Synthesis and Reactions of some acyl azides bearing Phosphorus substituents

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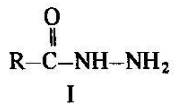
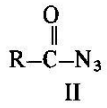
(Received 18th January 1982)

Summary: P-(Diphenylphosphino) benzoyl azide (IIa) and diphenylphosphinoacetyl azide (IIb) are prepared by the action of $NaNO_2$ and HCl on the corresponding acid hydrazides (I). The azides (II) are subjected to both base and acid-catalyzed decompositions. II reacts with hydrazine hydrate to give the precursor acid hydrazides(I). The reaction of (II) with benzylamine affords the corresponding amides (III). When (II) is allowed to react with anhydrous $AlCl_3$ in benzene, toluene or anisole, the corresponding anilides (IV) are obtained. The structures of the products are discussed in the light of their chemical and spectroscopic properties.

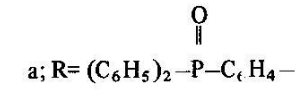
P-(Diphenylphosphino) benzoic hydrazide[1] (I_a) and diphenylphosphino-acetic acid hydrazide[2] (I_b) were recently prepared by the action of hydrazine hydrate on the corresponding esters. In this investigation, we report the conversion of these hydrazides into the corresponding azides with a study of the resulting phosphorus containing acyl azides.

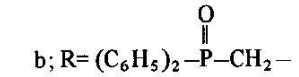


I



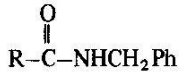
II



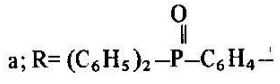


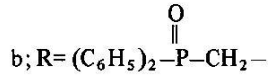
The hydrazide-azide route reported[3,4] for the conversion of acid hydrazides into the corresponding acyl azides (treatment with $NaNO_2$ & HCl) is applied to the above hydrazides (I), whereby the corresponding azides (II) are obtained. The structure of (II) is based upon: (i) analytical data, (ii) the IR spectra of these compounds show an absorption band at 2150 cm^{-1} characteristic[5] of the azido group, as well as, a $\nu_{C=O}$ at 1700 cm^{-1}, and (iii) the reactions carried out on them.

The azides (II) were subjected to both base and acid-catalyzed decompositions. Azides (II) react with hydrazine hydrate to give hydrazides (I), whose formation is confirmed by direct comparison (m.p. and m.m.p experiments). When decomposition of the azides (II) is effected with benzylamine, the corresponding N-benzylamides (III) are obtained.

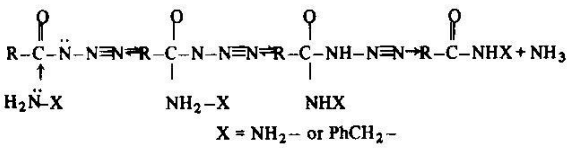


III





The IR spectra of these products show ν_{NH} at 3250 3300 cm^{-1}, as well as an amide $\nu_{C=O}$ at 1660 cm^{-1}. Furthermore, the electronic spectra of these compounds show similarity (Table 1). The formation of (I) and (III) may be represented by the following scheme:



X = NH_2– or $PhCH_2$–

Under Friedel-Crafts conditions, azides (II) react with benzene, toluene or anisole with the formation of the corresponding anilides (IV).

IV

a; R= $(C_6H_5)_2$–P(=O)–C_6H_4– , Ar = C_6H_5–

b; R= $(C_6H_5)_2$–P(=O)–C_6H_4– , Ar = $C_6H_4CH_3$(p-)

c; R= $(C_6H_5)_2$–P(=O)–C_6H_4– , Ar = $C_6H_4OCH_3$(p-)

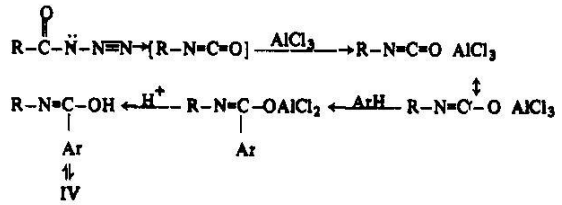
d; R= $(C_6H_5)_2$–P(=O)–CH_2– , Ar = C_6H_5–

e; R= $(C_6H_5)_2$–P(=O)–CH_2– , Ar = $C_6H_4CH_3$(p-)

f; R= $(C_6H_5)_2$–P(=O)–CH_2– , Ar = $C_6H_4OCH_3$(p-)

The structure of these products is inferred from: (i) Analytical data, (ii) The IR spectra of these products show ν_{NH} at 3200 cm^{-1}, as well as a $\nu_{C=O}$ at 1650 cm^{-1}, (iii) Similarity of the electronic spectra of these products (Table 1), and (iv) the reported[6] conversion of benzazide to the corresponding anilides under similar conditions.

We believe that the conversion of the azides (II) into the corresponding anilides (IV) might involve the intermediate formation of the isocyanate, [R–N=C=O], and the reaction may be represented by the following scheme:



Experimental

Melting points reported are uncorrected. IR spectra were recorded on a Unicam SP-1200 using KBr-wafer technique. Electronic spectra were measured on a Unicam SP-8000 spectrophotometer using ethyl alcohol solutions. *P*-(Diphenylphosphino) benzoic acid hydrazid[1] and diphenylphosphino-acetic acid hydrazide[2] were prepared according to the known procedures.

P-(Diphenylphosphino) benzoyl azide (IIa) *and diphenylphosphinoacetyl azide* (IIb).

To a suspension of the hydrazide (I_a) or (I_b) (2.0 g) in HCl (1 N, 100 ml), cooled in an ice-bath at 5°C, a cold sodium nitrite solution was added dropwise with stirring. After complete addition, the reaction mixture was left at room temperature for 1 hr. The product obtained was filtered off, washed thoroughly with water. II_a was obtained as a brown oil which could not be solidified; yield 85% (Found: C, 65.87; H, 3.99; N, 12.35 $C_{19}H_{14}N_3O_2P$ requires: C, 66.15; H, 4.04; N, 12.10); ν_{-N_3} 2150 cm^{-1}, $\nu_{C=O}$ 1700 cm^{-1}. II_b was recrystallized from pet.ether (60-80°) in colourless crystals, m.p. 85-86°C (dec.); yield 80% (Found: C, 58.65; H, 4.11; N, 14.45; $C_{14}H_{12}N_3O_2P$ requires : C, 58.94; H, 4.21; N, 14.77); ν_{-N_3} 2100 cm^{-1}, $\nu_{C=O}$ 1700 cm^{-1}.

Reaction of (II) *with hydrazine hydrate*

To a solution of the azide (II) (0.1 mole) in 200-ml dry benzene, hydrazine hydrate (0.3 mole) was added. The reaction mixture was stirred at room temperature for 1 hr. after which excess benzene was removed by distillation under reduced pressure. The product obtained was recrystallized from ethanol in colourless crystals ; yield 75%. The product was shown in each case by m.m.p to be the acid hydrazide (I).

Reaction of (II) *with benzylamine*

The reaction was carried out as described above. The reaction was completed as usual, and the product obtained (III) was recrystallized from the suitable solvent (cf. Table 1).

Table 1. *Physical data of the amides* (III) *and anilides* (IV).

Compound	M.P. °C	Formula	Analysis % Calc. (Found) C	H	N	UV Spectra λmax n.m	log ε
III_a	229-31(a)	$C_{26}H_{22}NO_2P$	75.9 (75.8)	5.4 (5.4)	3.41 (3.32)	265 273	3.75 3.54
III_b	208-10(a)	$C_{21}H_{20}NO_2P$	72.2 (72.1)	5.7 (5.5)	4.01 (3.89)	260 273	2.90 2.84
IV_a	224-26(b)	$C_{25}H_{20}NO_2P$	75.6 (75.8)	5.0 (4.9)	3.53 (3.67)	277	4.50
IV_b	240-42(b)	$C_{26}H_{22}NO_2P$	75.9 (75.7)	5.4 (5.1)	3.41 (3.29)	277	4.48
IV_c	229-30(b)	$C_{26}H_{22}NO_3P$	73.1 (73.3)	5.2 (5.3)	3.28 (3.17)	287	4.47
IV_d	217-18(b)	$C_{20}H_{18}NO_2P$	71.6 (71.4)	5.4 (5.5)	4.18 (4.37)	265 272	3.35 3.19
IV_e	204-5 (b)	$C_{21}H_{20}NO_2P$	72.2 (72.4)	5.7 (5.8)	4.01 (4.18)	265 272	3.34 3.18
IV_f	192-94(b)	$C_{21}H_{20}NO_3P$	69.0 (69.5)	5.5 (5.3)	3.83 (3.95)	265 272	3.30 3.24

(a) Crystallized from ethanol.
(b) Crystallized from benzene.
Yields of the products 70-85%.

Reaction of (II) *with anhydrous* $AlCl_3$ *in benzene, toluene or anisole*

To a stirred mixture of anhydrous $AlCl_3$ (0.3 mole) in dry benzene, toluene or anisole (100 ml), a solution of the azide (II, 0.1 mole) in the same dry hydrocarbon (100 ml) was added dropwise. After complete addition, the reaction mixture was stirred at room temperature for additional 3 hrs. The complex was decomposed with ice-cooled 15% hydrochloric acid, and then the mixture steam distilled to remove the excess hydrocarbon. The solid obtained was filtered off, washed thoroughly with water and finally recrystallized from the suitable solvent (cf. Table 1).

References

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