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AN UNUSUAL REACTION OF ISATOIC ANHYDRIDE WITH ACETYL- AND BENZOYL-METHYLENETRIPHENYLPHOSPHORANES

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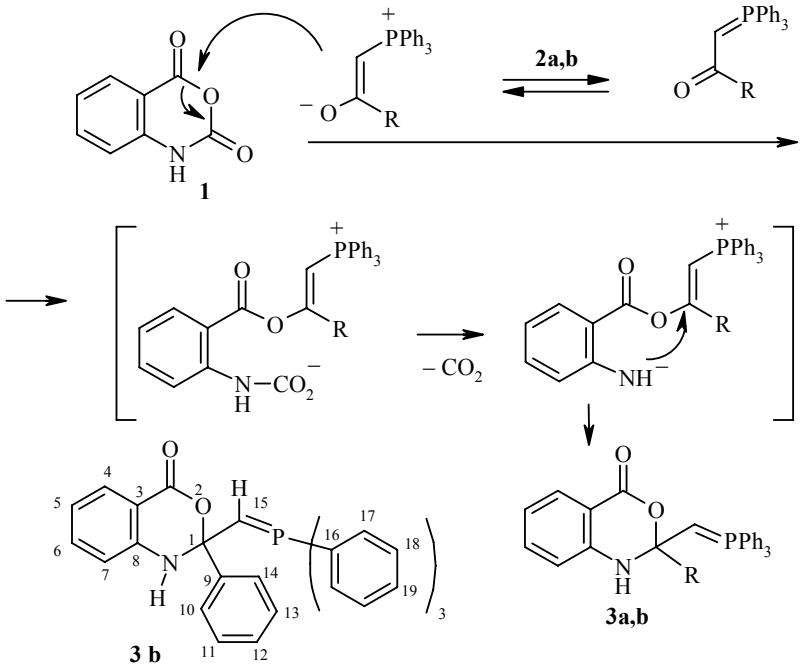
There are published data on the C-acylation of ethyl triphenylphosphoranylideneacetate with isatoic anhydride [3,1-benzoxazine-2,4(H)-dione] (**1**) leading to the formation of 3-(triphenylphosphoranylidene)-quinoline-2,4(1H,3H)-dione [1,2]. As a result of the reaction of compound **1** with 1-triphenylphosphoranylidene-2-propanone (acetylmethylenetriphenylphosphorane) (**2a**) or 2-triphenylphosphoranylidene-1-phenylethanone (benzoylmethylenephosphorane) (**2b**) we unexpectedly isolated the products from O-acylation of the latter followed by decarboxylation of the intermediate ylide and heterocyclization, i.e., the 2-substituted 2-(triphenylphosphoranylidenemethyl)-1,2-dihydro-4H-3,1-benzoxazin-4-ones **3a**,**b**.



2, **3 a** R = Me, **b** R = Ph

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The structure of compounds **3a**,**b** is confirmed by the NMR spectra and agrees well with previously obtained data on the structural features of ylides [3].

Compounds **3a**,**b** have bactericidal activity against standard strains of *Staphylococcus aureus* P-209 and *Escherichia coli* M_{17}, acting on bacterial cultures at a minimum suppressing concentration of up to 62.5 μg/ml.

Reaction of Isatoic Anhydride (1) with Acetyl- or Benzoylmethylenetriphenylphosphoranes. A mixture of isatoic anhydride **1** (0.82 g, 5.0 mmol) and acetylmethylenetriphenylphosphorane **2a** (1.59 g, 5.0 mmol) [4] or benzoylmethylenetriphenylphosphorane **2b** (1.90 g, 5.0 mmol) [4] in dioxane (80-100 ml) was boiled for 3-5 h (TLC). The solvent was evaporated, and the residue was rubbed with ether and tetrachloromethane and recrystallized from ethyl acetate. Compounds **3a** and **3b** were obtained.

2-Methyl-2-triphenylphosphoranylidenemethyl-1,2-dihydro-4H-3,1-benzoxazin-4-one (3a). Yield 1.40 g (64%); mp 139-140°C (ethyl acetate). IR spectrum (Specord M-80, thin layer in vaseline oil), ν, cm^{-1}: 3273 (NH), 1788, 1728 (C=O), 1592, 1570 (C=C_{arom}, Ph_3P=CH). ^{1}H NMR spectrum (RYa-2310, 60 MHz, DMSO-d_6, HMDS), δ, ppm: 1.88 (3H, s, CH_3); 3.78 (1H, br. s, NH); 4.15 (1H, br. s, CH in Ph_3P=CH–); 7.10-7.82 (19H, m, $3C_6H_5$, C_6H_4). Found, %: C 76.69; H 5.72; N 3.06; P 6.88. $C_{28}H_{24}NO_2P$. Calculated, %: C 76.87; H 5.53; N 3.20; P 7.08.

2-Phenyl-2-triphenylphosphoranylidenemethyl-4H-3,1-benzoxazin-4-one (3b). Yield 1.89 g (72%); mp 198-199°C (ethyl acetate). IR spectrum (Specord M-80, thin layer in Vaseline oil), ν, cm^{-1}: 3292 (NH), 1780, 1732 (C=O), 1620, 1584, 1502 (C=C_{arom}, Ph_3P=CH). ^{1}H NMR spectrum (Gemini-300, 300 MHz, in deuterochloroform, TMS), δ, ppm (*J*, Hz) (the numbering of the carbon atoms is arbitrary, see the scheme): 2.90 (1H, br. s, NH); 4.45 (1H, br. s, $C_{(15)}$H); 6.79 (1H, d, *J* = 8.4, $C_{(7)}$H); 6.91 (1H, t, *J* = 7.8, $C_{(12)}$H); 7.10-7.12 (3H, group of signals, $C_{(4)}$H, $C_{(5)}$H, $C_{(6)}$H); 7.20-7.26 (7H, group of signals, $C_{(10)}$H, $C_{(14)}$H, and 5CH in Ph_3P=); 7.31-7.35 (3H, group of signals, $C_{(11)}$; $C_{(13)}$; and 1CH in Ph_3P=); 7.43-7.50 (6H, group of signals, 6CH in Ph_3P=); 7.69-7.72 (3H, group of signals, 3CH in Ph_3P=). ^{13}C NMR spectrum (Gemini-300 BB, 75 MHz, TMS, deuterochloroform), δ, ppm (*J*, Hz) (the numbering of the carbon atoms is arbitrary, see the scheme): 51.4 ($C_{(15)}$, *J* = 111.0), 109.3 ($C_{(1)}$), 115.3 ($C_{(7)}$), 123.0, 128.8, 128.9, 136.2 ($C_{(4)}$-$C_{(6)}$, $C_{(12)}$), 126.0 ($C_{(16)}$, *J* = 91), 126.3, 127.3 ($C_{(10)}$, $C_{(11)}$), 128.4 ($C_{(18)}$, *J* = 13), 131.7 ($C_{(19)}$, *J* = 2), 132.5 ($C_{(17)}$, *J* = 11), 141.0, 146.9 ($C_{(3)}$, $C_{(9)}$), 159.4 ($C_{(8)}$), 184.2 ($C_{(2)}$). ^{31}P NMR spectrum (Gemini-300 BB, 121 MHz, H_3PO_4, deuterochloroform), δ, ppm: +16.6. Found, %: C 79.11; H 5.37; M 2.65; P 6.03. $C_{33}N_{26}NO_2P$. Calculated, %: C 79.34; H 5.25; N 2.80; P 6.20.

REFERENCES

1. D. T. Connor and M. von Strandtmann, *J. Org. Chem.*, **38**, 1047 (1973).
2. G. M. Coppola, *Synthesis*, 505 (1980).
3. E. N. Koz'minykh, E. S. Berezina, V. O. Koz'minykh, R. A. Aitken, N. Karodia, and T. Messil, *Zh. Obshch. Khim.*, **68**, 420 (1998).
4. F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).