# PHOSPHORYLATION OF SOME NEW ACENAPHTHENEQUINONE DERIVATIVES

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Acenaphthenequinone reacted with diazofluorene, diphenyldiazomethane, phenybenzoyldiazomethane, phenacyl chloride, o-nitrobenzyl chloride, and diazohydroindenedione to give new oxadiazole, ketoepoxide and dioxadiazepine derivatives. They reacted with triphenylphosphine and triethylphosphite to give new organophosphorus compounds containing a six-membered or four-membered phosphorane ring. The structures were elucidated using IR, UV, NMR, and mass spectra, and elemental analyses.

Keywords: acenaphthenequinone, dioxadiazepine, epoxides, oxadiazole, phosphorane, phosphorylation.

Many earlier studies have been reported on the reactions of phenanthrenequinones with diazomethane. Arndt [1] found that it gave the monoethylene oxide derivative when the reaction was carried out using ether and a small amount of methanol. Reinvestigation of the same reaction [2], using dioxirane containing a small amount of methanol, gave monospiroepoxy ketone, and in tetrahydrofuran with a small amount of lithium chloride the product was the bis-epoxide, while in the presence of a large amount of methanol ring expansion took place.

The reaction of some derivatives of diazomethane with phenanthrenequinone [2-4] gave a methylenedioxy derivative. The reaction of diphenyldiazomethane and di(*p*-chlorophenyl)diazomethane with phenanthrenequinone showed that the structures must be corrected to the ketoepoxide [5]. 3,6-Dibromo-9,10-phenanthrene reacted with diazoalkanes to give the corresponding ketoepoxide derivatives [6]. The *o*-methyl ether of isatin reacted with diazomethane to furnish a quinoline derivative as the major product, together with a spirooxirane derivative [7]. It has been reported [8] that *p*-chloroacetophenone reacted with diphenyl-diazomethane and diazofluorene in benzene in the presence of copper bronze to give nitrogen- and halogen-free new compounds and *p*-chlorophenol. The reaction of diazomethane derivatives with 1,2-naphthoquinone-4-sulfonic acid in benzene gave  $\alpha$ -ketoepoxides, cyclopropane, and methylenedioxy derivatives, accompanied

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by desulfonation reactions [9]. The reaction of 3,4-dimethoxyacetophenone with 2-diazo-1,3-dihydroindenedione, diphenyldiazomethane, and 9-diazofluorene in chlorobenzene proceeded with formation of new four-, five-, and six-membered rings. These compounds reacted with triphenylphosphine to give five- and six-membered heterorings *via* ring opening and cyclization [10]. A derivative of the 2,2-dihydro-1,2-oxaphospholane-4 ring system was obtained from the reaction of 3-benzylidene-2,4-pentanedione with trimethyl phosphate [11].

Triphenylphosphine and trimethylphosphite as nucleophiles reacted with ketoepoxides spiro(oxirane-2,9-phenanthrenes) to give heterocyclic hexaoxyphosphorane compound [12]. Triphenylphosphine reacted with 3,4-cyclopropane-1,2-ketoepoxide derivatives of naphthalene to give a four-membered heterophosphorus ring *via* cyclization (tetraoxyphosphorane) [13].

We investigated the reaction of the new compounds **1-3** with triphenylphosphine, where phosphorus is in a low oxidation state, in order to study the mechanism of the reaction.

In continuation of our previous work, the present work is directed toward studying the reactions of some quinones with diazomethane derivatives, phenacyl chloride, and *o*-nitrobenzyl chloride, and the reactions of the products with organophosphorus compounds to obtain new compounds of the expected biological activity.

Acenaphthenequinone reacted with 9-diazofluorene in benzene under reflux for 5 h to give an oxadiazole derivative **1**. The reaction mechanism may be as follows:



The IR spectrum of compound **1** shows the presence of the bands  $v_{C=O}$  at 1718 and  $v_{N=N}$  at 1622 cm<sup>-1</sup>. Diphenyldiazomethane, phenylbenzoyl diazomethane, phenacyl chloride, and *o*-nitrobenzyl chloride reacted with acenaphthenequinone to give yellow, green-yellow, and pale-brown ketoepoxide products **2a-d**.



**2** a  $R = R^1 = Ph$ , b R = Ph,  $R^1 = COPh$ ; c R = COPh,  $R^1 = H$ ; d  $R = o-O_2NC_6H_4$ ,  $R^1 = H$ 

The IR spectra for compounds **3a** and **3b** show  $v_{oxirane}$  at 1267 and 829 cm<sup>-1</sup> [14]. For compound **2a** its spectrum shows one  $v_{C=0}$  at 1720 cm<sup>-1</sup>, while the spectrum of compound **2b** shows two  $v_{C=0}$  at 1731 and 1681 cm<sup>-1</sup>. The mass spectrum for compound **2b** confirmed the suggested structure. The spectrum did not show the molecular ion peak; the base peak was m/e 167 (Scheme 1).

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Scheme 1



The IR spectrum for compound **2c** shows  $v_{C-H}$  at 2950, two  $v_{C=0}$  at 1728 and 1690, and  $v_{oxirane}$  at 1228, 852, and 827 cm<sup>-1</sup>. The IR spectrum for compound **2d** shows  $v_{C-H}$  at 2955–2852,  $v_{C=0}$  at 1728,  $v_{C-H}$  at 3378,  $v_{NO_2}$  at 1522 and 1340, and  $v_{oxirane}$  at 1187, 856, and 820 cm<sup>-1</sup>.

Acenaphthenequinone reacted with 2-diazo-1,3-dihydroindenedione in benzene under reflux to give dioxadiazepine **3**.

The suggested structure is based on the following data from elemental analysis, IR, and UV/Vis spectra.

Fluorenylidene derivative **1** reacted with triphenylphosphine to give a six-membered ring oxadiazaphosphorane **4**.

The reaction mechanism may be as follows:



Its IR spectrum shows a new absorption band due to  $v_{P-Ph}$  at 1440 and  $v_{C=0}$  at 1717 cm<sup>-1</sup>, indicating the presence of one C=O group. The mass spectrum shows the molecular ion peak  $[M-2]^+$  at *m/e* 634 (1.49%) and the base peak at *m/e* 356 (100%) (Table 1).

The reactions of triphenylphosphine with  $\alpha$ -ketoepoxide derivatives **2a**-**d** in tetrahydrofuran gave new products *via* nucleophilic attack of the trivalent phosphorus on the electron-deficient carbon followed by bond cleavage and cyclization with the formation of a four-membered heterophosphorus ring (tetraoxyphosphorane compounds) **5a**-**d**.

Fragment	m/e	Relative abundance, %
1	2	3
$N \approx N$ $O \qquad P = O$ $Ph_3$ $[M-2]^+$	634	1.49
$\begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \\ Ph \end{array} \begin{array}{c} O \\ P \\ C \\ P \\ Ph \\ Ph \end{array} \begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \end{array}$	552	1.25
$O$ $C_4H_6$ $N$ $N$ $N$	499	1.99

TADLE 1. THE TRAINERS OF TRADUCT 4 WITH THEIR 70 RELATIVE ADDITURINE	TABLE 1.	The Fragment	ts of Product 4	with their	% Relative	Abundances
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TABLE 1 (continued)

1	2	3
	356	100
	327	77.71
	277	4.36
P = O	254	6.23
C=N=N	191	1.74
	178	29.51%
	166	3.11%
(+) C.	163	74.89%
$C_{6}H_{5}^{+}$ $HC \equiv C - C \equiv C - C \equiv CH^{+}$	74	4.61%

The mechanism of the reaction may be as follows:



**5a**  $R = R^1 = Ph$ , **b** R = Ph,  $R^1 = COPh$ ; **c** R = COPh,  $R^1 = H$ ; **d**  $R = o-O_2NC_6H_4$ ,  $R^1 = H$ 

The IR spectrum for compounds **5a** shows  $v_{C=O}$  at 1726,  $v_{P-Ph}$  at 1437, and  $v_{P-O-C}$  at 1022 cm<sup>-1</sup>, while the IR spectrum for compound **5b** shows two bands  $v_{C=O}$  at 1727 and 1690,  $v_{P-Ph}$  at 1448, and  $v_{P-O-C}$  at 1034 cm<sup>-1</sup>. The UV/Vis spectrum for compound **5b** shows  $\lambda_{max}$  at 348 nm ( $\epsilon 2.0 \times 10^4$ ) and a shoulder at 350 nm ( $\epsilon 1.3 \times 10^3$ ). The IR spectrum for compound **5c** shows  $v_{C-H}$  at 2926, two  $v_{C=O}$  at 1727, 1690,  $v_{PPh}$  at 1449, and  $v_{P-O-C}$  at 1188 cm<sup>-1</sup>. For compound **5d** the IR spectrum shows  $v_{C-H}$  at 2968–2852, only one  $v_{C=O}$  at 1728,  $v_{P-Ph}$  at 1460, and  $v_{P-O-C}$  at 1187 cm<sup>-1</sup>. The UV/Vis spectrum for compound **5c** shows  $\lambda_{max}$  at 348 nm ( $\epsilon 2.0 \times 10^4$ ). The signal  $\delta 5.32$  ppm (1H) in the <sup>1</sup>H NMR spectrum of compound **5d** can be attributed to CH (methine) protons.

Triphenylphosphine reacted with dioxadiazepine derivative 3 to give 6-membered oxadiazaphosphorane 6.



The IR spectrum shows 3 bands  $v_{C=0}$  at 1774, 1722, 1673,  $v_{P-Ph}$  at 1437.6 and  $v_{P-O-C}$  at 1032 cm<sup>-1</sup>. The UV/Vis spectrum shows  $\lambda_{max}$  at 397 nm ( $\epsilon$  7.52×10<sup>2</sup>). The mass spectrum of compound **6** shows the molecular ion peak [M+1]<sup>+</sup> at *m/e* 617 (10.06%). The different fragments in each case are tabulated in Table 2 with their relative abundances.

Triethylphosphite reacted with compound **2b** to afford four-membered ring oxyphosphorane 7 *via* the same reaction mechanism. The IR spectrum of compound 7 shows new absorption bands at 2958 and 1030 cm<sup>-1</sup> due to  $v_{C-H}$  and  $v_{P-O-alkyl}$ .



Triethylphosphite reacted with dioxadiazepine derivative **3** to give the product cyclophosphorane **8**. The IR spectrum of compound **8** shows three  $v_{C=0}$  at 1775, 1731, 1672 and  $v_{P-O-alkyl}$  at 1030 and 1227 cm<sup>-1</sup>.

Fragment	m/e	Relative abundance, %
$O = C \qquad F = O \qquad F = $	617	10.06
$\begin{array}{c} O \\ O \\ H \\ C \\ + \\ H \\ H$	369	7.55
C = N - N = C + O + O + O + O + O + O + O + O + O +	337	10.69
$Ph \rightarrow P=O$ $P=O$ $Ph \rightarrow P=O$	278	15.72
$\begin{array}{c} \overbrace{(+)}\\ Ph \\ Ph \\ Ph \end{array} P = O$	277	55.97%
$ \begin{array}{c} Ph \\ Ph \\ Ph \\ P \\ H_2C \\ + \end{array} P $	199	23.27
H C C H HO H	149	41.51
$H \cdot P \longrightarrow C \equiv C - H$	57	52.20
$C_4H_3$ +	51	100

## TABLE 2. The Fragments of Compound 7 with their Relative Abundances

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Com-	Empirical	Found, % Calculated %			mn °C*	Vield %	
pound	formula	С	Н	N	Р	mp, c	i ieia, 70
1	$C_{25}H_{14}N_2O_2$	<u>80.88</u> 80.21	<u>3.64</u> 3.74	<u>7.52</u> 7.48		188-189	35.41
2a	$C_{25}H_{16}O_2$	$\frac{86.39}{86.20}$	<u>4.21</u> 4.59			167-168	49.42
2b	$C_{26}H_{16}O_3$	$\frac{82.65}{82.97}$	$\frac{4.28}{4.25}$			140-141	30.92
2c	$C_{20}H_{12}O_3$	<u>79.53</u> 80.00	$\frac{3.69}{4.00}$			138-139	63
2d	$C_{19}H_{11}NO_4$	$\frac{71.64}{71.92}$	$\frac{3.17}{3.47}$	$\frac{4.10}{4.41}$		~340	47
3	$C_{21}H_{10}N_2O_4$	<u>70.92</u> 71.18	$\frac{2.67}{2.82}$	$\frac{7.74}{7.90}$		112-113	57
4	$C_{43}H_{29}N_2O_2P$	<u>80.88</u> 81.15	$\frac{3.10}{2.98}$	$\frac{4.64}{4.55}$	$\frac{4.66}{4.87}$	208-209	73
5a	$C_{43}H_{31}O_2P$	<u>84.62</u> 84.59	$\frac{5.26}{5.08}$		$\frac{5.32}{5.08}$	120-121	69
5b	$C_{44}H_{31}O_3P$	$\frac{82.71}{82.75}$	$\frac{4.88}{4.85}$		$\frac{4.95}{4.85}$	130-131	53
5c	$C_{38}H_{27}O_3P$	$\frac{81.00}{81.13}$	$\frac{4.80}{4.77}$		<u>5.24</u> 5.51	207-208	53
5d	$C_{37}H_{26}NO_4P$	<u>75.99</u> 76.68	$\frac{4.74}{4.49}$	$\frac{2.32}{2.41}$	$\frac{5.30}{5.35}$	172-173	44
6	$C_{39}H_{25}N_2O_4P$	<u>75.65</u> 75.97	<u>3.96</u> 4.05	<u>4.31</u> 4.45	$\frac{5.40}{5.03}$	254-256	86
7	$C_{32}H_{31}O_6P$	$\frac{70.82}{70.84}$	<u>5.67</u> 5.71		<u>5.70</u> 5.71	123-124	60
8	$C_{27}H_{25}N_2O_7P$	$\frac{61.69}{62.30}$	$\frac{4.63}{4.80}$	$\frac{4.83}{5.38}$	<u>5.90</u> 5.96	90-91	75

TABLE 3. Physical Properties and Analyses of Products

\* Solvent of crystallization: petroleum ether 40-60° (compounds 1, 7, 8), ether (compounds 2a,b, 3, 4, 5a,b), EtOH (compound 2c), MeOH (compound 2d), THF (compound 5c,d, 6).

#### EXPERIMENTAL

Melting points were determined with Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Lab., Cairo University, Giza. FTIR spectra were recorded on a Bruker vector apparatus, Germany, and on Mattson 1000 spectrophotometer at the Microanalytical Lab., Cairo University, Giza. UV/Vis spectra were recorded using a vis Shimadzu UV-1601 spectrometer. Mass spectra were measured on a GCQ Finnigan MAT apparatus at Ain Shams University. <sup>1</sup>H NMR spectra were recorded on a Gemini 200 spectrometer in DMSO solution with TMS as an internal standard at Cairo University, Giza.

**Compound 1.** A mixture of acenaphthenequinone (0.47 g, 2.5 mmol), 9-diazofluorene (1.44 g, 7.5 mmol), and copper bronze (0.50 g, 7.8 mmol) in benzene (100 ml) was boiled under reflux for 10 h. Copper bronze was removed by filtration and copper oxide (1.98 g, 25 mmol) was added to the filtrate, which was then refluxed for 10 h. Copper oxide was removed by filtration, whereby an orange product 1 was obtained after crystallization from petroleum ether (40-60°C). The UV-Vis spectrum shows  $\lambda_{max}$  at 350 ( $\varepsilon = 2.0 \times 10^3$ ), 415.2 ( $\varepsilon = 1.6 \times 10^3$ ), and 462.5 nm ( $\varepsilon = 1.88 \times 10^3$ ).

**Compound 2a.** A mixture of acenaphthenequinone (0.91 g, 5 mmol) and diphenyldiazomethane (1.94 g, 10 mmol) was boiled under reflux in benzene (100 ml) for 10 h. A yellowish brown crystalline product **3a** was formed, filtered off, and recrystallized from ether. The UV/Vis spectrum showed  $\lambda_{max}$  at 350 ( $\epsilon 1.3 \times 10^4$ ) and 379 nm ( $\epsilon 8.43 \times 10^3$ ) for compound **2a**.

**Compound 2b.** A mixture of acenaphthenequinone (0.47 g, 2.5 mmol), phenylbenzoyl diazomethane (1.56 g, 7.5 mol), and copper bronze (0.50 g, 7.8 mmol) was refluxed in benzene for 20 h. Copper bronze was removed by filtration, whereby a yellowish-green product **3b** was formed and recrystallized from ether.

**Compounds 2c,d**. A mixture of acenaphthenequinone (6 mmol), phenacyl chloride (or *o*-nitrobenzyl chloride) (12 mmol), and K<sub>2</sub>CO<sub>3</sub> (7 mmol) in ethyl alcohol (30 ml) was refluxed for 3 h, whereby a yellow (or pale-brown) product was formed and recrystallized from THF. The UV/Vis spectrum for compound **2c** shows  $\lambda_{max}$  at 341 nm ( $\epsilon 2.5 \times 10^3$ ).

**Compound 3.** A mixture of acenaphthenequinone (0.47 g, 2.5 mmol) and 2-diazo-1,3-dihydrinoindenedione (0.86 g, 5 mmol) was refluxed in benzene (100 ml) for 20 h. A deep brown precipitate **4** was obtained and recrystallized from ether. The IR spectrum, being in accordance with the proposed structure, shows two  $v_{C=0}$  at 1720 and 1681 cm<sup>-1</sup>. UV/Vis spectrum shows  $\lambda_{max}$  at 407 ( $\epsilon$  5.06×10<sup>3</sup>) and a shoulder at 475 nm ( $\epsilon$ 2.3×10<sup>3</sup>).

**Compound 4.** A mixture of triphenylphosphine (0.13 g, 0.5 mmol) and compound **1** (0.18 g, 5 mmol) in THF (10 ml) was stirred for 3 h at room temperature, then left to stand overnight, whereby an orange precipitate **5** was separated, filtered off, and recrystallized from ether. The UV/Vis spectrum shows  $\lambda_{max}$  at 350 ( $\varepsilon 1.3 \times 10^4$ ), 407.5 ( $\varepsilon 10.5 \times 10^3$ ) and a shoulder at 472.8 nm ( $\varepsilon 2.4 \times 10^3$ ).

**Compounds 5a-d (General Method).** A mixture of  $\alpha$ -ketoepoxide derivative **2a-d** (1 mmol) and triphenylphosphine (1 mmol) in THF (10 ml) was stirred for 3 h at room temperature, whereby brown, pale-brown, yellowish-white, and pale-brown products **5a-d** were formed and recrystallized from THF.

**Compound 6**. A mixture of compound **3** (0.17 g, 0.5 mmol) and triphenylphosphine (0.13 g, 0.5 mmol) in THF (10 ml) was stirred at room temperature for 3 h, whereby a brown product **6** was formed and recrystallized from THF.

**Compounds 7 and 8 (General Method)**. A mixture of triethylphosphite (0.5 mmol) and compounds **2b** and **3** (0.5 mmol) in THF (10 ml) was stirred for 3 h at room temperature, then left to stand overnight, whereby yellowish-white and brown crystalline products **7** and **8** were separated, filtered off, dried, and recrystallized from petroleum ether ( $40-60^{\circ}$ C).

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