $Hg[C(N_2)P(O)(OMe)_2]_2$.

The silver derivative was prepared in an analogous manner, substituting a 50% molar excess of silver(I) acetylacetonate and carrying out the stirring and filtering operations in subdued light. The product was a yellow powder (95% yield), mp 125° (explodes), and was freely soluble in dichloromethane to give a deep orange solution. It was not shock sensitive. Ir (Nujol mull): 2310 (sh), 2270 (w), 2070 (s, C=N=N), 2030 (sh), 1525 (w), 1220 (s, P=O), 1185 (m), 1145 (m), 1055 (s), 1030 (s), 890 (s), 810 (s), and 745 (m) cm^{-1}.

Copper-Catalyzed Reactions of the Diazoalkanes with Olefins. A. Dimethyl α-Diazobenzylphosphonate.—A 200-ml three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was charged with the olefin (100 ml, freshly distilled from lithium aluminum hydride), 6–10 mmol of the diazo compound, and 3.80 g (60 mg-atoms) of copper powder (J. T. Baker "purified grade"). The mixture was stirred at reflux under nitrogen until the orange diazoalkane color had been discharged (usually about a 12–24-hr reaction time was involved). The usually pale yellow mixture was filtered through Celite and the product cyclopropane was obtained by crystallization (in the case of cyclohexene) or distillation (in the case of 1-heptene and allyltrimethylsilane).

The product from cyclohexene, 7-(dimethylphosphono)-7-phenylnorcarane, was converted to the phosphonic acid by refluxing 331 mg of the dimethyl ester in 4 ml of concentrated HBr for 15 min. The mixture was cooled and the resulting white precipitate was filtered, washed with cold water, and dried to give 282 mg (95%) of 7-phenyl-7-phosphononorcarane, mp 271–273°. Recrystallization from aqueous methanol gave white needles, mp 274–275°.

B. Dimethyl Diazomethylphosphonate.—To a stirred mixture of the olefin (100 ml), 30 ml of dichloromethane, and 3.8 g of copper powder maintained in an ice bath under a nitrogen atmosphere was added 10 mmol of dimethyl diazomethylphosphonate. The reaction mixture was stirred at 0° for 8 hr and overnight at room temperature. Fractional distillation of the filtered (through Celite) reaction mixture gave the cyclopropane (yields in Table I) and the crude carbene "dimer," 1,2-bis(dimethylphosphono)ethylene (presumed identity; not obtained in pure state)[11] in variable (15–30%) yields.

The presence of dichloromethane was required in order to obtain good yields. Thus, in the case of cyclohexene, reaction with the diazo compound in the absence of dichloromethane gave the expected norcarane in 20% yield and "carbene dimer" in 68% yield. In the presence of dichloromethane these yields were 39 and 28%, respectively.

The reaction with isobutylene was carried out −7° for 16 hr.

1,3-Dipolar Addition Reactions of Dimethyl α-Diazobenzylphosphonate. A. Reactions in Which the Initial Adduct Was Isolated.—The diazo compound and the 1,3-dipolarophile (10- to 50-fold excess) in dry benzene were kept at room temperature for 1 or 2 days. The reaction mixture, if still orange at that time, was heated at reflux until a color change to yellow had occurred. Evaporation at reduced pressure and crystallization of the residue followed. Pure products were obtained by recrystallization from benzene–heptane (adducts from acrylonitrile, diethyl maleate) or chloroform–carbon tetrachloride (adduct from methyl vinyl ketone).

B. Reactions in Which the Cyclopropane Was Isolated. (a) Reaction with Dimethyl α-Styrylphosphonate.—α-Styrylphosphonic acid was prepared by the procedure of Conant and Coyne[12] and was esterified with an excess of diazomethane in diethyl ether. The reaction mixture was washed with saturated $NaHCO_3$, dried, and evaporated. The residual yellow oil was short-path distilled (141° at 4.3 mm) and redistilled at 101° (0.1 mm) to give dimethyl α-styrylphosphonate in 62% yield. A trace of hydroquinone prevented yellowing of the sample on storage in the freezer. A center cut had $n^{25}D$ 1.5267.

Anal. Calcd for $C_{10}H_{13}O_3P$: C, 56.60; H, 6.17. Found: C, 56.66; H, 6.37. Ir (liq film): 3050 (sh), 3000 (m), 2945 (s), 2840 (m), 1600 (w), 1575 (w), 1495 (s), 1445 (m), 1250 (s), 1180 (m), 1100 (m), 1050 (s), 960 (m), 935 (m), 850 (s), 830 (s), 785 (s), 765 (s), 720 (m), 700 (s), and 680 (m) cm^{-1}.

A solution of this vinylphosphonate ester (1.06 g, 5.0 mmol) and the diazo compound (1.13 g, 5.0 mmol) in 10 ml of benzene was heated at reflux under nitrogen for 7 days. Distillation of the reaction mixture gave 0.42 g of unconverted vinylphosphonate ester and then a viscous yellow syrup, boiling range 178–190° at 0.04 mm. Redistillation gave pure product, bp 190° (0.04 mm), presumably a mixture of isomers. The syrup changed to a white powder, melting range 100–125°, after it had stood for 2 weeks.

(b) Reaction with Diethyl Vinylphosphonate.—A solution containing 5.0 mmol of the diazo compound and 50 mmol of the vinylphosphonate ester was heated on the steam bath for 3 hr. The now colorless reaction mixture was distilled to remove the unconverted vinylphosphonate ester, and the yellow oil which remained, whose ir spectrum indicated the presence of some pyrazoline (N–H absorption), was distilled using a Hickman still (oil bath 90–160° at 0.10–0.05 mm) to give the cyclopropane as a colorless oil (no N–H absorption in the infrared).

1,3-Dipolar Addition Reactions of Dimethyl α-Diazoethylphosphonate.—The diazo compound and the respective 1,3-dipolarophile (1:1 molar ratio) were dissolved in toluene. An exothermic reaction ensued. Subsequently the reaction mixture was heated for *ca.* 30 min on the steam bath, until the diazo compound color had been discharged. The pyrazolines produced were isolated by removal of the solvent at reduced pressure. Pure samples were obtained by recrystallization from carbon tetrachloride (adduct from methyl vinyl ketone) or cyclohexane–carbon tetrachloride (adducts from ethyl acrylate and acrylonitrile).

Registry No.—Dimethyl α-diazobenzylphosphonate, 28447-22-5; dimethyl benzoylphosphonate *p*-toluenesulfonylhydrazone, 28447-23-6; dimethyl diazomethylphosphonate, 28447-24-7; bromomethylphthalimide, 5332-26-3; dimethyl phthalimidomethylphosphonate, 28447-26-9; dimethyl *p*-toluenesulfonylaminomethylphosphonate, 28447-27-0; dimethyl α-diazo-3,5-dimethoxybenzylphosphonate, 28447-28-1; *anti*-dimethyl 3,5-dimethoxybenzoylphosphonate *p*-toluenesulfonylhydrazone, 28434-43-7; *syn*-dimethyl 3,5-dimethoxybenzoylphosphonate *p*-toluenesulfonylhydrazone, 28434-44-8; dimethyl 3,5-dimethoxybenzoylphospho-

(11) Hydrogenation and saponification of this compound gave ethylenediphosphonic acid, mp 218–220°, which was not depressed on admixture with authentic acid: M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 631 (1947); *Chem. Abstr.*, **42**, 5845*h* (1948).

(12) J. B. Conant and B. B. Coyne, *J. Amer. Chem. Soc.*, **44**, 2530 (1922).

nate, 28446-76-6; dimethyl α-styrylphosphonate, 1707-07-9; dimethyl α-diazoethylphosphonate, 26584-15-6.

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The Synthesis and Chemistry of 1′,1′,4′(S)-Trimethyl-3β-trityloxyandrost-5-eno[16β,17β-b]azetidinium Tosylate

MILTON HELLER AND SEYMOUR BERNSTEIN*

Organic Chemical Research Section, Lederle Laboratories, A Division of American Cyanamid Company, Pearl River, New York 10965

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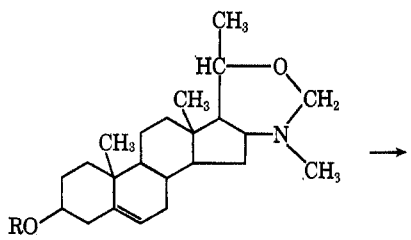
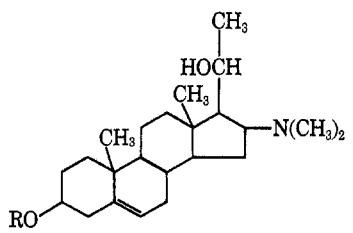
Treatment of 16β-dimethylamino-3β-trityloxypregn-5-en-20β-ol (**2b**) with *p*-toluenesulfonyl chloride in pyridine afforded 1′,1′,4′(*S*)-trimethyl-3β-trityloxyandrost-5-eno[16β,17β-*b*]azetidinium tosylate (**3a**). Reaction of the latter compound with refluxing ethanolamine (or potassium hydroxide in refluxing dioxane) yielded the Hofmann degradation product 16β-dimethylaminopregna-5,20-dien-3β-yl trityl ether (**4a**). The mother liquor of the ethanolamine reaction also contained the *N*-hydroxyethylamino compound **5a**. Reduction of **3a** with lithium aluminum hydride gave 16β-dimethylaminopregn-5-en-3β-yl trityl ether (**6**).

Published literature[1] in the steroid field has indicated that a tertiary amine grouping in a 1,4 relationship to a hydroxyl group may spontaneously cyclize under the influence of *p*-toluenesulfonyl chloride to form a pyrollidine ring. It was of interest, since 16β-dimethylaminopregn-5-ene-3β,20β-diol (**2a**)[2] was available, to know if the same conditions acting on this compound would produce an azetidine ring.[3] Such a transformation would establish a new heterocyclic-fused ring on the steroid system.

Since the 3β-hydroxyl group of the above-mentioned compound could conceivably interfere with a study of the reaction, it was thought best to protect this function preferentially. This was done by tritylation[4] of the *N*-methyloxazine **1a**[2] to form the 3-trityl ether **1b**,

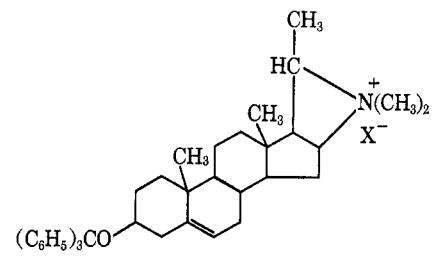


1a, R = H
b, R = $(C_6H_5)_3C$



2a, R = H
b, R = $(C_6H_5)_3C$

which was reduced with lithium aluminum hydride to afford 16β-dimethylamino-3β-trityloxypregn-5-en-20β-ol (**2b**). Reaction of **2b** with *p*-toluenesulfonyl chloride in pyridine at room temperature for 65 hr gave reasonable yields of the azetidine tosylate **3a**. This compound's structure was confirmed by its infrared spectrum, which



3a, X = O_3S—C_6H_4—CH_3
b, X = Br

had the tosylate ion bands previously reported,[1a] by the nmr spectrum confirming the quaternary alkylated nitrogen, and the mass spectrum which showed the expected molecular ion (minus *p*-toluenesulfonic acid) at *m/e* 586, and this ion minus the trityl grouping at *m/e* 343. Assuming a conventional rear-side attack of the nitrogen electrons to displace the C_{20}-β-toysl grouping, the resultant configuration of the steroidal C_{20}-methyl grouping on the azetidine ring would be *S*.

Since little is known of the chemistry of such azetidine systems, a modest chemical study of **3a** was undertaken. It has been shown that a condensed azetidinium ring structure, when it is nonplanar, will undergo reversal of the quaternization on reaction with nucleophiles.[5] In this case, however, treatment of **3a** with lithium bromide afforded only anion replacement to give the azetidinium bromide **3b**. The analogous iodide could be formed by treatment with sodium iodide, but the product was very labile to air and/or light and could not be characterized satisfactorily. This displacement reaction without ring opening may indicate that the azetidine ring is not distorted in

(1) (a) F. L. Weisenborn and D. Burn, *J. Amer. Chem. Soc.*, **75**, 259 (1953); (b) S. W. Pelletier and W. A. Jacobs, *ibid.*, **75**, 4442 (1953); (c) R. Ledger and J. McKenna, *Chem. Ind. (London)*, 1662 (1963); (d) L. Labler, J. Hora, and V. Cerny, *Collect. Czech. Chem. Commun.*, **28**, 2015 (1963).

(2) M. Heller and S. Bernstein, *J. Org. Chem.*, **32**, 3981 (1967).

(3) This is similar to the general method of preparing azetidines by ring closure of γ-haloamines: see J. A. Moore in "Heterocyclic Compounds With Three- and Four-Membered Rings," Part Two, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 891.

(4) R. T. Blickenstaff, *J. Amer. Chem. Soc.*, **82**, 3673 (1960).

(5) G. Fodor, *ibid.*, **88**, 1040 (1966).