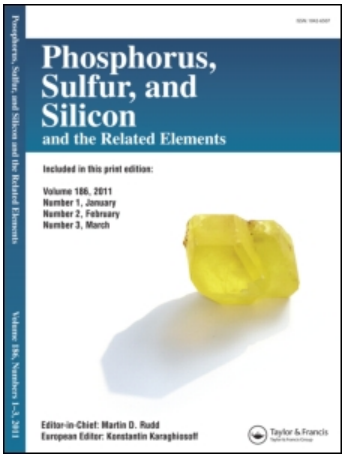

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Erol Çil[a]; Mustafa Arslan[a]; Fatih Aslan[b]; A. Ihsan Öztürk[b]
[a] Firat University, Elazig, Turkey [b] Harran University, S. Urfa, Turkey

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THE SYNTHESIS AND CHARACTERIZATION OF ARYLOXY-LINEAR PHOSPHAZENES

Erol Çil,[a] *Mustafa Arslan,*[a] *Fatih Aslan,*[b] *and A. Ihsan Öztürk*[b]
Firat University, Elazig, Turkey;[a] *Harran University, S. Urfa, Turkey*[b]

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The reactions of N-dichlorophosphoryl-P-trichloromonophosphazene with sodium o-methylphenoxide, sodium p-methylphenoxide, sodium α-naphthalenoxide, monosodium 4-(2-pyridylazo)resorcinol, and sodium 1-nitroso-2-naphthaleneoxide have been investigated. Experimental studies were carried out in argon atmosphere. The sodium aryloxides were prepared from naphthalene or phenol derivatives and metallic sodium. The phosphazene and phenolate or naphthaleneoxide were reacted at 0°C and then refluxed. After the reaction products were separated by using column chromatography, the structures of the compounds were defined by elemental analysis, IR, ^{1}H, ^{13}C, ^{31}P NMR, and mass spectroscopy.

Tetra- and pentasubstituted monophosphazenes were obtained from sodium o-methylphenoxide. Pentasubstituted derivatives also were obtained from sodium p-methylphenoxide and sodium α-naphthaleneoxide. Phosphazene or any phosphorus compound could not be isolated from the reaction of phosphazene with monosodium 4-(2-pyridylazo)resorcinol and sodium 1-nitroso-2-naphthaleneoxide.

Keywords: Linear phosphazenes; N-dichlorophosphoryl-P-trichloromonophosphazene; phenolysis of acyclic monophosphazene

Phosphazene are compounds that contain alternating phosphorus and nitrogen atoms in their skeleton. These compounds fall into three categories: the cyclo-, poly-, and monophosphazenes. The cyclo- and polyphosphazenes probably are the best known and most intensively studied phosphorus-nitrogen compounds because they are more stable

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Address correspondence to Mustafa Arslan, Firat University, Fen-Ed. Fak. Kimya Bolumu, Elazig 23169, Turkey. E-mail: marslan07@firat.edu.tr

than monophosphazenes. They are particularly interesting from the view point of their bonding structure and much of the physical-inorganic work carried out on these compounds has an important bearing on the skeletal bonding found in cyclic and polymeric phosphazenes.[1,2]

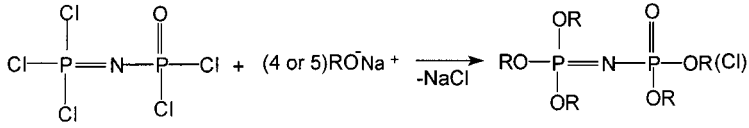
The short-chain species are generally difficult to synthesis, isolate, and study.[3] But phosphazenes possess a number of characteristics such as the using of drug components for chemotherapeutic applications and antibacterial activity.[4–6] These compounds are used in the structure of medical implants and drug delivery systems. N-di(alkoxy)phosphoryl-P-tri(alkoxy)monophosphazene, "pentaesters", especially those with different alkyl groups are biologically active compounds.[7]

N-dichlorophosphoryl-P-trichloromonophosphazene **1**, $Cl_3P{=}N{-}P(O)Cl_2$, which is the short-chain linear phosphazenes, is a very sensitive material to air and moisture. It can be obtained by several different reactions.[8–11] The reactions of compound **1** with amines and alcohols have been reviewed.[12–13] The replacement of one chlorine atom by the allyloxy group and the partial aminolysis of compound **1** with methylamine and *t*-butylamine,[14–15] diisopyropylamine,[16] and penta-substituted amines such as pyrrolidine, morpholine, and piperidine[17] have been reported. The partial replacement of chlorine atoms has been achieved with *o*-dichloro and *o*-dimethylphenol groups,[18] 2,4,6-*tert*-butylphenol, and 2,6-di-*tert*-butyl-4-methylphenol.[19] Pentasubstituted derivatives of compound **1** with alcohols such as ethyl, pyropyl, *n*-butyl, *i*-butyl, pentyl alcohol,[20] 4-phenylphenol,[21] 2,4,6-trimethylphenoxy,[22] benzyl, allyl, tetrahydrofurfuryl alcohol, and 2-isopyropyloxyethanol[23] have been obtained. Trisubstituted derivatives have been obtained from the reaction between **1** and mercaptans such as ethyl, pyropyl and octyl mercaptans.[24]

Here, we report the reactions of $Cl_3P{=}N{-}P(O)Cl_2$ with some alcohols yielding aryloxymonophosphazene. N-dichlorophosphoryl-P-trichloromonophosphazene was reacted with the sodium salts of *o*-methylphenol, *p*-methylphenol, 1-hydroxynaphthalene, 2-hydroxy-1-nitrosonaphthalene, and 4-(2-pyridylazo)resorcinol in argon atmosphere. Tetra- and penta substituted phosphazenes were obtained from the reaction of **1** with *o*-methylphenol. *p*-Methylphenol and 1-hydroxynaphthalene gave their penta-aryloxy derivatives. Phosphazene or any phosphorus compound could not be isolated from the reaction of phosphazene with 4-(2-pyridylazo)resorcinol and 2-hydroxy-1-nitrosonaphthalene. The structures of compounds were defined by IR, elemental analysis, ^1H, ^{13}C, ^{31}P NMR, and mass spectroscopy.

RESULTS AND DISCUSSIONS

All compounds were synthesized according to the reported procedures in the Experimental section. Compound **1** was reacted with the 1:10 ratio of sodium salts of *o*-methylphenol, *p*-methylphenol, α-hydroxynaphthalene, 2-hydroxy-1-nitrosonaphthalene, and 4-(2-pyridylazo)resorcinol. Major products were isolated from the reaction mixture by column chromatography. Tetra- and pentasubstituted monophosphazenes were obtained from *o*-methylphenol. Pentasubstituted derivatives also were obtained from *p*-methylphenol and α-hydroxynaphthalene as shown in the following reaction.



RO^-: $(o\text{-}CH_3)C_6H_4O^-$, $(p\text{-}CH_3)C_6H_4O^-$, $C_{10}H_7O^-$

Phosphazene or any phosphorus compound could not be isolated from the reaction of phosphazene with 4-(2-pyridylazo)resorcinol and 2-hydroxy-1-nitrosonaphthalene. All these compounds have been characterized by elemental analysis, ^1H, ^{13}C, ^{31}P NMR, mass spectrometer, and FT-IR. Although the starting compound is a very sensitive material to air and moisture, these compounds are stable. The physical properties, molecular weights and analytical data are given in Table I.

TABLE I The Physical Properties, Major Mass Peaks and Analytical Data for the $(RO)_3P{=}N{-}PO(OR)_2$ Compounds **1–5**

Comp.	RO^-	Color, state†	Yield (%)	Major m/z‡		Calcd	Found
1	—	w, s	51	—			
2	$o\text{-}CH_3C_6H_4O$	r, v	32	556 (M + 1),	C	60.54	60.99
				18 (H_2O)	H	5.08	5.55
				90 ($C_7H_6^+$)	N	2.51	2.14
3	$o\text{-}CH_3C_6H_4O$	r, v	8	—			
4	$p\text{-}CH_3C_6H_4O$	dy, v	68	628 (M + 1),	C	66.97	67.05
				107 ($C_7H_7O^+$)			
				91 ($C_7H_7^+$),	H	5.62	5.32
				77 ($C_6H_5^+$)	N	2.23	2.10
5	$\alpha\text{-}C_{10}H_7O$	r, v	25	808 (M + 1),	C	74.32	74.26
				107 ($C_7H_7O^+$)			
				91 ($C_7H_7^+$),	H	4.33	4.24
				77 ($C_6H_5^+$)	N	1.73	2.10

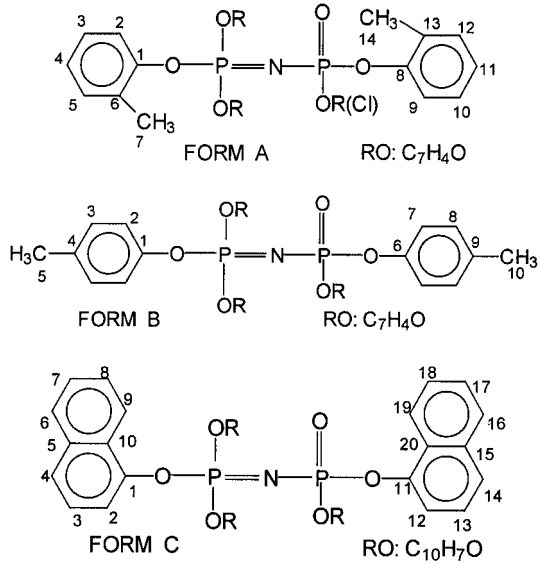
†w: white, s: solid, r: red, v: viscous, dy: dark yellow.

‡Only the first 3–4 peaks in the relative abundance order are shown.

The steric dimensions of the nucleophile influence the degree of halogen replacement and yield, with bulky side groups being the most difficult to introduce as substituents on the phosphazenes skeleton. Since the replacement of chlorine in chloromonophosphazene, $[Cl_3P{=}N{-}P(O)Cl_2]$, by *p*-methylphenoxy take place more readily than replacement by *o*-methylphenoxy, the yield of compound **4** is higher than of compound **3**, and the yield of tetrasubstituted monophosphazene **2** is also higher than pentasubstituted monophosphazene **3**.

P=O and P=N stretching vibrations in the IR spectra are characteristic of phosphazene and appeared near 1160–1230 cm^{-1} and 1180–1330 cm^{-1} respectively. The infrared spectrum of $Cl_3P{=}N{-}P(O)Cl_2$ consist of three strong bands above 650 cm^{-1}, which is beyond the region of P–Cl vibrations, so that these must be PNPO framework modes. The bands are centred at 770 cm^{-1} a region typical of ν_{P-N}, 1260 cm^{-1} which is almost certainly related to $\nu_{P=O}$ since the calculated value for $-N{=}P(Cl_2){=}O$ is 1286 cm^{-1}, and at 1330 cm^{-1} which is the expected region for $\nu_{P=N}$.[25] The simple analysis seems to suggest that the double bond is localized rather than delocalized. The nature of the substituents affects the stretching vibrations of P=O and P=N. The characteristic vibrations of the compounds are given in Table II.

The NMR data are presented in Tables III–V. Hydrogen and carbon atoms were numbered for compound **2** and **3** as form A and for **4** as form B and for compound **5** as form C (Scheme 1).



SCHEME 1

TABLE II The Characteristic Vibrations of the Compounds (cm^{-1})

Compound	$\nu_{C=C}$	$\nu_{C-H\ ar}$	$\nu_{C-H\ al}$	$\nu_{P=N}$	$\nu_{P=O}$	ν_{P-N}	ν_{P-O-C}	ν_{P-Cl}
1	—	—	—	1338	1263	770	—	650
2	1492	3031–3062	2931–2958	1355	1222	800	1106	675
3	1492	3031–3062	2931–2958	1370	1228	800	1106	—
4	1506	3031–3064	2861–2911	1378	1200	819	973	—
5	1508	3012–3056	2930–2950	1390	1224	796	958	—

^{31}P-NMR chemical shifts show that the phosphazene skeleton is intact. Starting and substituted phosphazenes give a AB spin pattern due to the two different phosphorus environments within the molecules. But the phosphorus signals in the aryloxy-substituted linear phosphazenes move to the higher field due to the substituents (Table III). The greater shielding is considered to be a consequence of the presence of the aryloxy groups on the phosphazene skeleton. The localization of the electron density on the phosphorus atoms causes a higher magnetic shielding and, thus, generates high field shifts in the position of the resonance of these phosphorus atoms.

In these aryloxy-substituted phosphazenes (**2–5**), there are essentially two sets of proton groups one in the phosphoryl [—P(O)$(OAr)_2$ or —P(O)(OAr)Cl] and the other in the phosphazene [$(ArO)_3$P=N—] moieties. The two environments can be distinguished in some cases, the latter being more shielded than the former. There are also two sets of carbon atoms. In the ^{1}H NMR spectra, the 2:3 ratio of integral intensities for the two sets of protons is observed for **2**, **4**, and **5**. There is the 1:3 ratio for 3. There also are the same ratios between the integral intensities of similar carbons. These observations indicate that aryloxy groups have replaced five or four chlorine atoms in **1**.

The nearest protons to the phosphorus atoms are very well characterized by the ^{1}H NMR spectra that show peaks at the lowest down field of the aromatic protons. Especially they are clearly observed in **2** and

TABLE III ^{31}P NMR Chemical Shifts Assignments

	Chemical shifts (δ, ppm)		Coupling constants (Hz) J_{PNP}	
Compound	P=N	P=O	P=N	P=O
1	−2.6	−10.6	21.3	21.3
2	−8.0	−21.6	65.7	66.5
3	−13.9	−21.5	72.2	72.2
4	−13.8	−20.7	75.8	75.8
5	−13.6	−21.8	75.0	75.0

TABLE IV ^{1}H NMR Chemical Shifts Assignments

Compound	Chemical shifts (δ) ppm, (coupling constants, J, Hz)†
1	—
2	2.16 (H_{14}), 2.19 (H_7), 7.05–7.36 (H other aryl), 7.35 (H_2), 7.37 (H_9)
3	2.10 (H_{14}), 2.19 (H_7), 6.97–7.28 (H aryl)
4	2.24 (H_{10}), 2.27 (H_5), 6.86–7.04 (H aryl)
5	7.97 (H_2, $^{3}J_{POCH}$: 8.6), 8.01 (H_{12}, $^{3}J_{POCH}$: 8.6), 7.1–7.8 (H other aryl)

†Coupling constants that can be calculated were given.

5 (Table IV). The alkyl protons resonate at $\delta = 2.16$ and 2.19, $\delta = 2.10$ and 2.19, $\delta = 2.24$ and 2.27 as two singlets for compounds **2**, **3**, and **4** respectively.

The ^{13}C NMR spectra were well-resolved first-order spectra from which the position of resonance of every carbon atom can be seen (Table V). It is noticed that the carbon atoms attached directly to the phosphorus atoms are generally observed at the lowest downfield. In these compounds (**2–5**), the $POAr_2$ and $PNAr_3$ environments can be distinguished in some cases. Especially, ipso carbons in the $-P(O)(OAr)_2$ are deshielded more than in the $(ArO)_3P{=}N-$.

TABLE V ^{13}C NMR Chemical Shifts Assignments

Compound	Chemical shifts (δ) ppm, (coupling constants, J, Hz)†
1	—
2	16.5 (C_7), 16.8 (C_{14}), 131.5(C_{12}), 132.2(C_5), 125.3 (C_{11}) 126.6(C_4), 127.0(C_{10}), 127.8(C_3), 121.0(C_9, $^{3}J_{POCC}$: 3.2), 120.3(C_2, $^{3}J_{POCC}$: 6.8), 130.1(C_6, $^{3}J_{POCC}$: 10.6), 130.3(C_{13}, $^{3}J_{POCC}$: 2.4), 149.3 (C_1, $^{2}J_{POC}$: 6.7), 150.1(C_8, $^{2}J_{POC}$: 6.7)
3	16.4 (C_7), 16.7 (C_{14}), 120.4(C_2), 120.7(C_9), 124.5 (C_{11}), 126.3(C_4), 127.0(C_{10}), 127.6(C_3), 130.1 (C_6, C_{13} $^{3}J_{POCC}$: 6.7), 131.5(C_{12}), 132.2(C_5), 149.4(C_1, $^{2}J_{POC}$: 91), 150.5(C_8, $^{2}J_{POC}$: 76)
4	21.14 (C_{10}), 21.18(C_5), 120.6 (C_2, $^{3}J_{POCC}$: 5.2) 120.8 (C_7, $^{3}J_{POCC}$: 4.9), 130.1(C_8,), 130.7 (C_3), 133.8 (C_9, $^{5}J_{POCCCC}$: 1.2), 136.0 (C_4, J_{POCCC}: 1.4), 148.5 (C_1, $^{2}J_{POC}$: 9.2), 150.0(C_6, J_{POC}: 7.7)
5	115.7(C_{12}, $^{3}J_{POCC}$: 2.8), 115.9(C_2, $^{3}J_{POCC}$: 3.5), 121.8(C_4), 122.8(C_{14}), 125.67 (C_{18}), 125.69(C_8), 125.88(C_{19}), 126.0(C_9), 126.35(C_{13}), 126.39(C_7), 126.46(C_{17}), 126.54(C_3), 127.1 (C_{16}), 127.2 (C_6), 127.7(C_{15}), 128.1(C_5), 135.0(C_{20}), 135.2(C_{10}), 146.6 (C_1, $^{2}J_{POC}$: 9.7), 148 (C_{11} $^{2}J_{POC}$: 7.9)

†Coupling constants that can be calculated were given.

The electron impact MS spectra of **2**, **4**, and **5** showed the parent ions at m/z 556 (M + 1, 45%), at 626 (M − 1, 2%)-628(M + 1, 2%) and 806 (M − 1, <1%)-808 (M + 1, <1%) respectively. The peaks at m/z values of 18 (dominant ion, 100%), 90, 82, and 107 correspond to the loss of H_2O, C_7H_6 (it is observed at the disubstituted aromatic compounds), C_6H_{10}, C_7H_7O for **2**. The dominant ion is at 107 ($C_7H_7O^+$, 100%) for **4**. Other peaks show the loss of C_7H_7 (at m/z 91, 96%) and C_6H_5 (at m/z 77, 55%). Compound **5** gives the dominant ion at m/z 107 ($C_7H_7O^+$, 100%). The peaks at 91 ($C_7H_7^+$, 78%) and 77 ($C_6H_5^+$, 54%) also are important and confirm the structure.

The liquid compounds were obtained from the reactions of compound **1** with 4-(2-pyridylazo)resorcinol monosodium salt, and also with sodium 1-nitroso-2-naphthaleneoxide. Their structures were tried to define by IR, ^1H, ^{13}C, ^{31}P NMR, and mass spectroscopy. There are no signals in the ^{31}P NMR. The reaction products couldn't be identified. The sodium ion is on the *ortho*-position with respect to the azo group in the structure of monosodium 4-(2-pyridylazo)resorcinol. In that case, the nucleophilic attack appears to be more difficult because the steric hindrance plays on important role in the reaction.

Although α-naphthaleneoxide reacted with the phosphazene, 1-nitroso-2-naphthaleneoxide did not. This observation can be presumed to be a consequence of the nitroso group. Nitroso group, which is an electron drawing group, will draw electron from the naphthalene ring and the electron density on the oxygene ion will tend to be on the ring. This causes the decreasing of the strength of the nucleophile.

As a result, tetra- and pentasubstituted arlyloxyphosphazenes were isolated from the nucleophilic substitution reaction between N-dichlorophosphoryl-P-trichloromonophosphazene and sodium *o*-methylphenoxide, sodium *p*-methylphenoxide, sodium α-naphthaleneoxide. The structures of arlyloxyphosphazenes were defined as 1-chloro,1-(*o*-methylphenoxy)phosphoryl-2,2,2-tris(*o*-methylphenoxy)phosphazene, 1,1-bis(*o*-methylphenoxy)phosphoryl-2,2,2-tris(*o*-methylphenoxy)phosphazene, 1,1-bis(*p*-methylphenoxy) phosphoryl-2,2,2-tris(*p*-methylphenoxy)phosphazene, 1,1-bis(α-naphthaleneoxy)phosphoryl-2,2,2-tris (α-naphthaleneoxy)phosphazene.

EXPERIMENTAL

General Remarks

Solvents were dried by conventional methods. All reactions were monitored by using Kieselgel 60 F254 (silica gel) precoated TLC plates and the separating conditions were determined. The separation of products

was carried out by flash column chromatography using Kieselgel 60 (60–230 mesh).

IR spectra were recorded with an ATI Unicam Mattson 1000 FTIR spectrophotometer. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded using a Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, 100.63, and 161.98 MHz respectively. All data were recorded for solutions in $CDCl_3$. The ^{1}H and ^{13}C chemical shifts were measured using $SiMe_4$ as an internal standard, the ^{31}P chemical shifts, using 85% H_3PO_4 as an external standard. Chemical shifts downfield from the standard are assigned positive δ values. Electron impact mass spectra were obtained by Micromass UK Platform-II spectrometer. Microanalysis was carried out by LECO 932 CHNS-O apparatus. The starting material, N-dichlorophosphoryl-P-trichloromonophosphazene, $Cl_3P{=}N{-}P(O)Cl_2$, was prepared by the method of Emsley, Moore and Udy and purified by vacuum distillation.[8]

Synthetic Procedures

The aryloxymonophosphazenes were synthesized as follows:

Reaction of 1 with Sodium o-Methylphenoxide

Small pieces of metallic sodium (0.93 g, 40 mmol) were slowly added to *o*-methyl phenol (4.40 g, 41 mmol) in 150 ml of toluene during 0.5 h with stirring at 20°C, with argon being passed over the reaction vessel. The alcoholate reaction were continued for 36 h at 45°C under reflux using a condenser fitted with a $CaCl_2$ drying tube. Excess of sodium was removed by filtration, and the solution of sodium *o*-methyl phenoxide was cooled to 0°C. Compound **1** (2.18 g, 8 mmol) in 50 ml of toluene was slowly added dropwise to the reaction vessel by stirring during 0.5 h, and the mixture was allowed to ambient temperature and then refluxed for 48 h. After the reaction was completed, the precipitated salt (NaCl) was filtered and the solvent was removed under vacuum. The oily residue was examined by TLC using n-hexane/ethylacetate (4:1) and two components, which were viscous and red coloured, and their R*f* values were 0.54 and 0.67, were detected. They were separated by using column chromatography. Compound **2** [1-chloro,1-(*o*-methylphenoxy)-phosphoryl-2,2,2-tris(*o*-methylphenoxy)phosphazene] and **3** [1,1-bis(*o*-methylphenoxy)phosphoryl-2,2,2-tris(*o*-methylphenoxy)phosphazene] were obtained in 8% (0.4 g) yield and 32% (1.62 g) yield respectively.

Reaction of 1 with Sodium p-Methylphenoxide

Conditions as for **(a)** using 0.59 g (25 mmol) metallic sodium, 2.809 g (26 mmol) of *p*-methylphenol, and 1.39 g (5 mmol) of compound

1 in diethyl ether (50 ml), eluent chloroform/ethylacetate (4:1, Rf = 0.35). The phenolate reaction was continued for 24 h at 30°C. The reaction of compound **1** with sodium *o*-methylphenoxide was carried out for 36 h at boiling ether. The viscous and dark yellow liquid compound is 1,1-bis(*p*-methylphenoxy)phosphoryl-2,2,2-tris(*p*-methylphenoxy)phosphazenes **4**. Yield is 68% (2.20 g).

Reaction of 1 with Sodium α-Naphthaleneoxide

Conditions as for **(b)** using 1.137 g (49 mmol) metallic sodium, 7.13 g (49 mmol) of α-hydroxynaphthalene, and 2.35 g (9 mmol) of compound **1** in diethyl ether (50 ml), eluent chloroform/ethylacetate (3:1, Rf = 0.92). The viscous and red liquid compound is 1,1-bis(α-naphthaleneoxy)-phosphoryl-2,2,2-tris(α-naphthaleneoxy)phosphazenes **5**. Yield is 25% (1.8 g).

Reaction of 1 with Monosodium 4-(2-Pyridylazo)resorcinol

Compound **1** (1.00 g, 4 mmol) in 50 ml of ether was slowly added dropwise to sodium 4-(2-pyridylazo)resorcinol (4.73 g, 20 mmol) at 0°C stirring during 0.5 h, and the mixture was allowed to ambient temperature and then refluxed for 168 h. The compound was eluted with the above conditions and the solvent was removed under vacuum. The oily residue was examined by TLC using n-hexane/ethylacetate (4:1) and three components, light green colored, with Rf values of 0.64, 0.47, 0.34, were detected. They were separated by using column chromatography.

Reaction of 1 with Sodium 1-Nitroso-2-naphthaleneoxide

Conditions as for **(b)** using 0.93 g (40 mmol) metallic sodium, 6.43 g (37 mmol) of 2-hydroxy-1-nitrosonaphthalene, and 2.00 g (7 mmol) of compound **1** in THF (50 ml), eluent chloroform. The naphtaleneoxide reaction was continued for 36 h at boiling THF. The reaction of compound **1** with sodium 1-nitrosonaphthaleneoxide was carried out for 72 h at boiling THF. Pure product was obtained as a viscous and red liquid (Rf = 0.84).

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