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The title reaction affords to the adducts **3** which upon alkaline treatment give compounds **5**, while by thermolysis give **6** and **7**. Hydrochloride salts of **3** in refluxing xylene afford to chlorohydrazones **10** as the major products. A mechanism is proposed for thermal decomposition of **3**.

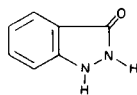
*J. Heterocyclic Chem.*, **19**, 641 (1982).

We are interested in the reactions of phosphonium ylides having hydrogen atoms attached to the ylide carbon (1). In this connection we allowed benzylidenetriphenylphosphoranes **1a,b** to react with benzenediazonium-2-carboxylate **2** (2) taking into account that the expected betaines **3** could easily decompose to give "inter alia" the benzoxadiazepinone derivatives **4**.

From the reaction mixture of **1a,b** and **2** the phosphonium betaines **3a,b** were isolated in high yields. The structures of **3a,b** were supported by elemental analysis, ir, nmr and mass spectra (see Experimental). Upon treatment with aqueous ethanolic 10% sodium hydroxide compounds **3** afforded the *o*-carboxyphenylhydrazones **5**, in quantitative yields. By refluxing in dry pyridine, or in xylene, or by heating above their melting points **3** yielded the 2-aryl-3-indazolinones **6**. In the case of thermolysis of **3b**, 3-(*p*-nitrophenyl)-4-oxycinnoline, **7b**, was also obtained in lower yield (3).

Compounds **4** were not isolated under the adopted experimental conditions.

In every case column chromatography of thermolyzed betaines **3** gave variable amounts of 3-indazolinone, **8**, which was proved to be produced during the chromatographic treatment.



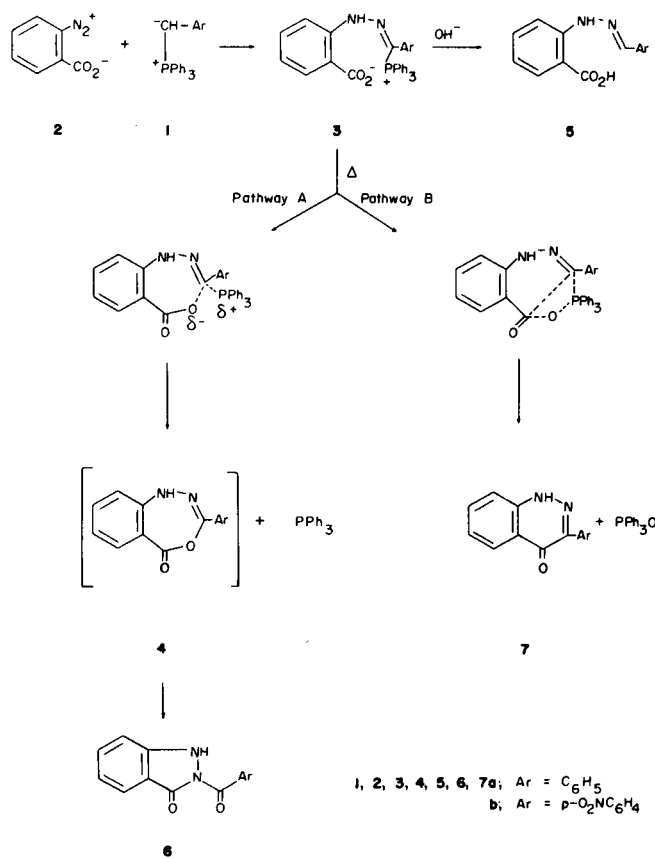
**8**

Structures of compounds **5**, **6** and **8** were confirmed by comparison with authentic samples prepared according to the literature methods (see Experimental).

The thermal fragmentation of **3** should proceed through an initial intramolecular nucleophilic attack of the carboxylate anion either at the carbon atom bonded to phosphorus (Pathway A), or at the phosphorus atom (Pathway B). Pathway A should involve the benzoxadiazepinone derivatives **4**, which in the adopted experimental conditions are not stable enough and isomerize to **6**. Pathway B affords **7** probably *via* a four center transition state, but only in the case of **3b**. A reason why **7a** was not formed, can be attributable to a reduced electrophilicity of

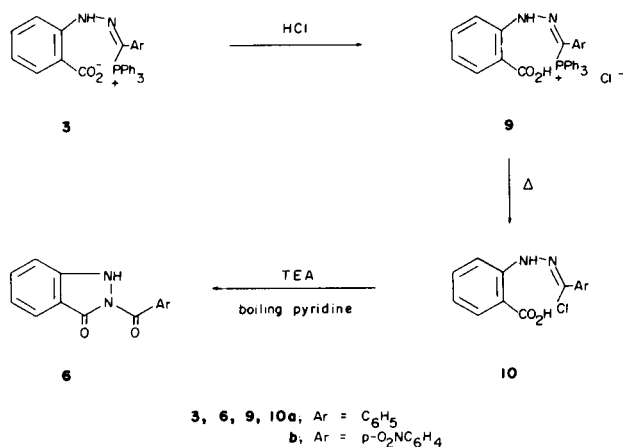
carbon atom of C=N double bond of **3a**. Accordingly triphenylphosphine and triphenylphosphine oxide were found among the reaction products.

Scheme 1



Betaines **3** added hydrogen chloride giving the stable hydrochlorides **9a,b** which in refluxing xylene afforded the *N*-( $\alpha$ -chlorobenzylidene)-*N'*-(*o*-carboxyphenyl)-hydrazines (**10a,b**) as the major products. The structures of compounds **10a,b** were determined both by spectral data and by its conversion into 2-aryl-3-indazolinones, **6**, by treatment with triethylamine in boiling pyridine.

Scheme 2



## EXPERIMENTAL

Melting points were determined with a Kofler apparatus and are uncorrected. The nmr spectra (solvent deuteriochloroform, unless otherwise stated) were recorded with a Variat A-60 spectrometer with TMS as the internal standard. Ir spectra (potassium bromide) were recorded with a Perkin-Elmer 137 spectrometer. Mass spectra were obtained with an AIE MS -9 instrument. The tlc was carried out on silica gel Merck F<sub>254</sub> plates. Chromatography was performed with silica gel Merck (0.05-0.2 mm).

Solvents were purified and dried according to the literature methods.

## Starting Materials.

Ylides **1a,b** were not isolated, but prepared directly in solution according to the Corey procedure (4) from 0.028 mole of the corresponding phosphonium chlorides with a solution of sodium methyl-sulfinil carbanion prepared in its turn under nitrogen from 0.028 mole of sodium hydride and 20 ml of dimethylsulphoxide. Ylides **1a,b** were also prepared by using phenyllithium as a base and dry ether as solvent.

Compound **2** was prepared by the procedure reported (5).

General Procedure to Obtain Adducts **3a,b**.

A solution of **1** obtained as reported above, was added with stirring at room temperature of 0.014 mole of **2** in small portions. After continual stirring for 30 minutes, the solvent was distilled under reduced pressure at room temperature and the residual brown oil was poured into cold 5% hydrochloric acid. The resulting solid gave the adducts **3** upon treatment with 100 ml of saturated aqueous sodium bicarbonate.

When the reactions between **1a,b** and **2** were carried out by using phenyllithium as a base and dry ether as a solvent the yields of **3a,b** were lower.

Adduct **3a**.

This compound was obtained as pale yellow crystals (3.5 g, 60%), mp 172°; ir (potassium bromide): 3285 (NH), 1625 (C=N), 1596 and 1320 (CO<sup>-</sup>) cm<sup>-1</sup>; nmr (DMSO): δ 6.8-8.7 (m, aromatic H, NH); ms: m/e 278 (Ph<sub>3</sub>PO), 262 (Ph<sub>3</sub>P), 105 (PhCO).

Anal. Calcd. for C<sub>32</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>P: C, 76.8; H, 5.0; N, 5.6. Found: C, 76.4; H, 5.2; N, 5.7.

Adduct **3b**.

This compound was obtained as yellow crystals (6.0 g, 78%) mp 172-173°; ir (potassium bromide): 3300 (NH), 1620 (C=N), 1596 (CO<sup>-</sup>), 1520 (assym NO<sub>2</sub>), 1345 (sym NO<sub>2</sub>) and 1326 (CO<sup>-</sup>) cm<sup>-1</sup>; nmr (DMSO): δ 7.1-8.9 (m, aromatic H, NH); ms: m/e 278 (Ph<sub>3</sub>PO), 262 (Ph<sub>3</sub>P), 150 (O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO).

Anal. Calcd. for C<sub>32</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>P: C, 70.4; H, 4.4; N, 7.7. Found: C, 70.5;

H, 4.5; N, 7.7.

Hydrochloride Salt Formation of **3a,b**.

Upon treatment of **3a,b** with concentrated hydrochloride acid at room temperature with stirring quantitative amounts of **9a,b** were recollected. The salt **9a** was obtained as pale yellow powder, mp 201-203°; the salt **9b** was obtained as colorless powder, mp 187-190°.

Alkaline Treatment of **3a,b**.

A solution of **3a,b** (2 mmoles) in ethanol (5 ml) containing 10% sodium hydroxide (10 ml) was stirred at room temperature for 1 hour and then poured into hydrochloric acid. The resulting precipitate was filtered and washed repeatedly with water. Crystallization from ethanol-water (2:1) gave benzaldehyde-2-carboxyphenylhydrazone **5a** (0.43 g, 90%), mp 228° (lit (6), mp 227-228°). Crystallization from ethanol gave 4-nitrobenzaldehyde-2-carboxyphenylhydrazone **5b** (0.54 g, 95%), mp 280° (lit (7), mp 283°).

Hydrazones **5a,b** were also isolated in fair yields by column chromatography of the crude solid obtained when the reaction mixtures of **1a,b** with **2** were poured into water instead of diluted hydrochloride acid.

Thermal Fragmentation of **3a,b**.

## a) By Heating Above Their Melting Points.

Four mmoles of dry **3a,b** were stratified at the bottom of a glass vessel and kept for 2 minutes in a thermostat heated at 180°. Column chromatography of the thermolized crude product yielded compounds **6a,b** as the major products, together with variable amounts of triphenylphosphine oxide and triphenylphosphine, stilbene derivatives (8) and 3-indazolinone (9). Crystallization from light petroleum gave 2-benzoyl-3-indazolinone **6a** (0.2 g, 20%), mp 170-172°; ir (potassium bromide): 1680 (CO) cm<sup>-1</sup>; nmr: δ 4.8 br (1H, s, NH); 7.1-8.0 (9H, m, aromatic H); ms: m/e 238 (M), 105 (PhCO).

Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 70.5; H, 4.2; N, 11.7. Found: C, 70.4; H, 4.4; N, 11.4.

Crystallization from benzene-ethyl acetate (1:1) gave 2-(4-nitrobenzoyl)-3-indazolinone **6b** (0.3 g; 30%), mp 228-230°; ir (potassium bromide): 1676 (CO), 1510 (assym NO<sub>2</sub>) and 1344 (sym NO<sub>2</sub>) cm<sup>-1</sup>; nmr: δ 7.1-8.2 (m, aromatic H), the NH signal was very broad and was not observed; ms: m/e 283 (M), 150 (O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO).

Anal. Calcd. for C<sub>14</sub>H<sub>9</sub>N<sub>3</sub>O<sub>4</sub>: C, 59.3; H, 3.2; N, 14.8. Found: C, 59.1; H, 3.5; N, 14.7.

Compounds **6a,b** were confirmed by comparison with authentic samples prepared by refluxing equimolar amounts of *o*-hydrazinobenzoic acid hydrochloride and benzoyl chloride in anhydrous pyridine for 4 hours.

## b) By Refluxing in Pyridine or Xylene.

Dry **3a,b** (0.4 mole) was refluxed in pyridine or xylene for 30 minutes. Column chromatography (eluents: light petroleum, benzene, ethyl acetate, methanol) of the crude products resulting from distillation of the solvent *in vacuo* gave the same products **6a,b** obtained from the thermolysis of **3a,b** above their melting points.

3-(*p*-Nitrophenyl)-4-oxycinnoline (**7b**).

From thermolized **3b**, compound **7b** was also isolated in small amount, mp 328-330°; ir (potassium bromide): 1672 (CO), 1630 (C=N), 1506 (assym NO<sub>2</sub>) and 1337 (sym NO<sub>2</sub>) cm<sup>-1</sup>; ms: m/e 267 (M), 237 (M-NO), 119.

Anal. Calcd. for C<sub>14</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>: C, 62.9; H, 3.4; N, 15.7. Found: C, 62.4; H, 3.6; N, 15.5.

Thermal Fragmentation of **9a,b**.

Four mmoles of **9a,b** were refluxed in xylene for 30 minutes. On cooling the resulting yellow solid was filtered. In the case of **9a** crystallization from methanol gave *N*-( $\alpha$ -chlorobenzilidene)-*N'*-(*o*-carboxyphenyl)hydrazine, **10a** (0.74 g, 69%), mp 194-196°; ir (potassium bromide): 2870 br (OH), 1675 (CO) and 1650 (C=N) cm<sup>-1</sup>; nmr: δ 7.2-8.6 (10H, m, aromatic H, NH); 11.6 (1H, s, COOH); ms: m/e 274 (M), 238 (M-HCl, 6a),

105 (PhCO).

*Anal.* Calcd. for  $C_{14}H_{11}ClN_2O_2$ : C, 61.3; H, 4.0; N, 10.2. Found: C, 61.1; H, 4.2; N, 10.1.

In the case of **9b** crystallization from acetic acid gave *N*-[ $\alpha$ -chloro-(*p*-nitrobenzylidene)]-*N'*-(*o*-carboxyphenyl)hydrazine, **10b** (0.8 g, 64%), mp 214-217°; ir (potassium bromide): 2890 br (OH), 1680 (CO), 1654 (C=N), 1520 (assym  $NO_2$ ) and 1336 (sym  $NO_2$ )  $cm^{-1}$ ; nmr:  $\delta$  7.2-8.6 (9H, m, aromatic H, NH); 11.2 (1H, s, COOH); ms: *m/e* 319 (M), 283 (M-HCl, 6b), 150 ( $O_2NC_6H_4CO$ ).

*Anal.* Calcd. for  $C_{14}H_{10}ClN_2O_4$ : C, 52.6; H, 3.1; N, 13.1. Found: C, 52.3; H, 3.2; N, 13.0.

Treatment of **10a,b** With TEA.

A solution of **10a,b** (4 mmoles) with TEA (16 mmoles) in dry pyridine was refluxed for 8 hours. Removal of the solvent by distillation under reduced pressure gave a residue which was poured into water and extracted with chloroform. The organic layer was dried and evaporated. Chromatography with elution of benzene-ethyl acetate (1:1) of the resulting solid gave compounds **6a,b** which were confirmed by comparison with an authentic sample.

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- (2) For the reactions between ylides and diazonium salts: A. W. Johnson, "Ylid Chemistry", Academic Press, New York, N.Y., 1966, p 109.
- (3) It is worth mentioning that no acyl-4-oxycinnolines were isolated from a similar reaction with acylmethylenetriphenylphosphorane (T. Kawashima and N. Inamoto, *Bull. Chem. Soc. Japan*, **45**, 3504 (1972).
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- (6) E. Fisher and R. Blochmann, *Ber.*, **35**, 2315 (1902).
- (7) F. D. Chattaway and G. H. Clemo, *J. Chem. Soc.*, 3041 (1923).
- (8) Stilbene derivatives clearly derive from the well known Wittig reaction.
- (9) 3-Indazolinone was formed during the chromatographic treatment as it was verified by tlc analyses.