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# Reaction of 2,4-Dinitrophenylhydrazones of Triphenyl(2-aroylethyl)phosphonium Bromides with Aqueous Alkali and Some Transformations of the Betaines Formed

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**Abstract**—Triphenyl(2-*p*-toluoylethyl)- and triphenyl(2-*p*-bromobenzoylethyl)phosphonium bromide 2,4-dinitrophenylhydrazones were established to form a bipolar compounds with a negatively charged nitrogen atom and a positively charged phosphonium atom, under the action of aqueous alkali at 0°C. When refluxed in acetonitrile, the product formed from triphenyl(2-*p*-toluoylethyl)phosphonium bromide undergoes cleavage by a five-membered ring mechanism to give triphenylphosphine and tolyl vinyl ketone 2,4-dinitrophenylhydrazone. The reactions of the above betains with methyl iodide give rise to N-alkylation and cleavage products, but, in addition, iodide analogs of the starting phosphonium salt 2,4-dinitrophenylhydrazones which are probably formed via N→C negative charge transfer, C-methylation, and reaction of the resulting products with *N*-betaines.

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Previously we found that triphenyl(2-aroylethyl) phosphonium salt oximes, unlike their aroylmethyl analogs, do not undergo cyclization under the action of proton acceptors. Attempted heterocyclization of hydrazones and phenylhydrazones of the mentioned salts failed [1, 2].

Proceeding with these studies we turned to reactions of 2,4-dinitrophenylhydrazones (2,4-DNPH) of (2-*p*-toluoylethyl)- and (2-*p*-bromobenzoylethyl) triphenylphosphonium bromides (compounds **Ia** and **Ib**, respectively) with aqueous alkali. It was expected that the presence of strong electronegative substituents in the phenylhydrazone group would make heterocyclization possible.

$$\underset{\underset{\text{N–NH–}C_6H_3(NO_2)_2}{\|}}{\text{Ar–C}}\text{–}CH_2\text{–}CH_2\text{–}\overset{+}{P}(C_6H_5)_3\ Br^- \xrightarrow{\bar{O}H} \underset{\underset{\text{N–}\bar{N}\text{–}C_6H_3(NO_2)_2}{\|}}{\text{Ar–C}}\text{–}CH_2\text{–}CH_2\text{–}\overset{+}{P}(C_6H_5)_3,$$

**Ia, Ib** **IIa, IIb**

**Ia, IIa**: Ar = $CH_3C_6H_4$; **Ib, IIb**: Ar = $BrC_6H_4$.

However, the reactions of salts **Ia** and **Ib** with aqueous alkali gave, instead of heterocycles, bipolar compounds **IIa** and **IIb** having the negative charge on nitrogen and the positive charge on phosphorus.

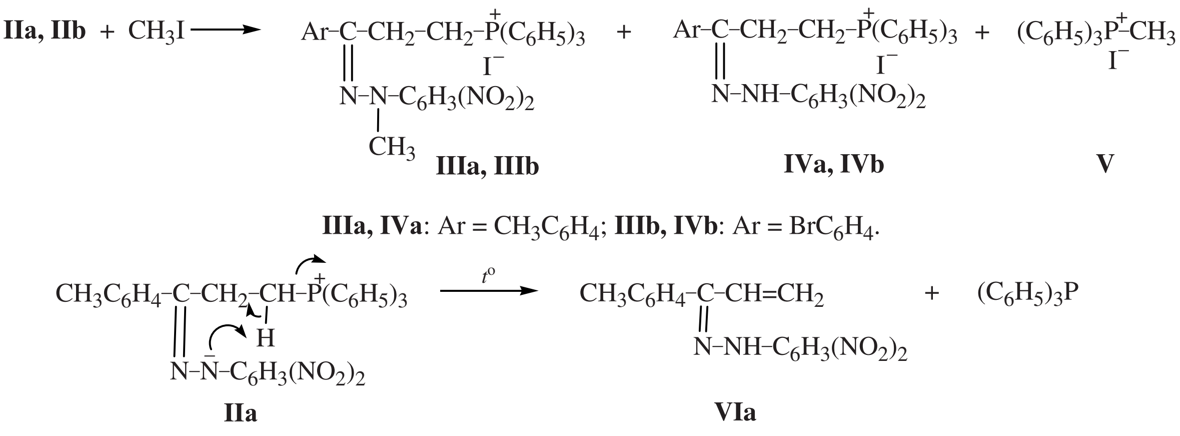
By heating betaines **IIa** and **IIb** with methyl iodide in acetonitrile solution we obtained, along with N-alkylation products **IIIa** and **IIIb**, compounds **IVa** and **IVb,** which are analogs of the starting salts, as well as methyltriphenylphosphonium iodide (**V**).

Heating compound **IIa** in acetonitrile in the absence of methyl iodide resulted in cleavage products, viz. triphenylphosphine and tolyl vinyl ketone 2,4-dinitrophenylhydrazone, probably formed by a five-membered ring mechanism (Scheme 1).

Compounds **IVa** and **IVb** are hardly formed in no other way that that involving N→C negative charge transfer, C-methylation, and reaction of the resulting products with *N*-betaines **IIa** and **IIb** (Scheme 2).

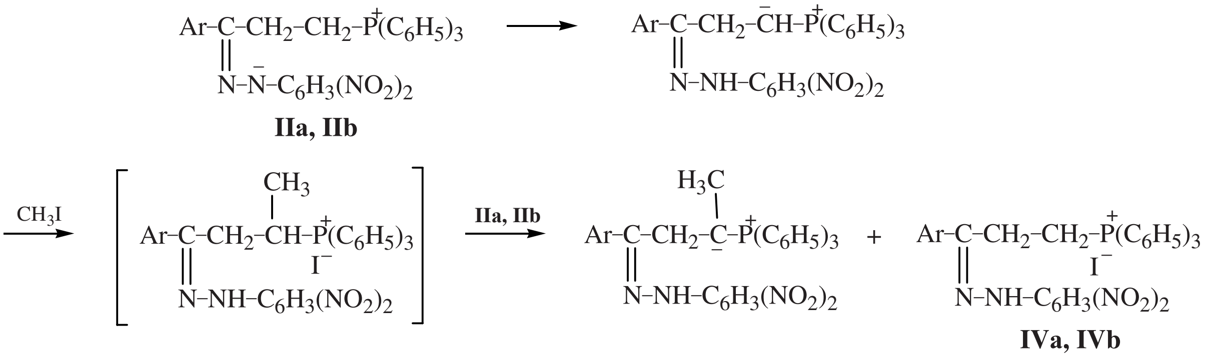
The proposed scheme is consistent with the data of Bestmann and Schulz [3, 4] on the formation of

**Scheme 1.**

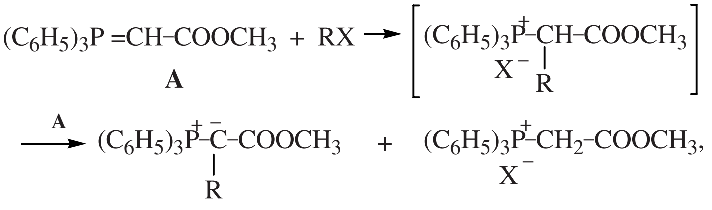


**IIIa, IVa**: Ar = $CH_3C_6H_4$; **IIIb, IVb**: Ar = $BrC_6H_4$.

**Scheme 2.**



**Scheme 3.**



R = alkyl, allyl, benzyl.

alkylated ylides in reactiona of ylides **A** with alkyl, allyl, and benzyl halides (Scheme 3).

## EXPERIMENTAL

The $^1H$ and $^{31}P$ NMR spectra were registered on a Varian MERCURY-300 instrument (300 MHz) against internal TMS.

**Triphenyl(2-*p*-toluoylethyl)phosphonium bromide 2,4-dinitrophenylhydrazone (Ia).** To an alcohol solution of 1.98 g of 2,4-dinitrophenylhydrazine we added 0.54 ml of 93% $H_2SO_4$ and 4.89 g of triphenyl (2-*p*-toluoylethyl)phosphonium bromide. The mixture was refluxed on a water bath for 30 h, and the precipitate that formed was filtered off, washed with alcohol, and dried in a vacuum. Yield 4.81 g (72%), mp 225–226°C. $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 2.40 s (3H, $CH_3$), 3.20 br. m (2H, $C\mathit{H}_2CH_2P^+$), 4.02 br.m (2H, $CH_2C\mathit{H}_2P^+$), 7.20 d (2H, $C_6H_4$, *J* 8.6 Hz), 7.50 d (2H, $C_6H_4$, *J* 8.6 Hz), 7.75–8.00 br. m (15H, $3C_6H_5$), 8.10 d (1H, 2,4-DNPH *o*-H, *J* 9.6 Hz), 8.40 d. d (1H, 2,4-DNPH *m*-H, *J* 9.6 and 2.5 Hz), 8.96 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz), 11.15 s (1H, NH). $^{31}P$ NMR spectrum, δ, ppm: 29.97. Found, %: C 61.0; H 4.52; Br 12.0; N 8.27; P 4.72. $C_{34}H_{30}BrN_4O_4P$. Calculated, %: C 60.99; H 4.48; Br 11.96; N 8.37; P 4.63.

**(2-*p*-Bromobenzoylethyl)triphenylphosphonium bromide 2,4-dinitrophenylhydrazone (Ib)** was prepared similarly to compound **Ia** from 1.98 g of 2,4-dinitrophenylhydrazine, 0.54 ml of 93% $\mathrm{H_2SO_4}$ and 5.54 g of (2-*p*-bromobenzoylethyl)triphenylphosphonium bromide. Yield 5.51 g (75%), mp 254–255°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.29 br. m (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2P^+}$), 3.89 br. m (2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{P^+}$), 7.58 d (2H, $\mathrm{C_6H_4}$, *J* 8.8 Hz), 7.62 d (2H, $\mathrm{C_6H_4}$, *J* 8.8 Hz), 7.75–7.97 m (15H, $\mathrm{3C_6H_5}$), 8.06 d (1H, 2,4-DNPH *o*-H, *J* 9.6 Hz), 8.45 d. d (1H, 2,4-DNPH *m*-H, *J* 9.6 and 2.5 Hz), 8.92 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz), 11.06 s (1H, NH). $^{31}$P NMR spectrum, δ, ppm: 29.71. Found, %: C 54.10; H 3.57; Br 21.97; N 7.75; P 4.01. $\mathrm{C_{33}H_{27}Br_2N_4O_4P}$. Calculated, %: C 53.95; H 3.68; Br 21.80; N 7.63; P 4.22.

**Reactions of compounds Ia and Ib with aqueous potassium hydroxide.** To a saturated alcohol solution of 0.67 g of compound **Ia** we added dropwise 1 ml of 1 N aqueous KOH under stirring in the cold. The precipitate that formed was filtered off, washed with water to pH 7, and dried under a vacuum to obtain 0.58 g (98.6%) of compound **IIa**, mp 165–166°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.34 s (3H, $\mathrm{CH_3}$), 3.05 br.m (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2P^+}$), 3.99 br.m (2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{P^+}$), 7.06 d (2H, $\mathrm{C_6H_4}$, *J* 8.6 Hz), 7.44 d (2H, $\mathrm{C_6H_4}$, *J* 8.6 Hz), 7.55 br. d (2H, 2,4-DNPH *o*- and *m*-H), 8.52 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz). $^{31}$P NMR spectrum, δ, ppm: 29.79. Found, %: C 69.27; H 5.12; N 10.12; P 5.37. $\mathrm{C_{34}H_{29}N_4O_4P}$. Calculated, %: C 69.39; H 4.93; N 9.52; P 5.27.

Compound **IIb** was prepared in a similar way from 0.73 g of compound **Ib** and 1 ml of 1N aqueous KOH. Yield 0.68 g (89%), mp 171–172°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.05 br. m (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2P^+}$), 4.00 br. m (2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{P^+}$), 7.38 d (2H, $\mathrm{C_6H_4}$, *J* 8.8 Hz), 7.45 d (2H, $\mathrm{C_6H_4}$, *J* 8.8 Hz), 7.58 br. d (2H, 2,4-DNPH *o*- and *m*-H), 7.70–7.88 m (15H, $\mathrm{3C_6H_5}$), 8.50 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz). $^{31}$P NMR spectrum, δ, ppm: 29.75. Found, %: C 60.81; H 4.09; Br 12.10; N 8.71; P 4.37. $\mathrm{C_{33}H_{26}BrN_4O_4P}$. Calculated, %: C 60.64; H 3.98; Br 12.25; N 8.58; P 4.75.

**Reactions of compounds IIa and IIb with methyl iodide.** To a saturated acetonitrile solution of 0.3 g of compound **IIa** we added 1 ml of methyl iodide. The mixture was refluxed for 5 h. The precipitate that formed was filtered off, washed with acetonitrile, and dried under a vacuum to obtain 0.07 g (19.6%) of compound **IVa**, mp 244–245°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.40 s (3H, $\mathrm{CH_3}$), 3.20 br. m (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2P^+}$), 4.02 br. m (2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{P^+}$), 7.20 d (2H, $\mathrm{C_6H_4}$, *J* 8.6 Hz), 7.50 d (2H, $\mathrm{C_6H_4}$, *J* 8.6 Hz), 7.70–8.00 br.m (15H, $\mathrm{3C_6H_5}$), 8.10 d (1H, 2,4-DNPH *o*-H, *J* 9.6 Hz), 8.40 d.d (1H, 2,4-DNPH *m*-H, *J* 9.6 and 2.5 Hz), 8.96 s (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz), 11.15 s (1H, NH). The $^{31}$P NMR spectrum, δ, ppm: 29.87. Found, %: C 57.11; H 4.19; I 17.85; N 7.98; P 4.21. $\mathrm{C_{34}H_{30}I \cdot N_4O_4P}$. Calculated, %: C 56.98; H 4.25; I 17.74; N 7.82; P 4.33.

The acetonitrile filtrate was diluted with ether. The precipitate that formed was filtered off and dried under a vacuum to obtain 0.21 g of a mixture of salts **IIIa** and **V** in yields of 0.17 g (48.0%) and 0.04 g (20%), respectively (by $^1$H and $^{31}$P NMR data). Compound **IIIa.** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.40 s (3H, $\mathrm{CH_3}$), 3.15 s (3H, N–$\mathrm{CH_3}$), 3.29 br.m (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2P^+}$), 3.65 br.m (2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{P^+}$), 7.25 d (2H, $\mathrm{C_6H_4}$, *J* 8.6 Hz), 7.44 d (1H, 2,4-DNPH *o*-H, *J* 9.6 Hz), 7.57 d (2H, $\mathrm{C_6H_4}$, *J* 8.6 Hz), 7.65-7.95 br.m (15H, $\mathrm{3C_6H_5}$), 8.32 d.d (1H, 2,4-DNPH *m*-H, *J* 9.6 and 2.5 Hz), 8.45 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz). $^{31}$P NMR spectrum, δ, ppm: 30.70.

Compound **IVb** was prepared similarly from 0.46 g of compound **IIb** and 1 ml of methyl iodide. Yield 0.08 g (16%), mp 254–255°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.29 br. m (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2P^+}$), 3.89 br. m (2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{P^+}$), 7.57 d (2H, $\mathrm{C_6H_4}$, *J* 8.8 Hz), 7.62 d (2H, $\mathrm{C_6H_4}$, *J* 8.8 Hz), 7.75–7.98 m (15H, $\mathrm{3C_6H_5}$), 8.06 d (1H, 2,4-DNPH *o*-H, *J* 9.6 Hz), 8.45 d. d (1H, 2,4-DNPH *m*-H, *J* 9.6 and 2.5 Hz), 8.92 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz), 11.06 s (1H, NH). $^{31}$P NMR spectrum, δ, ppm: 29.62. Found, %: C 50.32; H 3.85; Br 10.88; I 16.95; N 7.59; P 4.18. $\mathrm{C_{33}H_{27}BrIN_4O_4P}$. Calculated, %: C 50.70; H 3.46; Br 10.24; I 16.26; N 7.17; P 3.97.

From the acetonitrile filtrate we obtained 0.26 g of a mixture of salts **IIIb** and **V** in yields of 0.13 g (23,0%) and 0.13 g (46%), respectively (by $^1$H and $^{31}$P NMR data). Compound **IIIb.** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.16 s (3H, N-$\mathrm{CH_3}$), 3.35 br. m (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2P^+}$), 3.67 br.m (2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{P^+}$), 7.46 d (1H, 2,4-DNPH *o*-H, *J* 9.6 Hz), 7.70–7.88 br. m (19H, $\mathrm{C_6H_4}$, $\mathrm{3C_6H_5}$), 8.34 d.d (1H, 2,4-DNPH *m*-H, *J* 9.6 and 2.5 Hz), 8.45 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz). $^{31}$P NMR spectrum, δ, ppm: 30.85.

***p*-Tolyl vinyl ketone 2,4-dinitrophenylhydrazone (VIa).** An acetonitrile solution of 0.2 g of compound **IIa** was refluxed for 5 h. The precipitate that formed was filtered off, washed with acetonitrile, and dried under a vacuum to obtain 0.08 g (80.0%) of compound **VIa**, mp 220–221°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.42 s (3H, $CH_3$), 5.84 d. d (1H, =$CH_2$, *J* 9.0 and 4.6 Hz), 6.19 d. d (1H, =$CH_2$, *J* 6.2 and 4.6 Hz), 6.79 d. d (1H, CH=, *J* 9.6 and 6.1 Hz), 7.22 d (2H, $C_6H_4$, *J* 8.0 Hz), 7.65 d (2H, $C_6H_4$, *J* 8.0 Hz), 8.11 d (1H, 2,4-DNPH *o*-H, *J* 9.6 Hz), 8.35 d.d (1H, 2,4-DNPH *m*-H, *J* 9.6 and 2.5 Hz), 8.98 d (1H, 2,4-DNPH *m*-H, *J* 2.5 Hz), 11.54 s (1H, NH).

Triphenylphosphine (0.67 g, 75%) obtained from the acetonitrile filtrate was identified as iodomethylate. Its mixed sample with an authentic sample gave no melting point depression.

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