A New Method of Preparing Hydrazonyl Halides

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The triphenylphosphine – carbon tetrahalide (Br, Cl) system transforms *N*′-benzoyl-*N*-arylhydrazines (**1**), *N*,*N*-dimethyl-, and *N*-methyl-*N*-phenyl-*N*′-benzoylhydrazines (**3**) into the corresponding hydrazonyl halides **2** and **4**.

Tribromomethyltriphenylphosphonium bromide (**7**), formed by reacting triphenylphosphine with carbon tetrabromide, is capable of transforming *N*′-benzoyl-*N*-phenylhydrazine (**1***a*) into the corresponding hydrazonyl bromide (**2***b*) in the presence of triphenylphosphine.

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Le couple triphénylphosphine – tétrahalogénure de carbone (Br, Cl) transforme les *N*′-benzoyl *N*-arylhydrazines (**1**) ainsi que les *N*,*N*-diméthyl- et *N*-phényl *N*′-benzoylhydrazines (**3**) en halogénures (**2** et **4**) d'hydrazonyle correspondants.

Le bromure de tribromométhyltriphénylphosphonium (**7**) obtenu par réaction de la triphénylphosphine avec le tétrabromure de carbone peut transformer, en présence de triphénylphosphine, la *N*′-benzoyl *N*-phénylhydrazine (**1***a*) en bromure d'hydrazonyle correspondant (**2***b*).

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The two most important methods for the preparation of aromatic hydrazonyl halides (α-halogenobenzaldehyde arylhydrazones, **2**) are the action of phosphorus pentachloride on *N*′-benzoyl-*N*-arylhydrazines (**1**) and the halogenation of benzaldehyde arylhydrazones. The applicability of these methods is limited; the first can only be applied to hydrazonyl chlorides and the latter is generally accompanied by halogenation in the *N*-aryl part of the hydrazone (*cf.* ref. 1).

The recent work by Appel *et al.* (2) in transforming secondary amides (RCONHR′) into the corresponding imidoyl halides (RCXNR′) by use of the triphenylphosphine – carbon tetrahalide system ($Ph_3P–CX_4$) has prompted us to examine the applicability of this method also to the hydrazonyl system.

Applying the $Ph_3P–CX_4$ system to **1** affords **2** (see eq. 1) in 40–65% yield.

$$[1]\quad \underset{\mathbf{1}}{\text{PhCONHNHAr}} \xrightarrow{\text{Ph}_3\text{P–CX}_4} \underset{\mathbf{2}}{\text{PhCX=NNHAr}}$$

a Ar = Ph; X = Cl
b Ar = Ph; X = Br
c Ar = $2\text{-NO}_2C_6H_4$; X = Cl
d Ar = $3\text{-NO}_2C_6H_4$; X = Cl
e Ar = $4\text{-NO}_2C_6H_4$; X = Cl

Typically, CCl_4 (1 equiv.) was added to a stirred suspension of **1***a* (1 equiv.) and Ph_3P (1.25 equiv.) in dry CH_3CN. After 6 h the precipitate was filtered off and recrystallized to give **2***a* in 58% yield. The previously unknown α-bromobenzaldehyde phenylhydrazone (**2***b*, 33%) was prepared in a similar manner; the yield of **2** was increased slightly when the reaction time was extended to 20 h. The method is not limited to aromatic hydrazonyl halides but may also be applied to the preparation of aliphatic hydrazonyl halides of type **4** (see eq. 2).

$$[2]\quad \underset{\mathbf{3}}{\text{PhCONHN(CH}_3\text{)R}} \xrightarrow{\text{Ph}_3\text{P–CX}_4} \underset{\mathbf{4}}{\text{PhCX=NN(CH}_3\text{)R}}$$

a R = Ph; X = Cl
b R = CH_3; X = Cl
c R = CH_3; X = Br

Thus reacting the $Ph_3P–CBr_4$ system with *N*,*N*-dimethyl-*N*′-benzoylhydrazine (**3***b*) affords after 2 h α-bromobenzaldehyde dimethylhydrazone (**4***c*; 39%), which has previously been prepared (but not isolated) by *in situ* bromination of the corresponding hydrazone ($PhCHNN(CH_3)_2$) (3). A mass spectrum taken of the reaction mixture confirmed the presence of bromoform and triphenylphosphine oxide.

The active reagents, transforming **1** and **3** into **2** and **4**, respectively, may be the charge-transfer complex (**5**), and the dihalogeno triphenylphosphorane (**6**), as shown by Appel *et al.* (2) in the transformation of amides into imidoyl halides.

$$\underset{\mathbf{5}}{\overset{+\delta}{\mathrm{Ph_3P}} \ldots \mathrm{X} \ldots \overset{-\delta}{\mathrm{CX_3}}} \qquad\qquad \underset{\mathbf{6}}{\mathrm{Ph_3PX_2}}$$

The sparingly soluble tribromomethyltriphenylphosphonium bromide (**7**) precipitated out instantly (88%) in dry CH_3CN by mixing CBr_4 (1 equiv.) with Ph_3P (1 equiv.) in the absence of **1** or **3** (see eq. 3); with 2 equiv. of Ph_3P the yield of **7** was reduced to 69%. This shows that under these experimental conditions only a certain part of the Ph_3P–CBr_4 system is converted to **6** (X = Br) and dibromomethylene triphenylphosphorane (**8**) (4). Compound **7** itself was capable of transforming **1***a* into the corresponding hydrazonyl bromide **2***b* (42% after recrystallization) only in the presence of Ph_3P (see eq. 4).

$$[3] \qquad \mathrm{CBr_4 + Ph_3P \rightarrow \underset{\mathbf{7}}{(Ph_3PCBr_3)Br}}$$

$$[4] \qquad \underset{\mathbf{1}a}{\mathrm{PhCONHNHPh}} \xrightarrow{\mathrm{(Ph_3PCBr_3)Br\ +\ Ph_3P}} \underset{\mathbf{2}b}{\mathrm{PhCBr{=}NNHPh}}$$

The formation of **2***b* may then be explained in terms of the action of **6** (X = Br) on **1***a*, where **6** (X = Br) is formed according to reaction 5, which has been proposed by Appel *et al.* (2) in accordance with the observations by Ramirez *et al.* (4) and Rabinowitz and Marcus (5) on the reaction of Ph_3P with CBr_4 and CCl_4, respectively; (see ref. 6 for a general review).

$$[5] \qquad \underset{\mathbf{7}}{\mathrm{(Ph_3PCBr_3)Br}} + \mathrm{Ph_3P} \rightarrow \underset{\mathbf{6}}{\mathrm{Ph_3PBr_2}} + \underset{\mathbf{8}}{\mathrm{Ph_3P{=}CBr_2}}$$

This is further substantiated by the observation that dibromomethyltriphenylphosphonium bromide (**9**) is formed in 52% yield (after recrystallization), by refluxing compound **7** (1 equiv.) with Ph_3P (1 equiv.) in wet CH_3CN (see eq. 6).

$$[6] \qquad \underset{\mathbf{7}}{\mathrm{(Ph_3PCBr_3)Br}} + \mathrm{Ph_3P} \xrightarrow[\mathrm{CH_3CN,\ H_2O}]{} \underset{\mathbf{9}}{\mathrm{(Ph_3PCHBr_2)Br}}$$

The formation of **9** may be explained as an addition of HBr to the ylide **8** (**8** + HBr → **9**), where **8** is formed according to reaction 5. Similarly the reduction of bromomethyltriphenylphosphonium bromide to methyltriphenylphosphonium bromide by the action of Ph_3P has been reported (7).

Experimental

All melting points were taken on a Reichert melting point microscope. The aromatic hydrazonyl halides were normally recrystallized from acetonitrile.

α-Halogenobenzaldehyde Arylhydrazones

Carbon tetrachloride (1.95 ml, 20.0 mmol) was added to a stirred suspension of compound **1***a* (4.24 g, 20.0 mmol) and Ph_3P (6.55 g, 25.0 mmol) in CH_3CN (40 ml, dried by passage through an alumina column and introduced directly from the columm into the reaction flask). After 6 h the solution was cooled, crystallization was initiated by scratching, and the product filtered off. Recrystallization gave compound **2***a* in 58% yield, m.p. 128–131° (lit. (8) 129.5–130.5°). Extension of the reaction time to 20 h increased the yield of **2***a* to 64%.

Compound **1***c* (reaction time 20 h) gave **2***c* (59%), m.p. 162–164°.

Anal. Calcd. for $C_{13}H_9ClN_3O_2$: C, 56.69; H, 3.66; N, 15.24. Found: C, 56.85; H, 3.97; N, 15.48.

Compound **1***d* (reaction time 20 h) gave **2***d* (60%), m.p. 162–165°.

Anal. Found: C, 56.40; H, 3.86; N, 15.45.

Compound **1***e* (reaction time 20 h) gave **2***e* (55%), m.p. 189–192° (acetonitrile–acetone, 1:1) (lit. (9) 189–191°).

Carbon tetrabromide (6.03 g, 20.0 mmol), compound **1***a* (20.0 mmol), and Ph_3P (25.0 mmol) were mixed. After 6 h the clear solution was evaporated to dryness and extracted four times with ether, the ether was removed *in vacuo* and the residue recrystallized from ethanol to give compound **2***b* (33%), m.p. 109–111°. Extension of the reaction time to 20 h increased the yield of **2***b* to 40%.

Anal. Calcd. for $C_{13}H_{11}BrN_2$: C, 56.22; H, 4.03; N, 10.24. Found: C, 56.74; H, 4.03; N, 10.18.

α-Halogenobenzaldehyde N-Methyl-N-phenyl- and N,N-Dimethylhydrazones

Carbon tetrachloride (1.95 ml, 20.0 mmol) was added to a stirred suspension of compound **3***a* (4.52 g, 20.0 mmol) and Ph_3P (6.55 g, 25.0 mmol) in CH_3CN, (40 ml; dried as described above) with the exclusion of moisture. After 2 h, the solution was evaporated. The solid material was extracted four times with ether and the ether was removed *in vacuo*; this was followed by distillation to give **4***a* (77%), b.p. 138–143°/0.05 mm; δ 3.39 (CH_3, in $CDCl_3$) (lit. (10) δ 3.40).

Carbon tetrachloride (20.0 mmol), compound **3***b* (11) (3.28 g, 20.0 mmol), and Ph_3P (25.0 mmol) (reaction time 2 h) gave compound **4***b* (58%), b.p. 58–60°/0.05 mm; δ 2.84 (CH_3) ($CDCl_3$).

Anal. Calcd. for $C_9H_{11}ClN_2$: C, 59.18; H, 6.07; N, 15.34. Found: C, 58.78; H, 6.18, N, 15.34.

Carbon tetrabromide (20.0 mmol), compound **3***b* (20.0 mmol), and Ph_3P (25.0 mmol) (reaction time 2 h) gave compound **4***c* (39%), b.p. 82–85°/0.5 mm; δ 2.80 (CH_3) ($CDCl_3$). A mass spectrum of the reaction mixture showed both the presence of bromoform (*m/e* 254/256) and triphenylphosphine oxide (*m/e* 278).

Anal. Calcd. for $C_9H_{11}BrN_2$: C, 47.59; H, 4.88; N, 12.34. Found: C, 48.02; H, 5.23; N, 12.38.

The Reaction of Triphenylphosphine with Carbon Tetrabromide

Carbon tetrabromide (6.03 g, 20.0 mmol) was added to a stirred suspension of Ph_3P (5.25 g, 20.0 mmol) in

CH_3CN (25 ml; dried as described above). After 15 min the solution was filtered and washed carefully with ether to give compound **7** (88% yield), m.p. 230–232° (lit. (4) 246–247°).

Anal. Calcd. for $C_{19}H_{15}Br_4P$: C, 38.42; H, 2.55. Found: C, 38.57; H, 3.00.

Compound **7** crystallized from ethanol as a solvate, m.p. 242–244°.

Anal. Calcd. for $C_{19}H_{15}Br_4P{\cdot}C_2H_5OH$: C, 39.41; H, 3.31; Br, 49.95. Found: C, 39.20; H, 2.90; Br, 51.27.

Recrystallization of the solvated form from nitromethane gave m.p. 236–238°.

Anal. Found: C, 38.28; H, 2.95.

Carbon tetrabromide (20.0 mmol) was added to a stirred suspension of Ph_3P (10.50 g, 40.0 mmol) in CH_3CN (25 ml; dried as described above). This gave after 15 min **7** (69%), m.p. 228–230°.

Anal. Found: C, 38.91; H, 2.95.

The Reaction of N′-Benzoyl-N-phenylhydrazine with Tribromomethyltriphenylphosphonium Bromide

Compound **1***a* (2.12 g, 10.0 mmol), crude **7** (5.94 g, 10.0 mmol), and Ph_3P (2.62 g, 10.0 mmol) were stirred together under dry conditions at room temperature for 3 days in CH_3CN (20 ml; dried as described above). The mixture was evaporated to dryness, the residue extracted four times with ether, and the ether removed *in vacuo*; this was followed by recrystallization from ethanol to give compound **2***b* (42%), m.p. 108–110°; i.r. identical to that of **2***b* prepared above.

Compound **2***b* was not isolated nor detected (t.l.c.) by repeating the foregoing experiment in the absence of Ph_3P.

The Reaction of Tribromomethyltriphenylphosphonium Bromide with Triphenylphosphine

Crude **7** (2.97 g, 5.0 mmol) and Ph_3P (1.31 g, 5.0 mmol) were refluxed together for 30 min in CH_3CN (10 ml). The red solution was allowed to cool to room temperature and then filtered. The solid obtained (2.32 g) was recrystallized to give compound **9** (52%). Compound **9** crystallized from acetonitrile as a solvate, m.p. 144–147°.

Anal. Calcd. for $C_{19}H_{16}Br_3P{\cdot}CH_3CN$: C, 45.35; H, 3.44; N, 2.52; Br (ionic), 14.37. Found: C, 45.18; H, 3.76; N, 2.96; Br (ionic), 14.37.

Heating compound **9** at 170° overnight gave m.p. 235–238° (lit. (12) 235°).

Anal. Calcd. for $C_{19}H_{16}Br_3P$: C, 44.30; H, 3.13. Found: C, 44.30; H, 3.19.

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