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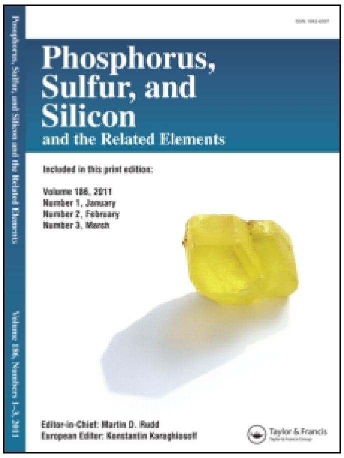

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REACTIONS OF PHTHALIMIDOBENZOIC ACID AZIDES WITH TRIMETHYL PHOSPHITE AND TRIS (DIALKYLAMINO) PHOSPHINES

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REACTIONS OF PHTHALIMIDOBENZOIC ACID AZIDES WITH TRIMETHYL PHOSPHITE AND TRIS (DIALKYLAMINO) PHOSPHINES

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Trimethyl phosphite (**3a**) and/or tris (dialkylamino) phosphines (**3b**, **c**) react with *o*-, and *m*-phthalimidobenzoic acid azides (**1a**, **b**) to give the new iminophosphorane derivatives (**4a–4f**). Possible reaction mechanism are considered and the structural assignments are based on compatible analytical and spectroscopic results.

Key words: *o*- and *m*-Phthalimidobenzoic acid azides (**1a**, **b**), trimethyl phosphite (**3a**), tris(dialkylamino)phosphines (**3b**, **c**) and iminophosphorane derivatives (**4a–4f**).

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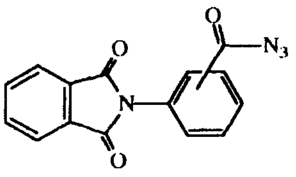
INTRODUCTION

Phthalimidobenzoic acid azides (**1a**, **b**) have been reported to react with triphenylphosphine to give the stable aminophosphorane derivatives (**2a**, **b**).[1] As iminophosphoranes are widely used in the synthesis of amides,[2] amines,[2,3] and a variety of compounds containing carbon-to-carbon double bonds,[4-8] it was of interest to extend our study on the behaviour of *o*- and *m*-phthalimidobenzoic acid azides (**1a**, **b**) towards another phosphorus reagents namely trimethyl phosphite (**3a**) and tris(dialkylamino)phosphines (**3b**, **c**).



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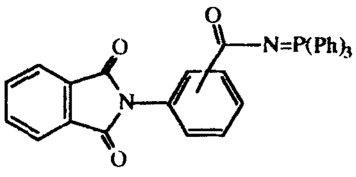


2

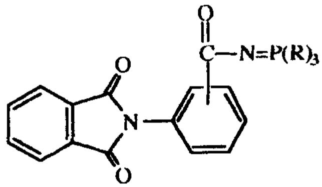
$P(R)_3$

1 & 2 a, *ortho* (*o*-)
b, *meta* (*m*-)

3 a, R = OCH_3
b, R = $N(CH_3)_2$
c, R = $N(C_2H_5)_2$

RESULTS AND DISCUSSION

We have found that the reaction of *o*-phthalimidiobenzoic acid azide (**1a**) with one mole equivalent of trimethyl phosphite (**3a**) in dry benzene proceeds at room temperature to give pure adduct formulated as (**4a**). The structure of compound (**4a**) is deduced from its analysis, ^{1}H-NMR, ^{31}P-NMR, ^{13}C-NMR and mass spectral data.



4 a, R=OCH_3 (*o*-); d, R=OCH_3 (*m*-);
b, R=$N(CH_3)_2$ (*o*-); e, R=$N(CH_3)_2$ (*m*-);
c, R=$N(C_2H_5)_2$ (*o*-); f, R=$N(C_2H_5)_2$ (*m*-)

The IR spectrum of (**4a**) shows strong bands at 1355 cm^{-1} (N=P), 1700 (acid azide C=O), at 2200 cm^{-1} (for azido group), 1775 and 1720 cm^{-1} (C=O, coupling bands of cyclic imides).[9-11] Moreover, its IR spectrum exhibits an absorption band at 1230 cm^{-1} (P—O—CH_3).[12] The ^1H NMR spectrum of (**4a**) shows a signal at δ = 3.7 [d, 9H, $P(OCH_3)_3$] for the 9 aliphatic protons of three equivalent methoxy groups with a coupling constant value of J_{HP} = 11 Hz. The aromatic protons appeared as a multiplet at δ 7.15–8.20 (m, 8H, Ar). Compound (**4a**) exhibits δ = +22.3 in its ^{31}P-NMR spectrum which clearly indicates an iminophosphorane structure. ^{13}C-NMR of adduct (**4a**) ($CDCl_3$) reveals signals at 175.6 (d, C=O), 170.3 (s, C=O), 57.08 (d, OCH_3). The mass spectrum of the adduct (**4a**) yielded a prominent ion peak M^+ at 388 which supports structure (**4a**).

Similarly, iminophosphorane derivatives (**4b–f**) were isolated from the reaction of *m*- and *o*-phthalimidobenzoic acid azides (**1a, b**) with trimethyl phosphite (**3a**) and tris(dialkylamino)phosphines (**3b, c**).

The identity of the new products (**4a–f**) is attested from their analysis, IR, ^1H-NMR and mass spectroscopic data (cf. Tables I and II). The reaction between the

TABLE I

Analytical data and physical properties of the products **4a–f**

Compound	Yield[a] %	m.p. °C	Mol. Form. (M. wt)	Analysis, Found (calcd.) %				M^+ m/z %
				C	H	N	P	
4a	73	182-183[c]	$C_{18}H_{17}N_2O_6P$ (388.34)	55.60 (55.67)	4.45 (4.41)	7.15 (7.21)	7.85 (7.90)	388 (3.5)
4b	60	157-158[b]	$C_{21}H_{26}N_5O_3P$ (427.49)	59.12 (59.00)	6.2 (6.13)	16.23 (16.39)	7.17 (7.24)	427 (35)
4c	80	147-148[c]	$C_{27}H_{38}N_5O_3P$ (511.65)	63.40 (63.38)	7.5 (7.48)	13.61 (13.69)	6.10 (6.05)	511 (4)
4d	75	218-. 219[c]	$C_{18}H_{17}N_2O_6P$ (388.34)	55.60 (55.67)	4.43 (4.41)	7.23 (7.21)	7.81 (7.90)	388 (8)
4e	70	125-126[b]	$C_{21}H_{26}N_5O_3P$ (427.49)	59.12 (59.00)	6.2 (6.13)	16.25 (16.39)	7.20 (7.24)	427 (25)
4f	90	137-138[b]	$C_{27}H_{38}N_5O_3P$ (511.65)	63.40 (63.38)	7.5 (7.48)	13.63 (13.69)	6.13 (6.05)	511 (0.3)

a. Yield are approximately

Solvent of crystallization: b. Petroleum ether (40-60°) c.Petroleum ether (60-80°)

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TABLE II

IR and ^{1}H-NMR data for compounds **4a–f**

Compound	^{a}IR in cm^{-1}	^{1}H (δ, ppm)
4a	1355 (N = P), 1230 (P - O - CH_3)	3.70 (d, 9H, J_{HP} = 11 Hz), 7.15 - 8.20 (m, 8H, Ar)
4b	1350 (N = P), 1320, 860 (P - $N(CH_3)_3$)	2.80 (d, 18H, J_{HP} = 10.1 Hz), 7.20 - 8.20 (8H, Ar)
4c	1360 (N = P), 1330, 850 (P - $N(C_2H_5)_3$)	1.20 (t, 18H), 3.08 (q, 12H, N-CH_2-CH_3) 7.20 - 8.15 (8H, Ar)
4d	1350 (N = P), 1220 (P - O - CH_3)	3.75 (d, 9H, J_{HP} = 11 Hz), 7.15-8.30 (m, 8H, Ar)
4e	1340 (N = P), 1325, 855 (P - $N(CH_3)_3$)	2.70 (d, 18H, J_{HP} = 10.2 Hz), 7.25-8.2 (8H, Ar)
4f	1350 (N = P) 1335, 860 (P - $N(C_2H_5)_3$)	1.10 (t, 18H, N-CH_3), 3.08 (q, 12H, N-CH_2-CH_3) 7.20 - 8.20 (8H, Ar)

(a) The IR spectrum of compounds 4a-f showed bands at 1700-1710 (acid azide, C=O), and 1770-1720 cm^1 (C = O, coupling bands of cyclic imides)

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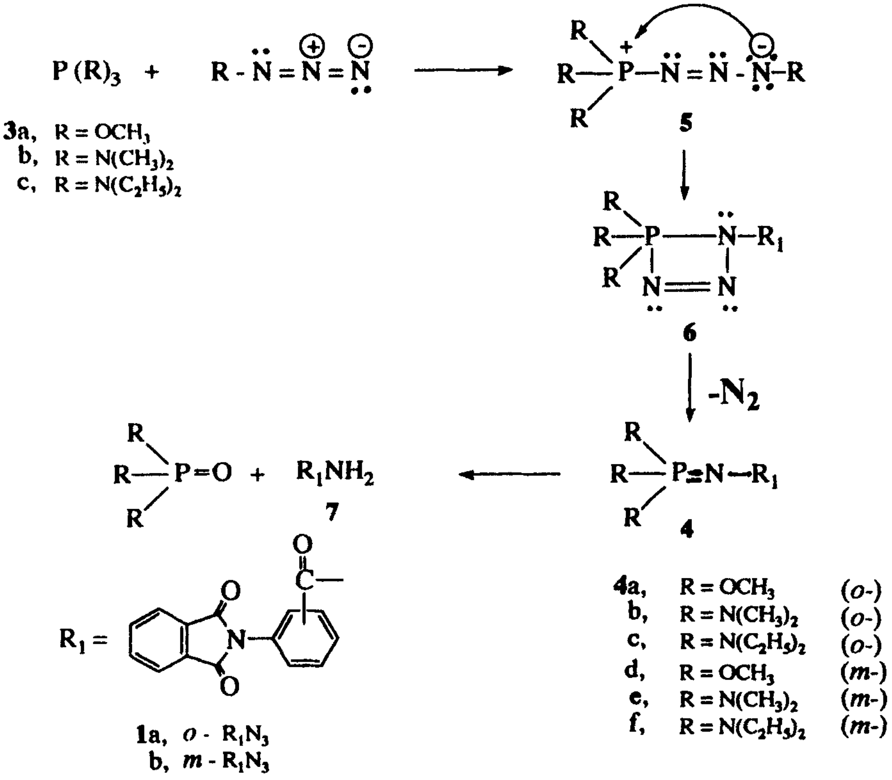
above mentioned phosphorus reagents (**3a–c**) and phthalimidobenzoic acid azides (**1a**, **b**), conceivably takes place by an addition of the trivalent phosphorus to the terminal nitrogen of the azide to form the unstable phosphazide **5** (Scheme I). Though, phosphazide adducts in some cases are isolable from the reaction of certain P^{III} azide,[2,5,13] these intermediate adducts **5** in the present case decompose to the iminophosphoranes at room temperature. A four-membered cyclic transition state like **6** is by no means unusual.

Judging from the effect of substituents on the P^{III} (**3a–c**), the more nucleophilic tris(dimethylamino)phosphine (**3b**) is the more vigorous in its reaction.

From the results of the present investigation, it could be noted that *o*- and *m*-phthalimidobenzoic acid azides (**1a**, **b**) behave towards alkyl phosphite (**3a**) and tris(dialkylamino)phosphines (**3b**, **c**) in a manner similar to the reaction of the same azide with triphenylphosphines in which the iminophosphorane derivatives (**4a–f**) are the sole reaction products.

EXPERIMENTAL

All melting points are uncorrected. The appropriate precautions in handling moisture-sensitive compounds were undertaken. Benzene and petroleum ether (b.p. 40–60°) were dried over sodium. The starting azides (**1a**, **b**) were prepared according to established procedures. Trimethyl phosphite was



SCHEME I

purified by treatment with sodium followed by fractional distillation. Tris(dialkylamino)phosphines (**3b, c**)[14] were freshly distilled before use. The IR spectra were recorded with a Perkin-Elmer spectrophotometer 157 G. The ^{1}H-NMR spectra were run in $CDCl_3$ on a Varian spectrometer at 90 MHz using TMS as an internal reference. The ^{31}P-NMR spectra were taken in $CDCl_3$ (vs. H_3PO_4 as external standard) on Varian CET 20,32 MHz spectrometer. The mass spectra were performed at 70 ev on MS-50 Kratos (A.E.I.) spectrometer.

General Procedure

A solution of phthalimidobenzoic acid azides (**1a, b**) (0.01 mol) in dry benzene (10 ml), was added dropwise to a solution of phosphite or phosphine reagents (**3a–c**) in 10 ml of the same solvent at room temperature. The yellow color which appeared during the course of the reaction faded rapidly and N_2 was evolved. The solution was then stirred for 5 hours at room temperature. The precipitated material was filtered off and crystallized to give the iminophosphoranes **4a–f**. Yields, physical and analytical data of the products are given in Table I and Table II.

Action of hydrochloric acid on **4d**: A mixture of the iminophosphorane **4d** (0.34 g, 0.001 mole) and dilute HCl (7 ml, 5%) was refluxed for 3 h. The reaction mixture was cooled, neutralized with sodium bicarbonate and then extracted with ether. After distilling off the ether, the solid residue was crystallized from ethyl alcohol to give *m*-phthalimidobenzoylamine (**7**) (75% yield), m.p., mixed m.p. with authentic sample (240–242°C) and comparative IR spectra.[15]

Action of sodium hydroxide on **4d**: A mixture of **4d** (0.34 g, 0.001 mole) and ethanolic sodium hydroxide (7 ml, 5%) was refluxed for 1 h. After cooling, the reaction mixture was neutralized with hydrochloric acid and extracted with ether. The solvent was distilled off, and the residue was crystallized from ethyl alcohol to give **7**, m.p., mixed m.p. (240–241°C).[15]

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