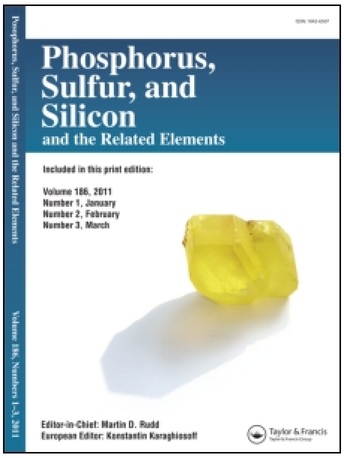

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ORGANOPHOSPHORUS COMPOUNDS, 9.[1] THE REACTION OF YLID-PHOSPHORANES WITH NITROSONAPHTHOLS

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ORGANOPHOSPHORUS COMPOUNDS, 9.[1] THE REACTION OF YLID-PHOSPHORANES WITH NITROSONAPHTHOLS

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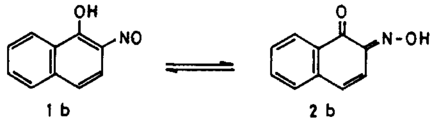
α-Nitroso-β-naphthol (**1a**) reacts with ylid-phosphoranes **3a–c** to give the corresponding imines **4a–c**. On the other hand, β-nitroso-α-naphthol (**1b**) undergoes deoxygenative dimerization by the same reagents to yield the azo-derivative **6**. The appropriate symmetrically disubstituted ethylene **7** was also isolated and identified in each reaction. Structures **4**, **6** and **7** were attested by compatible analytical and spectroscopic results.

Key words: Nitroso-naphthols; ylid-phosphoranes; reactions; deoxygenative dimerization.

INTRODUCTION

Although the behaviour of quinones toward ylid-phosphoranes (Wittig-reagents) has been extensively studied,[2] the behaviour of nitroso-compounds toward the same reagents has received only limited attention.[3] Since nitrosonaphthols of type **1** can exist not only in the benzenoid structure **1** but also in the tautomeric quinonoid form **2** and undergo reactions characteristic of both forms,[4–7] it appeared of interest to examine their reaction with stable ylid-phosphoranes **3** to

1a 2a



1b 2b

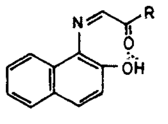
establish whether the nitroso-, or the carbonyl function would be preferentially attacked by the reagents.

$$(C_6H_5)_3P{=}CH{-}R \rightleftharpoons (C_6H_5)_3\overset{\oplus}{P}{-}\overset{\ominus}{C}H{-}R$$

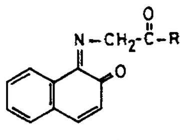
3 a, R = $COOCH_3$
b, R = $COOC_2H_5$
c, R = COC_6H_5

RESULTS AND DISCUSSION

We have found that α-nitroso-β-naphthol **1a** reacts with methylenetriphenylphosphoranes **3a–c**, in boiling benzene to give brown crystalline products formulated as **4a–c**, respectively. Triphenylphosphine oxide (TPPO) was also isolated and identified in each case. Compounds **4** are chromatographically pure and possess sharp melting points. Structure **4** was attested by the following evidences: (a) Compatible elemental analyses and molecular weight determinations (MS) were obtained for all products. (b) The IR spectra of **4** (in KBr) showed only weak absorption around 3400 cm^{-1} for the OH group. This is probably due to proximity of the OH to the carbonyl function (chelation).[8] However, compounds **4a–c** dissolve freely in dilute aqueous alkali and exhibit a violet color reaction with alcoholic ferric chloride solution. Moreover, the IR spectrum of 1-(carbmethoxymethylimino)-2-hydroxynaphthalene (**4a**) disclosed the presence of strong absorption bands at 1730 cm^{-1} (C═O, ester) and 1330 cm^{-1} (C—O, stretching).[8] (c) The PMR spectrum of **4a** (in $CDCl_3$) showed signals at δ4.15 (3H, OCH_3, s) and δ7.82 (6H, aromatics, m). The azomethine proton appeared at δ8.51 (1H, s) while the OH proton showed a singlet (exchangeable with D_2O) at δ13.33 ppm. Based upon these arguments, an alternative tautomeric structure like **5** can be disregarded.

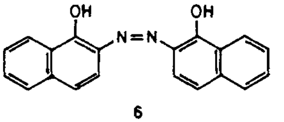


4 a, R = OCH_3
b, R = OC_2H_5
c, R = C_6H_5



5, R as in 4

The reaction of β-nitroso-α-naphthol **1b** with ylid-phosphoranes **3a–c** was also conducted in boiling benzene. In each case, a brown substance was separated in *ca.* 60% yield from the reaction medium and proved to have structure **6** (*vide infra*). TPPO and the appropriate symmetrical disubstituted ethylene **7** could also be isolated and identified in each reaction. Evidences for structure **6** are: (a) It gave correct elemental analyses and molecular weight determination (MS) which corresponded to $C_{20}H_{14}N_2O_2$. (b) It dissolves freely in 10% NaOH aq., and gives a violet color reaction with 1% alcoholic $FeCl_3$. (c) The —N═N— absorption band characteristic for azo-compounds[8] was present at 1570 cm^{-1} in the IR spectrum of **6**. Besides, the absorption bands due to the carbonyl functions which were observed in the IR spectra of compounds **4a–c** in the region 1750–1700 cm^{-1}, were absent in the spectrum of **6**. Moreover, the PMR spectrum of **6** (in $CDCl_3$) showed only a multiplet in the region δ8.11–6.57 due to the aromatics



6

E R–CH=CH–R
7a, R = $COOCH_3$
b, R = $COOC_2H_5$
c, R = COC_6H_5

while the OH protons appeared as D_2O-exchangeable broad singlet centered at δ13.35 ppm. (d) The mass spectrum of **6** showed the molecular ion peak at m/z 314 (M^+, $C_{20}H_{14}N_2O_2$, 50%). Loss of 2H radicals from M^+, which is frequently observed in the behaviour of condensed aromatics under electron impact,[9] yielded the radical cation at m/z 312 (base peak) which loses then N_2 molecule to give the ion peak at m/z 284 ([$C_{20}H_{12}O_2)^+$, 12%].

CONCLUSION

The present study clearly shows that α-nitroso-β-naphthol behaves toward the stable[2] ylid phosphoranes **3** in a manner different from that of β-nitroso-α-naphthol toward the same reagents. Besides, it is safe to cite that each substance reacts with **3** exclusively in the benzenoid nitroso-form (**1a** or **1b**) and not in the tautomeric quinone-oxime structure (**2a** or **2b**) at least under the prevailing experimental conditions. Although the initial step in the reaction of **1a** or **1b** with **3** involves nucleophilic attack by the nitroso-oxygen atom on the phosphonium center of the reagent, the consequences of the initial step vary markedly according to the nature of the nitroso-compound. The unexpected behaviour of **1b** toward ylid-phosphoranes **3** leading to the azo-derivative **6** and ethylenes **7** represents a new finding and supplement to the wide aspects[2] of utilizing Wittig reagents in the preparative purposes.

EXPERIMENTAL SECTION

Melting points: Not corrected, IR spectra: Perkin Elmer 157G (KBR); ^1H NMR spectra: Brucker WH-90 (solvent, $CDCl_3$, TMS as internal reference); MS: Kratos MS-50; Elemental analyses: Microanalysis Lab., National Research Centre (Cario). All reactions were carried out under nitrogen and dry conditions. Starting materials: α-Nitroso-β-naphthol is commercially available from BDH. Fumaric acid esters (dimethyl and diethyl) are commercially available from Aldrich. β-Nitroso-α-naphthol was prepared by the established method.[10]

Reaction of α-Nitroso-β-naphthol (*1a*) *with Wittig-Reagents* **3**. A mixture of **1a** (1.73 g; 0.01 mol) and ylid **3a**[11] (3.34 g; 0.01 mol) in benzene (100 ml) was refluxed for 20 hr. The reaction mixture was then concentrated at 60°C under reduced pressure. The solid product was redissolved in methanol (100 ml) and evaporated to dryness in the presence of silica gel (8 g). The mixture was then added to a column previously charged with silica gel in cyclohexane. The column was developed with cyclohexane containing increasing amounts of diethyl ether.

Fraction: (up to 8:2) eluted 1.61 g (70.51%) of a brown substance recrystallized from pet. ether (b.r. 60:80°C) to give **4a** as brown crystals mp. 140–142°C.

$C_{13}H_{11}NO_3$ (229.239)

Calcd.	C 68.11;	H 4.83;	N 6.11	
Found	67.99;	4.79;	6.08	M.W. 229 (MS).

$IR_{(cm^{-1})}$: Bands at 3400 (—OH), 1730 (C=O, ester), 1330 (C—O, stretching).

^1H $NMR_{(\delta)}$: Signals at 4.15 (3H, —OCH_3, s); 7.48–8.17 (6H, aromatics, m); 8.51 (1H, N=CH, s); 13.33 (1H; OH, s).

Fraction: (up to 6:4) afforded 2.42 g (87.4%) of colorless needles, mp. 156°C, confirmed to be triphenylphosphine oxide[12] (mp. & mixed mp., comparative IR spectra).

Similarly, **4b** and **4c** were obtained upon reacting ylids **3b**[11] and **3c**,[13] respectively with **1a** and working-up of the reaction mixture as mentioned above. TPPO was also isolated (*ca.* 85%) and identified in each reaction.

Compound **4b** was obtained as brown crystals (1.59 g, 65.72%), mp. 85°C, from cyclohexane-light pet. ether (1:1 v/v).

$C_{14}H_{13}NO_3$ (243.266)
Calcd. C 69.12 H 5.38 N 5.75
Found 68.87 5.29 5.68 M.W. 243 (MS).

$IR_{(cm^{-1})}$: Bands at 3345 (—OH); 1735 (C=O, ester); 1330 (C—O, stretching).

$^1H\,NMR_\delta$: Signals at 1.52 (3H, —CH_3, t; $J_{H.H} = 8$ Hz); 4.62 (2H, CH_2, q); 7.51–8.17 (6H, arom., m); 8.62 (1H, N=CH, s); 13.28 (1H, OH, s, exchang. with D_2O).

Compound **4c** (1.71 g, 62.53%) was isolated as brown crystals mp. 110–112°C, from benzene-light pet. ether (1:1 v/v).

$C_{18}H_{13}NO_2$ (275.31),
Calcd. C 78.53 H 4.75 N 5.08
Found 78.78 4.69 5.12 M.W. 275 (MS).

$IR_{(cm^{-1})}$: Bands at 3350 (—OH); 1710 (C=O, aryl-carbonyl).

$^1H\,NMR_\delta$: Signals at 7.37–8.40 (11 H, arom., m)' 8.91 (1 H, N=CH, s); 13.47 (1 H, OH, s).

Compounds **4a–c** are freely soluble in aq. NaOH (10%) and give violet color with alc. $FeCl_3$ solution (1%).

Reaction of β-Nitroso-α-naphthol (*1b*) *with Wittig-Reagents* **3**. A mixture of **1b** (1.73 g, 0.01 mol) and ylid-phosphorane (**3c**) (3.8 g, 0.01 mol) in benzene (100 ml) was refluxed for 40 hr. The reaction mixture was worked-up in the same way as described in the case of **1a** and the column was carried out with cyclohexane containing increasing amounts of diethyl ether.

Fraction: (9:1) yielded 887.8 mg (52.8%) of yellow crystalline material, mp. 110°C from ethyl alcohol, proved to be *E*-dibenzoyl ethylene[14] (**7c**) (mp. & mix. mp. and comp. IR).

Fraction: (8:2) produced 970 mg (61.81%) of brown crystals mp. 180°C from cyclohexane, shown to be **6**.

$C_{20}H_{14}N_2O_2$ (314.35)
Calcd. C 76.42 H 4.49 N 8.91
Found 76.37 4.46 8.82 M.W. 314 (MS).

$IR_{(cm^{-1})}$: Bands at 3340 (—OH), 1570 (N=N).

$^1H\,NMR_\delta$: Signals at 6.57–8.11 (12 H, arom., m), 13.35 (2 H, OH, s).

Fraction: (up to 6:4) gave 2.35 g (84.7%) of colorless needles mp. 156°C from ethyl alcohol, and confirmed to be triphenylphosphine oxide (mp. & mixed mp., comp. IR spectra).

Compound **6** is freely soluble in aq. NaOH (10%) and gives violet color with alc. $FeCl_3$ solution (1%).

When the above reaction was carried out using **3a** and/or **3b** instead of **3c** in benzene, TLC monitoring indicated the disappearance of the reactants after 20 hr. working-up the reaction mixture in the usual manner resulted in the isolation of dimethyl (**7a**)- and/or diethyl- (**7b**) fumarate (*ca.* 50%) along with **6** (*ca.* 26%) and TPPO (*ca.* 85%) respectively.

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