

Studies of Phosphazenes: Part II*—Reactions of Hexachlorocyclotriphosphazatriene with N-Methylaniline

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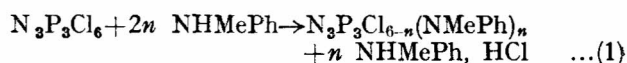
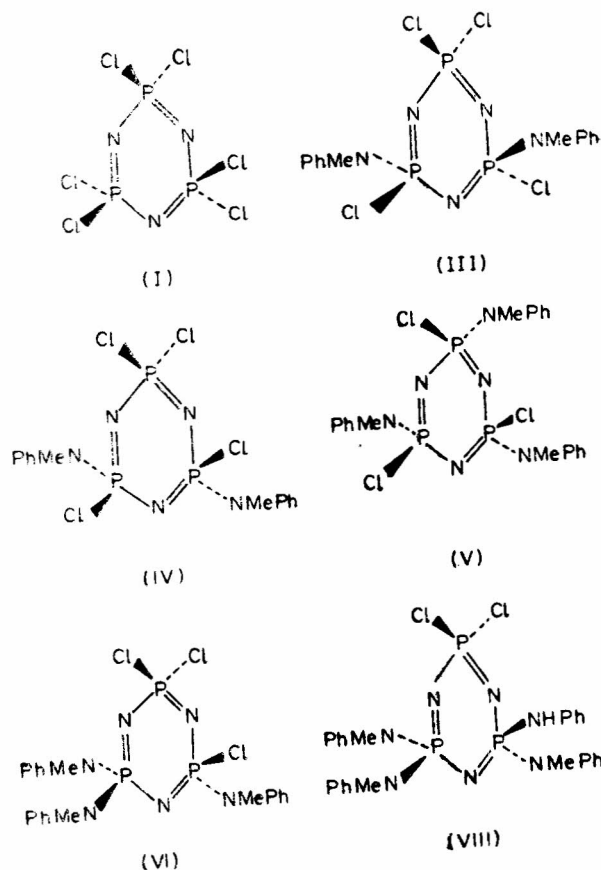
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Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, reacts with N-methylaniline in boiling organic solvents to give the derivatives, $N_3P_3Cl_{6-n}(NMePh)_n$ ($n = 1, 2, 2, 3, 3, 6$). The dealkylated compound, $N_3P_3Cl_4(NHPh)(NMePh)_2$ was obtained only from reactions carried out in boiling xylene. Structures have been assigned to these derivatives on the basis of their 1H NMR spectra. Comparisons are made with the reactions of hexachlorocyclotriphosphazatriene and other secondary amines.

THE reactions of 2,2,4,4,6,6-hexachlorocyclo-triphosphazatriene, $N_3P_3Cl_6$ (I), with primary and secondary aliphatic amines have been studied in great detail¹. Both geminal and non-geminal modes of chlorine atom replacement have been observed although these are rarely exclusive. The factors which determine the replacement pattern are not yet completely understood but several hypothesis have been suggested to rationalize the observations¹⁻³.

Very little information is available on the reactions of I with aromatic amines and only the aniline system has been thoroughly explored^{4,5}. We report here the results of our investigation on the reaction of I with the aromatic secondary amine, N-methylaniline. A previous account of this reaction is available in the literature but pure N-methylanilino derivatives were not isolated⁶.

Six N-methylanilino derivatives, $N_3P_3Cl_{6-n}(NMePh)_n$, $n = 1, 2, 2, 3, 3, 6$ (II-VII), have been isolated from the reaction of I with N-methylaniline in boiling organic solvents (Eq. 1). The reaction is very slow and lengthy reaction times are essential to obtain the higher substituted derivatives (V-VII). Even after 4-5 days, the yield of the mono-compound (II) is very poor in boiling benzene. An improved yield of this compound and of the bis-isomers (III, IV) is possible if methyl cyanide is used as the reaction medium. Reactions in methyl cyanide are complete within a few hours provided the reaction stoichiometry [amine/hexachloride (I)] does not exceed 4:1. The two bis-isomers, $N_3P_3Cl_4(NMePh)_2$ (III, IV), invariably crystallize together and it is very difficult to separate them by either fractional crystallization or column chromatography. Pure samples of these isomers were only obtained by preparative GLC. GLC investigations of several 4:1 reaction mixtures show that the two bis-isomers are formed in comparable amounts.



Reactions involving higher stoichiometries (e.g. 6:1 to 12:1) give a complex mixture of the bis-, tris- and hexa-N-methylanilino derivatives (III-VII). Unreacted N-methylaniline is always present in the reaction mixtures even after several days heating in boiling methyl cyanide or toluene. The use of triethylamine as a hydrogen chloride acceptor appears to have little effect on the rate of the re-

*Part I, Krishnamurthy, S. S., Sau, A. C., Vasudeva Murthy, A. R., Keat, R., Shaw, R. A. & Woods, M., *J. chem. Soc. Dalton*, (1976), 1405.

action or on the distribution of the products. The separation of pure products from these reaction mixtures is particularly tedious and involves lengthy column chromatographic procedures. Small quantities of the two *tris*-isomers, $N_3P_3Cl_3(NMePh)_3$ (V, VI) and the hexakis compound, $N_3P_3(NMePh)_6$ (VII) were isolated in this way. TLC and GLC studies of several reaction mixtures indicated that no other chloro-N-methylanilino-derivatives were present.

A small quantity of the dealkylated product, $N_3P_3Cl_2(NHPh)(NMePh)_2$ (VIII) was obtained only from the reaction in boiling xylene. It could be separated from other derivatives by column chromatography. The compounds isolated from the above reactions are shown in Table 1.

Structures have been assigned to the N-methylanilino-derivatives (III-VI, VIII) on the basis of their 100 MHz 1H NMR spectra (Fig. 1, Table 1). As observed previously⁷ for the chlorodimethylamino derivatives, $N_3P_3Cl_{6-n}(NMe_2)_n$, the number of different N-methyl proton environments and the value of the apparent coupling constant, $^3J^*_{(P-H)}$, are reliable guides to the disposition of the substituents. The bis-isomers (III, IV) have similar $^3J^*_{(P-H)}$ values to the mono-compound (II) and consequently assigned non-geminal structures. It is suggested that the isomer with the higher chemical shift has a *cis*-structure. This assignment is consistent with the anticipated shielding effect of two *cis*-N-methylanilino-substituents. The GLC retention time of the *cis*-isomer (IV) is longer than that of the *trans*-isomer (III) and this evidence furnishes additional support for the structural assignments. GLC data for the non-geminal bis-dimethylamino derivatives, $N_3P_3Cl_4(NMe_2)_2$ have been similarly interpreted⁸.

The *tris*-isomer (V) exhibits only one N-methyl doublet (coupling to phosphorus) in its NMR and a 2-*cis*-4-*cis*-6-structure is indicated. The appearance of a broad hump between the sharp outer lines (Fig. 1) of the doublet is a characteristic feature of many multi-spin systems and is particularly common in the spectra of cyclophosphazene derivatives¹. More detailed accounts of this phenomenon "virtual coupling" are given elsewhere⁹. The N-methyl proton signal of the *tris*-isomer (VI) appears as three overlapping doublets with $^3J^*_{(P-H)}$ values of 15.0, 11.0 and 11.0 Hz (Fig. 2) and clearly shows that

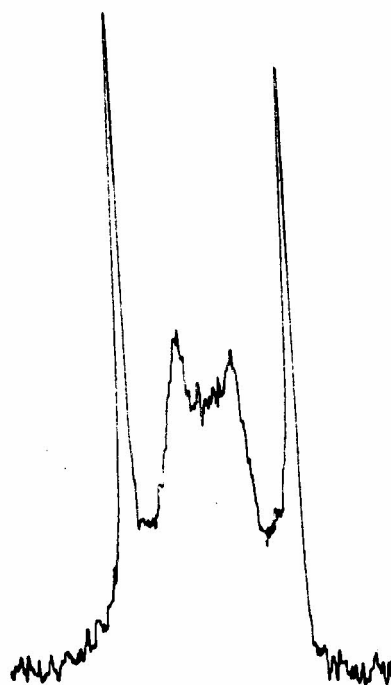


Fig. 1 — 1H NMR spectrum of *cis*- $N_3P_3Cl_3(NMePh)_3$ (V) (N-methyl signals only)

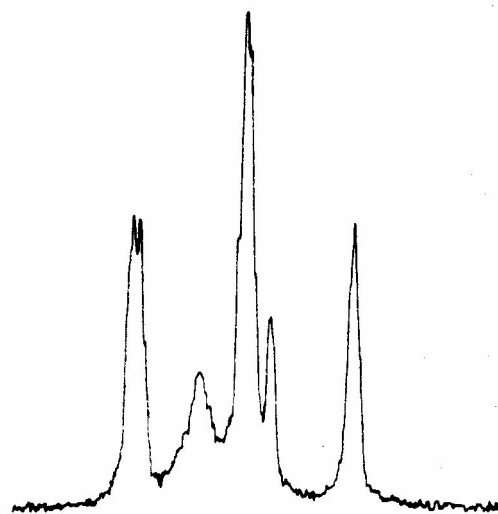


Fig. 2 — 1H NMR spectrum of *gem*- $N_3P_3Cl_3(NMePh)_3$ (VI) (N-methyl signals only)

TABLE 1 — NMR DATA FOR SOME N-METHYLANILINO-DERIVATIVES OF $N_3P_3Cl_6$ (I) IN $CDCl_3$ SOLUTION

Compound	m.p. (°C)	τNH	$^3J^*_{(P-H)}$ (Hz)	Structure‡
II $N_3P_3Cl_5(NMePh)$	63	6.83	15.0	
III $N_3P_3Cl_4(NMePh)_2$	84	6.84†	15.5	2,2,4,6: 4- <i>trans</i> -6
IV $N_3P_3Cl_4(NMePh)_2$	88	6.88†	15.5	2,2,4,6: 4- <i>cis</i> -6
V $N_3P_3Cl_3(NMePh)_3$	168	6.92†	15.5	2,4,6: 2- <i>cis</i> -4- <i>cis</i> -6
VI $N_3P_3Cl_3(NMePh)_3$	87	6.86†, 6.85, 6.97	15.0 } 11.0 } 11.0 }	2,2,4: 4,6,6
VII $N_3P_3(NMePh)_6$	142	6.98†	11.0	
VIII $N_3P_3Cl_2(NHPh)(NMePh)_2$	98	7.03	11.0	2,2:4: 4,6,6

†Virtual coupling.

‡For nomenclature see ref. 15.

(a) $\tau NH = 5.6$; $^3J_{(P-H)} = 9.5$ Hz.

this isomer has a geminal 2,2,4-structure. The doublets at τ 6.85 and 6.97 with the $^3J^*_{(P-H)}$ values of 11.0 Hz are assigned to the geminal $\equiv P(NMePh)_2$ groups. The doublet at high field is clearly due to the geminal N-methylanilino-group *cis* to the non-geminal one.

The IR spectrum of VIII has a broad band at 3200 cm^{-1} (N-H stretch) which is absent in the spectra of the other compounds obtained. The NMR spectrum contains a doublet at τ 5.6 which disappears after the sample has undergone exchange with deuterium oxide. The relative intensities of the signals observed in the spectrum suggest that this compound contains three N-methylanilino and one anilino-groups. Mass spectrometry confirms that derivative (VIII) is bis-chloroanilino-*tris*-N-methylanilinocyclotriphosphazatriene, $N_3P_3Cl_2(NHPh)(NMPH)_3$ [m/e (found) = 615.1147; m/e (calc.) = 615.1157].

A detailed examination of the 1H NMR spectrum suggests that this dealkylated derivative (VIII) has a geminal structure as shown. Although the resolution of the N-methyl proton environments is poor (a doublet with very broad outer lines is observed), the apparent coupling constant $^3J^*_{(P-H)}$ is approximately 11.0 Hz and indicates that $\equiv PCl(NMePh)$ groups are absent. An independent experiment shows that the geminal *tris*-isomer, $N_3P_3Cl_3(NMePh)_3$ (VI) reacts very slowly with two moles of aniline in boiling xylene to give $N_3P_3Cl_2(NHPh)(NMePh)_3$ (VIII). Aniline invariably reacts with chloro-cyclotriphosphazatriene derivatives by the geminal mode of replacement⁵ and hence this experimental observation supports the structural assignment. An analogous reaction [*gem*- $N_3P_3Cl_3(NMe_2)_3 + 2PhNH_2$] was reported earlier⁵ and found to give the geminal product, $N_3P_3Cl_2(NHPh)(NMe_2)_3$.

The reactions of $N_3P_3Cl_6$ (I) with dimethylamine¹, diethylamine¹⁰, piperidine¹ and pyrrolidine¹ proceed largely by the non-geminal replacement of chlorine atoms. *Trans*-structures predominate at the bis- and *tris*-stage of replacement although the yield of geminal *tris*-derivatives can be enhanced in an aromatic reaction medium¹¹. The tetra-derivatives have either *cis*- or *trans*-non-geminal structures^{1,10}.

Both geminal and non-geminal modes of replacement have been observed for the reaction of I with N-methylaniline with the latter dominating initially. After the bis-stage of replacement, the reaction is particularly slow and GLC evidence indicates that the geminal *tris*-compound (VI) is the major product formed in toluene, xylene and also in methyl cyanide. In general, reactions of secondary amines with I in boiling methyl cyanide yield very little geminal products. It is possible that the formation of the geminal isomer (VI) is influenced by the presence of unreacted N-methylaniline in these reactions and that this aromatic amine fulfils a role comparable to that of an aromatic reaction medium¹¹. The weakly basic character of N-methylaniline may also exert a significant influence on the replacement pattern (cf ethyleneimine¹²).

The reactions of phosphorus (V) halides with N,N-dialkylanilines at 130-60° were reported recently and dealkylation was shown to occur in many

cases³. For example, phosphoryl chloride reacted with N,N-dimethylaniline to give the anilino derivative, $P(O)(NHPh)(NMePh)_2$. Hence, the formation of small amounts of the dealkylated derivative, $N_3P_3Cl_2(NHPh)(NMePh)_3$ (VIII) in boiling xylene (2 days) is not unduly surprising. It is also well known that N-methylaniline undergoes dealkylation to aniline under comparable conditions¹⁴.

Experimental Procedure

Hexachlorocyclotriphosphazatriene (I) was purified by recrystallization from light petroleum (b.p. 60-80°) to constant m.p. 113°. Organic solvents were purified by conventional methods. The light petroleum used refers to the fraction b.p. 60-80° unless stated otherwise. N-Methylaniline was purified by distillation from zinc dust under reduced pressure.

Some typical reactions are described below in detail. Other reactions are summarized in Table 2. Table 3 gives analytical data, TLC R_f values and GLC retention times. Thin-layer and column chromatographic procedures were the same as described previously¹⁶. A Varian aerograph, series 1800, was used for the qualitative and quantitative GLC experiments. A steel column (15' \times 1/8") containing 7% Dexil 300 GC liquid phase on chromosil W-HP was used. The operating temperature was 265°.

1H NMR spectra were recorded with a Jeol MH 100 spectrometer in $CDCl_3$ with TMS as the internal reference. The infrared spectra were recorded in potassium bromide pellets using a Carl-Zeiss UR 10 spectrophotometer. The mass spectrometric data for compound (VIII) were obtained from the PCMU Service, Harwell, UK. Melting points were obtained from a Reichert Kofler apparatus fitted with a polarizing microscope.

Reactions of hexachlorocyclotriphosphazatriene (I):
(a) *With two equivalents of N-methylaniline in toluene* — N-Methylaniline (3.2 g, 0.03 mole) was added to a boiling solution of the hexachloride (I) (5.0 g, 0.014 mole) in toluene (25 ml) and the mixture heated under reflux for 24 hr. N-Methylaniline hydrochloride was filtered off and the solvent removed from the filtrate to give a brown, oily residue. TLC of this residue showed the presence of three compounds. The oil was chromatographed on silica gel (125 g) using a light petroleum-benzene (9:1) eluent. Pentachloro-N-methylanilinocyclotriphosphazatriene (II) m.p. 63°, (2.25 g; 38%) was obtained from the column and recrystallized from light petroleum. Elution with light petroleum-benzene (3:1) gave a mixture of the bis-isomers (III, IV). Further elution with light petroleum-benzene (1:1) gave an oily residue which could not be purified. This experiment was repeated using methyl cyanide as the reaction medium. The mono-compound (II) (2.6 g; 43%) was obtained by seeding the light petroleum extract with an authentic sample of II and cooling at 0°.

(b) *With four equivalents of N-methylaniline in methyl cyanide* — N-Methylaniline (6.4 g; 0.06 mole) was reacted with the hexachloride (I) (5.0 g; 0.014 mole) in methyl cyanide (25 ml) for 20 hr as in (a). The oily residue obtained was extracted with light

TABLE 2 — REACTIONS OF $N_3P_3Cl_6$ (I) WITH N-METHYLANILINE^a

$N_3P_3Cl_6$		HNMePh		Reaction solvent (ml)	Reaction time (hr)	Yield ^b		
(g)	(mmole)	(g)	(mmole)			(g)	No.	(%)
5	14	3.2	30	C_6H_6 (50)	75	0.50	I	10
						0.75	II	13
						0.15	III + IV	2.0
5	14	1.6 ^c	15	C_6H_6 (25)	40	0.60	II	10
						0.10	III + IV	1.5
5	14	3.2	30	$C_6H_5CH_3$ (25)	10	1.25	II	21
						0.15	III + IV	2.0
5	14	3.2	30	CH_3CN (25)	20	2.60	II	43
						0.15	III + IV	2.0
2.5	7	3.2	30	$C_6H_5CH_3$ (25)	35	0.20	II	7.0
						0.20	III + IV	6.0
10	28	12.8	120	$C_6H_5CH_3$ (75)	60	1.00	III + IV	7.0
						0.05	V	0.3
						0.30	VI	2.0
						0.15	III + IV	2.0
						0.025	VIII	0.3
10	28	12.8	120	CH_3CN (100)	48	2.0	III + IV	14
						0.02	V	0.1
						0.50	VI	3.0
						0.25	III + IV	7.5
5	14	9.6	90	$C_6H_5CH_3$ (25)	20	0.45	VI	8.5
						0.45	III + IV	12
3.5	10	6.4	60	CH_3CN (100)	10		IV	9
							V	1
							VI	78
5	14	12.8	120	$C_6H_5CH_3$ (40)	96	0.15	V	2.0
						0.25	VI	3.0
5	14	12.8	120	CH_3CN (30)	48		III	4
							IV	5
							V	2
							VI	89
5	14	25.6	240	$C_6H_5CH_3$ (40)	48	0.20	VII	2.0
5	14	25.6	240	$C_6H_4(CH_3)_2$ (100)	96	0.50	VI	6.0
						0.25	VII	2.5

(a) N-Methylaniline was added dropwise to a boiling solution of $N_3P_3Cl_6$ (I).

(b) Refers to pure products isolated by column chromatography and/or fractional crystallization; the low yields are a result of considerable loss of material in the chromatographic procedures.

(c) Relative percentage yield estimated from GLC traces.

TABLE 3 — ANALYTICAL, TLC AND GLC DATA

Compound	Found (%)			Formula	Reqd (%)			TLC* R _f	GLC† retention time (min)
	C	H	N		C	H	N		
II	20.0	1.9	13.6	$C_7H_8Cl_5N_4P_3$	20.1	1.9	13.4	0.85	4.7
III	34.2	3.2	14.1	$C_{14}H_{16}Cl_4N_5P_3$	34.4	3.3	14.3	0.81	9.8
IV	34.3	3.4	14.3	$C_{14}H_{16}Cl_4N_5P_3$	34.4	3.3	14.3	0.80	11.4
V	44.8	4.3	15.2	$C_{21}H_{24}Cl_2N_6P_3$	45.1	4.3	15.0	0.70	44
VI	45.0	4.3	15.0	$C_{21}H_{24}Cl_2N_6P_3$	45.1	4.3	15.0	0.73	29
VII	65.5	6.4	16.3	$C_{42}H_{48}N_9P_3$	65.4	6.3	16.3	0.66	86
VIII	53.4	5.4	15.4	$C_{27}H_{30}Cl_2N_7P_3$ ‡	52.6	4.9	15.9	0.28	—

*Eluent: benzene (silica gel).

†See experimental.

‡Accurate mass measurement on parent ion (see text).

petroleum (b.p. 40-60°). TLC indicated the presence of two compounds with very similar R_f values and also the mono compound (II). The light petroleum extract was concentrated and the solution cooled to 0°. Two crystalline crops, m.p. 83-86° (1.5 g; 21%) were obtained but GLC indicated the presence of two components. Attempts to separate these components by fractional crystallization and column chromatography were unsuccessful. A preparative

scale GLC separation of 150 mg of the mixture using the conditions described above gave 2,2,4,6-tetrachloro-4-*trans*-6-bis-(N-methylanilino)cyclotriphosphazatriene (III), m.p. 84° (62 mg) and 2,2,4,6-tetrachloro-4-*cis*-6-bis(N-methylanilino)cyclotriphosphazatriene (IV), m.p. 88° (69 mg).

(c) With six equivalents of N-methylaniline in methyl cyanide — N-Methylaniline (9.6 g; 0.09 mole) was reacted with the hexachloride (I) (5.0 g; 0.014 mole)

in methyl cyanide (50 ml) for 20 hr as in (a). The oily product was washed with water and extracted with light petroleum-benzene (1:1). The extract was chromatographed on silica gel (100 g). Elution with light petroleum-benzene (1:1) gave initially a mixture of the bis-isomers (III, IV) (0.5 g; 7%) and then 2,2,4-trichloro-4,6,6-tris-N-methylanilino-cyclotriphosphazatriene (VI), m.p. 87° (0.15 g; 2%) which was recrystallized from light petroleum (b.p. 40-60°). Elution with light petroleum-benzene (2:3) gave an oily material which also contained the tris-compound (VI). This oil could not be purified.

(d) *With eight equivalents of N-methylaniline in methyl cyanide* — N-Methylaniline (13.0 g; 0.12 mole) was reacted with the hexachloride (I) (5.0 g; 0.014 mole) in methyl cyanide (30 ml) for 48 hr as in (a). The oily residue was extracted (i) with boiling hexane and (ii) with hot benzene. Two crystalline crops were obtained from the hexane extract which on recrystallization from a light petroleum-methylene chloride mixture gave 2,4,6-trichloro-2-cis-4-cis-6-tris-(N-methylanilino)cyclotriphosphazatriene (V), m.p. 168° (0.3 g; 4%). TLC of the residual hexane extract and of the benzene extract indicated the presence of traces of compounds (III, IV, V) and also compound (VI). GLC of the combined extracts confirmed that the major component present was compound (VI) (89%). The latter was obtained (0.4 g; 5%) after column chromatography as in (c) as well as numerous oily residues.

(e) *With eight equivalents of N-methylaniline in xylene* — N-Methylaniline (13.0 g; 0.12 mole) was reacted with the hexachloride (I) (5.0 g; 0.014 mole) in boiling xylene (30 ml) for 48 hr as in (a). N-Methylaniline hydrochloride was filtered off and the xylene removed from the filtrate by distillation at 5-10 mm pressure. The residual brown oil was extracted with hot benzene and chromatographed on silica gel (100 g). Elution with light petroleum-(b.p. 40-60°)-benzene (3:1) gave an oil containing compounds (III, IV, V). Crystallization of the oil in a light petroleum (b.p. 40-60°) methylene chloride mixture gave the tris-compound (VI) (0.25 g; 4%). A further quantity of compound (VI) (0.075 g) was obtained on elution with light petroleum(b.p. 40-60°)-benzene (1:1) and after crystallization from a light petroleum-benzene mixture. Elution of the column with light petroleum(b.p. 40-60°)-benzene (1:3) gave 2,2-dichloro-4-monoanilino-4,6,6-tris(N-methylanilino)cyclotriphosphazatriene(VIII), m.p. 98° (0.15 g, 2%) which was recrystallized from light petroleum.

(f) *With twelve equivalents of N-methylaniline in methyl cyanide* — N-Methylaniline (19.5 g; 0.18 mole)

was reacted with the hexachloride (I) (5.0 g; 0.014 mole) in methyl cyanide (75 ml) for 85 hr as in (a). The oily product was extracted with hot light petroleum-benzene mixture and chromatographed on silica gel (120 g). Elution with light petroleum (b.p. 40-60°)-benzene (1:1) gave an oil which could not be crystallized. Elution with benzene gave hexa-N-methylanilinotriphosphazatriene (VII), m.p. 142° (0.25 g; 2%) which was recrystallized from a light petroleum (b.p. 40-60°)-methylene chloride mixture. A similar experiment in boiling xylene was monitored by GLC. Compound (VI) (60%) and compound (VII) (30%) were the major products of the reaction.

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