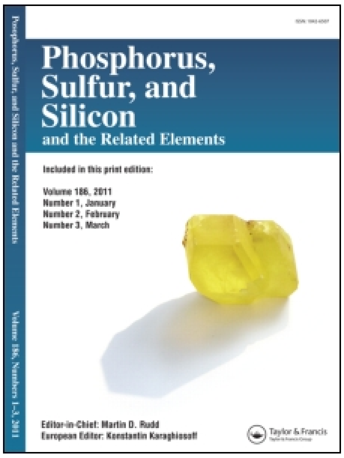

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 67.[1] THE REACTIONS OF OCTACHLOROCYCLO-TETRAPHOSPHAZATETRAENE WITH DIETHYL BIS(HYDROXYMETHYL)MALONATE. COMPARISON OF PRODUCT TYPE AND OF THE ^{31}P, ^{1}H AND ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA WITH THOSE OF THE DERIVATIVES OF PROPANE-1,3-DIOL AND 2,2-DIMETHYLPROPANE-1,3-DIOL

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 67.[1] THE REACTIONS OF OCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH DIETHYL BIS(HYDROXYMETHYL)MALONATE. COMPARISON OF PRODUCT TYPE AND OF THE ^{31}P, ^{1}H AND ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA WITH THOSE OF THE DERIVATIVES OF PROPANE-1,3-DIOL AND 2,2-DIMETHYLPROPANE-1,3-DIOL

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The reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, with diethyl bis(hydroxymethyl)-malonate, $(HOCH_2)_2C(CO_2Et)_2$, gave the following isolated and characterized derivatives: $N_4P_4Cl_6[(OCH_2)_2C(CO_2Et)_2]$, $N_4P_4Cl_4[(OCH_2)_2C(CO_2Et)_2]_2$, (two isomers), $N_4P_4Cl_2[(OCH_2)_2C(CO_2Et)_2]_3$ and $N_4P_4[(OCH_2)_2C(CO_2Et)_2]_4$. ^{31}P, ^{1}H and ^{13}C n.m.r. spectroscopic investigations showed all derivatives to have spiro structures. The isomeric bis derivatives have 2,2,4,4- and 2,2,6,6-structures. A comparison is made of product type and of the nuclear magnetic resonance spectra with those of the derivatives of propane-1,3-diol and 2,2-dimethylpropane-1,3-diol.

Key words: Octachlorocyclotetraphosphazatetraene; diethyl bis(hydroxymethyl)malonate; spiro compounds; isomers; n.m.r. studies; comparisons.

INTRODUCTION

We have earlier compared the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with three diols: propane-1,3-diol, $(HOCH_2)_2CH_2$, **(1)**, 2,2-dimethylpropane-1,3-diol, $(HOCH_2)_2CMe_2$, **(2)**, and diethyl bis(hydroxymethyl)malonate $(HOCH_2)_2(CO_2Et)_2$ **(3)**.[2] All three are based on a three carbon atom chain separating the two hydroxy functions. The diol **(2)** releases electrons, whilst the diol **(3)** withdraws electrons, both relative to diol **(1)**. Notable differences in product type and product distribution were observed.[2-4] We have already reported the reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, **(4)**, with the diols **(1)**[5] and **(2)**[1]; we now describe its reaction with the third one, **(3)**, and compare the results of the higher homologue **(4)**, with the same three diols.

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RESULTS AND DISCUSSION

We have isolated from the reaction of the octachloride, **(4)**, and the diol, **(3)**, five products: $N_4P_4Cl_6[(OCH_2)_2C(CO_2Et)_2]$, **(5A)**, $N_4P_4Cl_4[(OCH_2)_2C(CO_2Et)_2]_2$ (two isomers), **(6A, 7A)**, $N_4P_4Cl_2(OCH_2)_2C(CO_2Et)_2]_3$, **(8A)**, and $N_4P_4[(OCH_2)_2C(CO_2Et)_2]_4$, **(9A)**. We now discuss their structures based on n.m.r. spectroscopic studies.

^{31}P n.m.r. Studies

As in an earlier study,[5] we observed spectra of four types: A_2MX (A_2BX), A_2X_2 (A_2B_2), AA'XX' (AA'BB') and A_4. Compound **(5A)** has a spectrum of the A_2MX type. It is clearly a monospiro derivative, $N_4P_4Cl_6[(OCH_2)_2C(CO_2Et)_2]$. A proton coupled spectrum allows in this case (as in all the others) unambiguous assignments, which phosphorus nuclei do or do not have alkoxy groups attached. The spectrum of compound **(8A)** is more complex than that of **(5A)**, but can probably be best described to be of the A_2BX type. It is therefore the trispiro derivative, $N_4P_4Cl_2[(OCH_2)_2C(CO_2Et)_2]_3$. Compound **(6A)** displays two triplets; the A_2X_2 nature of the spectrum characterizes this as the 2,2,6,6-bis spiro-derivative,

TABLE I

^{31}P n.m.r. data of diol derivatives

Compound	δ $\underline{P}$spiro[a]	δ $\underline{P}Cl_2$[a]	$^2J(\underline{P}spiro\text{-}\underline{P}Cl_2)$[b]	$^2J(\underline{P}X_2\text{-}\underline{P}X_2)$[b]
(4)	−6.5			
(5A)	−11.4	−5.5(1)[c] −3.55(2)	61.1	29.4 (X_2 = Cl_2)[d]
(5B)	−10.5	−5.5(1) −4.3(2)	59.0	29.9 (X_2 = Cl_2)
(5C)	−10.8	−5.4(1) −4.0(2)	58.1	29.6 (X_2 = Cl_2)
(6A)	−10.6	−1.2	60.3	
(6B)	−9.6	−2.3	57.9	
(6C)	−9.7	−1.6	57.2	
(7A)	−6.6	−4.5	59.5	83.0 (X_2 = spiro) 35.6 (X_2 = Cl_2)
(7B)	−6.6	−4.7	58.2	82.85 (X_2 = spiro) 36.5 (X_2 = Cl_2)[c]
(7C)	−6.7	−4.6	55.9	82.8 (X_2 = spiro) 34.5 (X_2 = Cl_2)
(8A)	−2.0(1) −5.6(2)	−2.5	52.9	81.2 (X_2 = spiro)
(8B)	−2.1(1) −5.7(2)	−2.6	53.7	79.4 (X_2 = spiro)
(8C)	−2.1(1) −5.7(2)	−2.6	53.7	80.6 (X_2 = spiro)
(9A)	−2.3			

[a] In p.p.m.

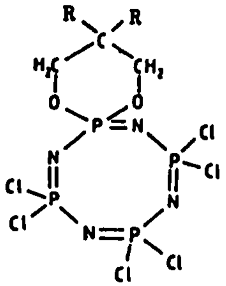
[b] In Hz.

[c] Relative number of nuclei in brackets.

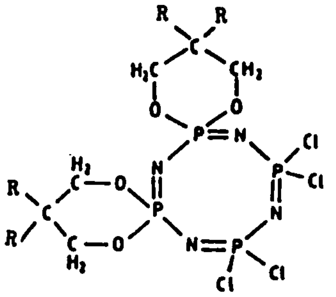
[d] $^4J(\underline{P}spiro\text{-}\underline{P}Cl_2)$ − 1.1 Hz.

[c] This coupling constant was placed erroneously in an earlier publication (Reference 5) against compound **(6B)**, 2,2,6,6-$N_4P_4Cl_4[(OCH_2)_2CH_2]_2$.

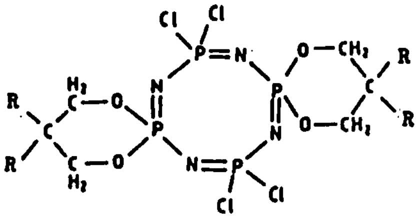
$N_4P_4Cl_4[(OCH_2)_2C(CO_2Et)_2]_2$. Its isomer, **(7A)**, has a symmetric spectrum, rather more complex than that of compound **(6A)**. Its AA'XX' appearance characterizes this as the 2,2,4,4-bis spiro-derivative, $N_4P_4Cl_4[(OCH_2)_2C(CO_2Et)_2]_2$. Finally, the single line spectrum of compound **(9A)** clearly establishes this as the tetrakis spiro-derivative, $N_4P_4[(OCH_2)_2C(CO_2Et)_2]_4$. The data are given in Table I together with those of the analogous derivatives based on the diols **(1)** and **(2)**.



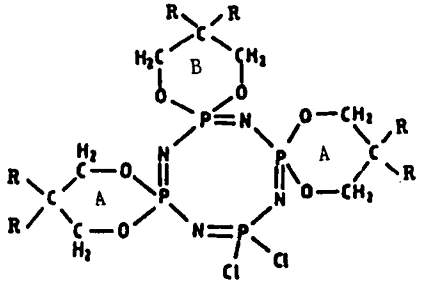
(5A, R = CO_2Et
B, R = H
C, R = Me)



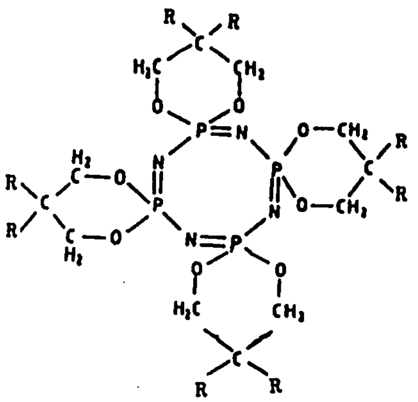
(7A, R = CO_2Et
B, R = H
C, R = Me)



(6A, R = CO_2Et
B, R = H
C, R = Me



(8A, R = CO_2Et
B, R = H
C, R = Me)



(9A, R = CO_2Et)

^1H n.m.r. Studies

The data for the malonate derivatives are given in Table II together, for comparison purposes, with the POC$\underline{H}_2$ data of the corresponding derivatives of the diols (**1**) and (**2**). Within the malonate series we note the increased shielding of the protons of the POC$\underline{H}_2$ groups as chlorine atoms are replaced by malonate residues. A similar, but lesser, effect is observed for the COC$\underline{H}_2$ and C$\underline{H}_3$ proton. On comparing the POC$\underline{H}_2$ proton chemical shifts of similar derivatives based on the three diols (**1–3**), we note an increase shielding of 0.35 to 0.4 p.p.m. on passing from the malonate to the propane series and a further similar increase in shielding on passing to the dimethylpropane series. As with the derivatives of diol (**2**),[1] the malonate derivatives show two environments for the 2,2,4,4-bis spiro compound (**7A**) and three environments for the tris spiro derivative (**8A**).

^{13}C n.m.r. Studies

The ^{13}C n.m.r. data for the malonate derivatives are given in Table III together, for comparison purposes, with the data for the ring carbon nuclei of the other two series based on the diols (**1**) and (**2**). For all three diol derivatives a small shielding

TABLE II

^{1}H n.m.r. data of diol derivatives

Compound	δ POC$\underline{H}_2$[a]	δ COC$\underline{H}_2$[a]	δ CH$_2$C$\underline{H}_3$[a]	$^3J(\underline{P}\text{-}\underline{H})$[b]
(**1**)	4.11	4.25	1.28	
(**2**)	3.85			
(**3**)	3.47			
(**5A**)	4.82	4.30	1.31	14.1
(**5B**)	4.48			13.5
(**5C**)	4.06			13.4
(**6A**)	4.77	4.27	1.28	14.0
(**6B**)	4.46			13.4
(**6C**)	4.05			13.4
(**7A**)	[c]	4.31	1.32	12.8
		4.26	1.27	12.6
(**7B**)	4.49			13.2
(**7C**)	4.02			11.4
	3.91			10.7
(**8A**)	[d]	4.24	1.24	11.6
		4.19	1.24	11.4
		4.18	1.22	11.6
(**8B**)	4.38			13.1
(**8C**)	4.13[c]			11.05[c]
	3.89[c]			11.1[c]
	4.04[f]			13.5[f]
(**9A**)	4.71[g]	4.25	1.28	13.6

[a] In p.p.m.

[b] In Hz.

[c] Complex signal approx. 4.65–4.82.

[d] Complex signal approx. 4.62–4.79.

[c] Data for spiro ring (**A**).

[f] Data for spiro ring (**B**).

[g] Indication of a quintet structure.

TABLE III

^{13}C n.m.r. data for diol derivatives

Compound	δ PO$\underline{C}H_2$[a]	δ $CH_2\underline{C}$[a]	δ $\underline{C}$=O[a]	δ CO$\underline{C}H_2$[a]	δ CH_2CH_3[a]	$^2J(\underline{P}O\underline{C})$[b]	$^3J(\underline{P}OC\underline{C})$[b]
(1)	61.9[c]	61.2	169.5	63.1	14.0		
(2)	61.8[c]	34.9					
(3)	70.5[c]	36.5					
(5A)	68.9(d)[d]	54.5(d)	165.25(s)	63.0(s)	13.9(s)	6.5	5.2
(5B)	68.0(d)	26.1(d)				5.9	7.0
(5C)	77.1(d)	32.6(d)				5.9	5.7
(6A)	68.6(d)	54.4(d)	165.4(s)	62.9(s)	13.9(s)	6.6	5.1
(6B)	67.7(t)	26.2(t)				5.9	7.0
(6C)	76.8(t)	32.4(t)				5.9	5.6
(7A)	68.5(t)	54.4(t)	165.7(s)	62.8(s)	13.9(s)	5.1	4.4
			165.3(s)	62.75(s)	13.9(s)		
(7B)	67.5(t)	26.2(t)				5.4	6.45
(7C)	76.8(t)	32.4(t)				5.6	5.6
(8A)	[c]	[f]	165.9(s)	62.6(s)	13.8(s)	[g]	[g]
			165.7(s)	62.6(s)	13.8(s)		
			165.3(s)	62.5(s)	13.8(s)		
(8B)	67.3(2)[h](t)	26.35(2)(t)				5.5	6.1
	66.9(1)(d)	26.4(1)(d)				5.5	5.5
(8C)	76.8(2)(t)	32.5(2)(t)				5.6	5.7
	76.9(1)(t)	32.4(1)(t)				5.6	5.7
(9A)	68.0(t)	54.6(t)	165.0(s)	62.4(s)	13.8(s)	5.5	4.2

[a] In p.p.m.

[b] In Hz.

[c] Refers to HO$\underline{C}H_2$.

[d] S = singlet, d = doublet, t = triplet.

[c] Complex group of lines at approx. 69 p.p.m.

[f] Complex groups of lines at approx. 54.5 p.p.m. [h] Numbers in brackets refer to relative numbers of nuclei.

effect with increased substitution of ≡Pspiro groups is observed for the PO$\underline{C}H_2$ nuclei. Even smaller shielding effects are observed for the CO$\underline{C}H_2$ nuclei, whilst the carbonyl nuclei, $\underline{C}$=O, show a very small deshielding effect. Again as for the ^1H n.m.r. spectra, compounds **(7A)** and **(8A)** show two, respectively three, different environments for the relevant nuclei.

Comparing the chemical shifts of the ring carbon nuclei between the three diol series, at first, the resemblances between derivatives based on R = H and R = CO_2Et and the contrast for derivatives based on R = Me for the PO$\underline{C}H_2$ nuclei seems somewhat surprising. However, a comparison with organic compounds (although based on alkane chains)[6] shows similar deshielding effects of Me and CO_2R substituents. In the previous,[6] as in the present study, the β-effect (PO$\underline{C}H_2$ nuclei) is large for the Me substituents and very small for CO_2R, whilst the α-effect ($CH_2\underline{C}$ nuclei) is very much larger for the CO_2R substituent than for Me. The relevant effects in p.p.m. (all deshielding) are for the present study (with the organic data per substituent in brackets); α-effect Me 6(**9**), CO_2R 28(**20**); β-effect Me 11(**9**), CO_2R 1(**2**). Thus the trends can be seen to be comparable.

MASS SPECTRA

When determining the mass spectra of the malonate derivatives no molecular ions, M^+ were observed. Instead $(\underline{M} + \mathbf{1})^+$, and $(\underline{M} + \mathbf{2})^+$ were found. A recent paper reported that for a very small number of compounds (10 out of 1400 examined), the molecular ion, $\underline{M}^+$, was generally absent, but the mono-protonated species $(\underline{M} + \underline{H})^+$ was present in excess of 10% of the base peak. The common structural feature in these 14 compounds was the presence of a carbonyl group and the phenomenon was described as self-induced chemical ionization under electron ionization conditions. The compounds described here, as those in a recent study,[2] contain a number of carbonyl groups.

SUMMARY

Diethyl bis(hydroxymethyl)malonate is prone to base and acid catalysed hydrolysis. The same may be true of its phosphazene derivatives. This instability may contribute to the smaller number of derivatives isolated in the trimer system.[2] It is tempting, however, to relate the changes in product in the present study, as well as in the earlier one on the trimer system,[2] to the electron-supplying/withdrawing capacity of the substituents R. In the trimer system[2] for R = Me, ansa products were considerable, for R = H, they were only minor, for R = CO_2Et, none were observed. The greater similarity between the reaction products of $N_3P_3Cl_6$, with the diols **(1)**[3] and **(2)**,[4] compared to those observed with the malonate, **(3)**, is also mirrored in the reactions of its homologue, $N_4P_4Cl_8$, **(4)**. In this system the diols **(1)**[5] and **(2)**,[4] did not yield tetrakis spiro derivatives, whilst in the malonate system, reported here, it is a major compound. The malonate derivatives of the phosphazenes may, because of the functionality of their organic substituents prove useful intermediates, especially for incorporating into polymer systems.

The shielding of the $POC\underline{H}_2$ protons is affected by the substituents R and the order is the predicted one: Me > H > CO_2Et. It is, however, possible that the magnetic anisotropy of the carbonyl group may cause some apparent anomalies, such as the relative closeness of the $PO\underline{C}H_2$ chemical shifts for R = H and R = CO_2Et, and hence comparisons within the same series, e.g., $\underline{A}$, $\underline{B}$, or $\underline{C}$ are less prone to such effects. The ^1H and ^{13}C spectra of the $PO\underline{CH}_2$ groups demonstrate that the electron-withdrawing power of the phosphazene moiety decreases when electron-withdrawing chlorine atoms are replaced by the more electron-supplying spirodioxy groups.

Whilst six- and seven-membered spiro derivatives based on the octachloride, **(4)**, and derived from aliphatic and aromatic diols are readily isolated,[5,8] those diols which gave rise to five-membered spiro derivatives with the trimer,[3,9] gave only breakdown products with the tetramer.[5] The subject has been recently reviewed.[10]

EXPERIMENTAL

Chemicals were obtained as follows: acetonitrile light petroleum (b.p. 40–60°C), dichloromethane (May & Baker Ltd.), benzene, tetrahydrofuran (Fluka Ltd.), deuteriated solvents for n.m.r. spectroscopy, diethyl bis(hydroxymethyl)malonate (Aldrich Chem. Co. Ltd.), pyridine, (B.D.H. Chemical Co. Ltd.), octachlorocyclotetraphosphazatetraene (Shin Nisso Kato Co. Ltd.). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60F 254 (silica gel) precoated t.l.c. plates and sprayed with Ninhydrin (0.5 w/v%) in butanol solution, and developed at approximately 130°C. Separation of products were carried out by flash column chromatography[11] using Kieselgel 60. Melting points were

TABLE IV

Experimental Details

	Starting Compound [$N_4P_4Cl_8$ **(4)**]		Reactant **(3)**					
ion	g (mmol) in CH_3CN	(cm^3)	g (mmol) in CH_3CN	(cm^3)	Pyridine g (mmol)	Eluent ratios	Chromatographic recrystallization solvent	Product No.
)	9.1(19.7)	130	8.65(39.0)	35	15.58(197)	Benzene-THF (10:1)	CH_2Cl_2-benzene (5:1)	**(5A)**
)	2.5(5.4)	60	9.50(43.0)	35	6.83(86)	Benzene-THF (10:1)	CH_2Cl_2-light petroleum (1:3)	**(6A)** **(7A)** **(8A)** **(9A)**
)	10.0(22)	150	19.38(88)	40	13.92(244)	Benzene-THF (10:1)	CH_2Cl_2-light petroleum (1:3)	**(6A)** **(7A)** **(8A)** **(9A)**

TABLE V

Analytical Data

			Elemental Analysis (%)			Found (Calc.)		
Compound	Formula	M.p. (°C)	C	H	N	P	Cl	Mass $\underline{M}^{+}$ ($\underline{M}$
(5A)	$C_9H_{14}N_4O_6P_4Cl_6$	80	17.45(17.70)	2.63(2.31)	8.87(9.17)	19.51(20.28)	34.32(34.42)	609(608
(6A)	$C_{18}H_{28}N_4O_{12}P_4Cl_4$	94	28.54(28.52)	3.65(3.72)	7.52(7.39)	16.36(16.34)	19.17(18.71)	758(756
(7A)	$C_{18}H_{28}N_4O_{12}P_4Cl_4$	128	28.60(28.52)	3.66(3.72)	7.61(7.39)	16.25(16.34)	19.44(18.71)	757(756
(8A)	$C_{27}H_{42}N_4O_{18}P_4Cl_2$	54	35.95(35.82)	4.78(4.68)	6.19(6.19)	13.57(13.82)	9.02(7.83)	905(904
(9A)	$C_{36}H_{56}N_4O_{24}P_4$	130	40.98(41.08)	5.21(5.36)	5.18(5.32)	11.86(11.77)		1053(105

[a] Based on mass of most abundant isotopes.

carried out on a Reichert-Kofler micro heating stage and a Mettler FB 82 hot stage connected to a FP8000 central processor with a polarising microscope.

^{1}H n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 199.5 MHz.), and a Brucker WH-400 spectrometer (Operating at 400.13 MHz.—Queen Mary College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm n.m.r. tubes. Measurements were carried out using a $CDCl_3$ lock, TMS as internal reference and sample concentrations of 15–20 mg/cm^3. ^{31}P n.m.r. spectra were recorded using a JEOL JNM FX-60 spectrometer (operating at 24.15 MHz.), and a Bruker WH400 spectrometer operating at 161.98 MHz.—Queen Mary College 85% H_3PO_4 was used as an external reference. ^{13}C n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 50.1 MHz.) and a Brucker WH400 spectrometer (operating at 100.62 MHz.—Queen Mary College, London), TMS was used as an internal reference.

The mass spectra were recorded using a VG 7070H Mass Spectrometer with Finnigan INCOS Data System at University College, London and a VG ZAB IF mass spectrometer at the School of Pharmacy.

Microanalyses were carried out by University College, London microanalytic service.

The reaction of **(4)**:

(a) with two mol equivalents of **(3)** *in acetonitrile.* To **(4)** (9.1 g, 19.7 mmol) in acetonitrile (130 cm^3) in a 500 cm^3 round-bottom 2-necked flask was added dropwise pyridine (15.58 g, 197 mmol). **(3)** (8.65 g, 39 mmol) dissolved in acetonitrile (35 cm^3) was added dropwise (1h). The flask was fitted with a condenser carrying a $CaCl_2$ drying tube and the mixture was refluxed with stirring (1h). It was then allowed to stand at room temperature overnight, the precipitated solids were removed by filtration and the filtrate had the solvent removed by a rotary evaporator under reduced pressure. Traces of solvent and amine were removed under high vacuum. The residue was examined by t.l.c. using benzene/THF (10:1) as mobile phase; one compound, **(5A)** was detected. It was separated by column chromatography (column length 65 cm, diameter 4 cm, 100 g silica gel for a 3 g mixture) using the same eluent as for t.l.c. Compound **(5A)** was recrystallized from dichloromethane-benzene (5:1).

(b) with four mol equivalents of **(3)** *in acetonitrile.* Reaction conditions are given in Table IV. The procedure was the same as for reaction **(a)**. Four compounds were detected by t.l.c. using benzene/THF (10:1) as mobile phase. They were separated by column chromatography. The compounds were eluted in the following order **(6A)**, **(7A)**, **(8A)** and **(9A)**. They were recrystallized from dichloromethane-light petroleum (1:3).

(c) with an excess of **(3)** *in acetonitrile.* Reaction conditions are given in Table IV. The procedure was the same as for reaction **(a)**. Four compounds were detected by t.l.c. using benzene/THF (10:1) as mobile phase. They were separated by column chromatography. The compounds were eluted in the following order: **(6A, 7A, 8A** and **9A)**. They were recrystallized from dichloromethane-light petroleum (1:3). Analytical data are given in Table V.

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