The Reaction of a Phosphorus Ylide with Aroyl Cyanides

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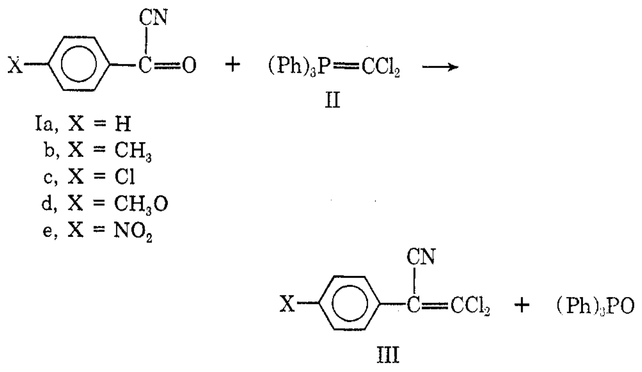
The reaction of aroyl cyanides with dichloromethylenetriphenylphosphorane, prepared *in situ* from carbon tetrachloride and triphenylphosphine, provides a convenient synthesis of 2-aryl-3,3-dichloroacrylonitriles. Aroyl cyanides studied in this reaction were benzoyl, 4-methylbenzoyl, 4-chlorobenzoyl, 4-methoxybenzoyl, and 4-nitrobenzoyl cyanide. Only 4-nitrobenzoyl cyanide failed to yield the desired product.

The Wittig reaction has provided an exceptionally versatile technique for the preparation of olefinic compounds. The literature bears proof of this with numerous examples of reactions of phosphorus ylides with aldehydes, ketones, acid chlorides, esters, anhydrides, and nitriles.[1] Except for our previous report,[2] there are no examples of the reaction phosphorus ylides with acyl cyanides. In particular, the reaction of dichloromethylenetriphenylphosphorane (II) with aroyl cyanides (I) offers a unique synthesis of 2-aryl-3,3-dichloroacrylonitriles (III). Previous methods of synthesis of β-halogenated acrylonitriles have not been particularly suitable for the preparation of α-alkyl or aryl derivatives, as most of these procedures start with the corresponding acrylamide or acrolein derivative, which are equally unavailable.[3]



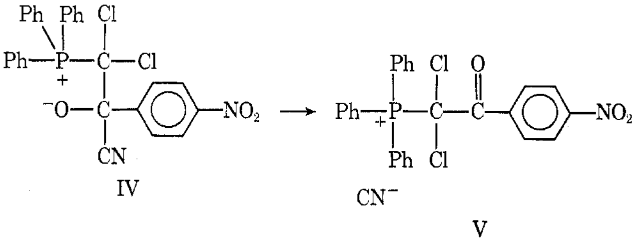
Dichloromethylenetriphenylphosphorane (II), synthesized by the reaction of carbon tetrachloride with triphenylphosphine[4] or by the decomposition of chloroform by potassium *tert*-butoxide in the presence of triphenylphosphine,[5] has been shown to react with representative aldehydes and ketones.[6] Except for a recent communication by Raulet and Levas,[7] the reactions of II have not been studied beyond the initial reports. In these most recent findings it was shown that II reacted preferentially with the ketone carbonyl of ethyl pyruvate to give ethyl 3,3-dichloro-2-methylacrylate.[7]

Results and Discussion

The 2-arylacrylonitriles (III) were obtained by mixing the aroyl cyanide (0.50 mol) and triphenylphosphine (1.0 mol) in a large excess of dry carbon tetrachloride under an inert atmosphere and then heating the mixture to reflux for 2–4 hr or stirring at room temperature for 48–72 hr. Work-up of the reaction mixture was initiated by the addition of ligroin to precipitate most of the triphenylphosphine oxide. The filtrate was concentrated and the residue was purified by distillation or recrystallized from a suitable solvent. Products IIIa, b, and d were obtained in 60–70% yield. Compound IIIc was obtained in only 20% yield; however, higher yields are undoubtedly possible.

Although most of the reaction mixtures darkened considerably as the reaction proceeded, the mixture of 4-nitrobenzoyl cyanide (Ie), carbon tetrachloride, and triphenylphosphine became black immediately at room temperature. Reaction conditions were varied in an attempt to obtain a product from this reaction; however, only tars resulted. It was apparent from several tests that a highly colored reaction was occurring between triphenylphosphine and Ie, even in the absence of carbon tetrachloride. In an attempt to avoid this side reaction a solution of triphenylphosphine and carbon tetrachloride was heated to 60° for 2 hr before Ie was added. This procedure also yielded only tarry by-products.

The failure of this reaction to yield the desired product is puzzling, since II has been shown to react smoothly with 4-nitrobenzaldehyde to give an 83% yield of 1,1-dichloro-2-(4-nitrophenyl)ethylene.[6] Two possible side reactions which may account for the absence of the desired product are a reduction of the nitro group by II[8] or by the loss of cyanide ion from the intermediate betaine to give an acylated phosphonium salt. This latter reaction path is not completely unexpected, since acyl chlorides are known to react with phosphorus ylides to form phosphonium salts similar to V.[9]



Several of the prominent bonds of the infrared spectra of the compounds prepared in this study are given in Table I, as this information does not appear in the literature. The most notable feature of the infrared spectra of the aroyl cyanides is the unexpected shift of the nitrile stretching frequency to the 2227–2218-cm^{-1} region typical of α,β-unsaturated alkyl or aryl nitriles. The intensity of the nitrile absorption was quite strong,

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TABLE I
INFRARED SPECTRA OF AROYL CYANIDES AND 3,3-DICHLORO-2-ARYLACRYLONITRILES

Compd	Frequency, cm^{-1}			
	ν_{CN}	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{=CCl}$
Ia	2220	1680		
Ib	2225	1665		
Ic	2227	1680		
Id	2218	1675		
Ie	2225	1683		
IIIa	2227		1564	926
IIIb	2222		1609	926
IIIc	2220		1592	925
IIId	2217		1603	936

unlike most nitriles bearing oxygen on the α carbon.[10] The carbonyl absorption appeared as a strong band in the 1680-cm^{-1} region characteristic of an α,β-unsaturated ketone and 30–100 cm^{-1} below the region typical of aryl esters and aroyl halides.[10] The nitrile and geminal dichlorovinyl stretching frequency of the acrylonitriles III showed only slight influence from the para substituent, shifting some ±6 cm^{-1} from the region 2222 and 932 cm^{-1}, respectively. By contrast, the olefinic stretching band appeared as a strong band between 1564 and 1609 cm^{-1}.

The reaction of ylide II with aliphatic acyl cyanides under the conditions used in this study gives very low yields of the desired coupled products. The appearance of resinous products and the odor of hydrogen cyanide tend to indicate that aldol type reactions are occurring owing to acidic conditions of the reaction media. Aldol condensations in the Wittig reaction of aliphatic aldehydes have been reported previously owing to the presence of strong base.[11] We are attempting to avoid this side reaction by adding reagents to maintain essentially neutral conditions during the course of the reaction.

Experimental Section

All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colo. A Beckman IR-8 was used to obtain the infrared spectra, which were calibrated at 2849.9 and 1601.0 cm^{-1} by a polystyrene film. All ylide reactions were carried out under a dry nitrogen atmosphere, until an infrared spectrum of an aliquot showed no carbonyl absorption.

Aroyl Cyanides.—The following aroyl cyanides were prepared by known literature procedures: benzoyl cyanide, bp 209–210° (lit.[12] bp 208–209°); 4-methylbenzoyl cyanide, mp 49–49.5° (lit.[13] mp 50–52°); 4-methoxybenzoyl cyanide, mp 58–60° (lit.[13] mp 58–59°); 4-chlorobenzoyl cyanide, mp 40–41.5° (lit.[14] mp 41–42.5°); 4-nitrobenzoyl cyanide, mp 115–117° (lit.[15] mp 116°). Of the various procedures reported for the preparation of aroyl cyanides, that given by Asinger, *et al.*,[13] affords the highest yields and is recommended. The addition of an inert solvent, such as *o*-xylene or *o*-dichlorobenzene, offers the advantage of moderating the reaction and permitted easy separation of the product from the cuprous salts. Subsequent removal of the solvent by distillation or recrystallization presented no difficulty.

3,3-Dichloro-2-phenylacrylonitrile (IIIa).—Into a three-necked flask fitted with condenser, drying tube, thermometer, and nitrogen inlet was added 500 ml of dry carbon tetrachloride, 202 g (0.770 mol) of triphenylphosphine, and 50.5 g (0.385 mol) of Ia. The reaction mixture was stirred (magnetic stirrer) at room temperature for 65 hr and then 600 ml of ligroin (bp 63–75°) was added. A yellow precipitate of triphenylphosphine oxide was removed and the filtrate was concentrated under reduced pressure. Additional precipitate was removed and then the liquid residue was quickly distilled at 0.5 mm. The distillate was carefully refractionated, yielding 50.3 g (67%) of IIIa, bp 92–94° (0.4 mm). The previously reported[2] boiling point should read bp 101–104° (1.0 mm). The ir spectrum of IIIa was identical with that of the known compound.[2]

3,3-Dichloro-2-(4-methylphenyl)acrylonitrile (IIIb).—In a manner similar to that described above, 45 ml of dry CCl_4, 18.4 g (0.070 mol) of triphenylphosphine, and 5.0 g (0.0345 mol) of Ib were mixed and heated to reflux (60°) for 2.5 hr. After cooling to room temperature, 90 ml of ligroin was added and the precipitate of triphenylphosphine oxide was removed. The precipitate was washed with 100 ml of ether and the filtrate was concentrated under reduced pressure. The residue was added to the liquid residue obtained from the concentration of the CCl_4/ligroin filtrate and distilled through a short-path distillation apparatus, giving 5.0 g (68%) of a slightly yellow product, bp 150° (1.25 mm). A second distillation gave colorless IIIb, bp 98° (0.6 mm), n^{25}_D 1.5895.

Anal. Calcd for $C_{10}H_7Cl_2N$: C, 56.63; H, 3.33; N, 6.60; Cl, 33.44. Found: 56.86; H, 3.33; N, 6.51; Cl, 33.79.

3,3-Dichloro-2-(4-chlorophenyl)acrylonitrile (IIIc).—Dry CCl_4 (36 ml), 15.8 g (0.060 mol) of triphenylphosphine, and 5.0 g (0.030 mol) of Ic were mixed, giving an immediate yellow-colored solution. After stirring overnight at room temperature the mixture was heated to reflux for 4 hr, where the solution darkened rapidly. Ligroin (55 ml) was added on cooling to room temperature and a gummy solid was filtered off. The solid was washed with an additional 50 ml of hot ligroin and then the combined filtrates were treated with decolorizing charcoal and concentrated under vacuum. The yellow-orange residue was recrystallized from ligroin, decolorized again from methanol, and then recrystallized twice from anhydrous methanol to give 1.4 g (20%) of colorless crystals of IIIc, mp 84.5–85.0°.

Anal. Calcd for $C_9H_4Cl_3N$: C, 46.49; H, 1.73; Cl, 45.75; N, 6.02. Found: C, 46.56; H, 1.67; Cl, 45.95; N, 5.96.

3,3-Dichloro-2-(4-methoxyphenyl)acrylonitrile (IIId).—In a manner similar to that described for the preparation of IIIc, 32.6 g (0.124 mol) of triphenylphosphine, 10.0 g (0.062 mol) of Id, and 80 ml of CCl_4 gave 8.5 g (60%) of light yellowish-green platelets, mp 105–108°. Repeated recrystallization from methanol and ligroin sharpened the melting point to 107.5–108° but did not remove a light yellowish-green coloration.

Anal. Calcd for $C_{10}H_7Cl_2NO$: C, 52.66; H, 3.09; Cl, 31.09; N, 6.19. Found: C, 52.64; H, 3.00; Cl, 31.43; N, 6.14.

Attempted Preparation of 3,3-Dichloro-2-(4-nitrophenyl)acrylonitrile.—Three attempts were made to condense II with Ie. (1) The reagents were mixed and stirred overnight at room temperature, then warmed briefly. (2) Benzene was added to CCl_4 (2:1 ratio) to dissolve Ie and then triphenylphosphine was added. The dark mixtures was stirred at room temperature for 20 hr and then heated to reflux for 2 hr. (3) The CCl_4 and triphenylphosphine were heated to 60° for 2 hr and then Ie was added and heating was continued for 1 hr.

In each case the resulting black reaction mixture failed to show any typical $Cl_2C=$ absorption in the infrared. Work-up gave black residues from which only triphenylphosphine oxide could be isolated. Similar tarry residues were obtained when nitrobenzene or *p*-nitrobenzoyl chloride was used instead of *p*-nitrobenzoyl cyanide.

Registry No.—Ib, 14271-73-9; Ic, 13014-48-7; Id, 14271-83-1; IIIb, 37447-51-1; IIIc, 37447-52-2; IIId, 37447-53-3; triphenylphosphine, 603-35-0; dichloromethylenetriphenylphosphorane, 6779-08-4.

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