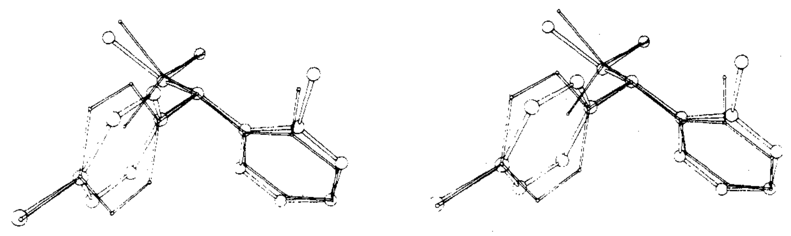

Figure 3. Stereoscopic view comparing I (larger atoms) and II,[2] with least-squares fitting of C1, C4, C7, C10, C13, and C11.[7]

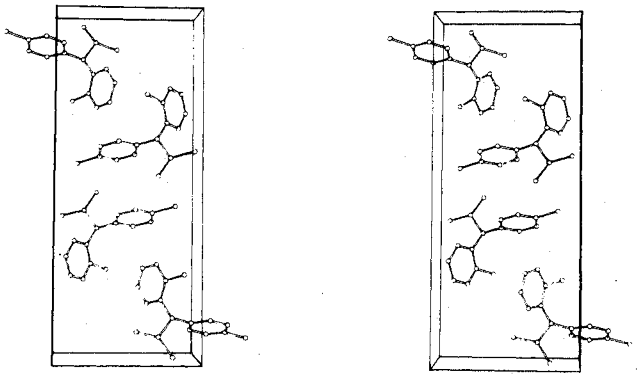

Figure 4. Stereoscopic view of a unit cell, *a* axis projection, *b* axis horizontal, *c* axis vertical.

Table I
Fractional Coordinates and Estimated Standard Deviations

Atom	*x/a*	*y/b*	*z/c*
Cl1	0.5464 (3)	0.1565 (2)	0.4397 (1)
Cl2	−0.0152 (3)	0.6226 (2)	0.2480 (1)
Cl3	−0.0429 (2)	0.6983 (2)	0.4756 (1)
Cl4	−0.0342 (3)	0.9429 (2)	0.4061 (1)
C1	0.2296 (8)	0.5599 (5)	0.3880 (2)
C2	0.4400 (8)	0.5569 (5)	0.4133 (2)
C3	0.5343 (9)	0.4340 (6)	0.4288 (2)
C4	0.4250 (9)	0.3116 (5)	0.4196 (2)
C5	0.2212 (9)	0.3101 (5)	0.3929 (2)
C6	0.1268 (8)	0.4348 (5)	0.3781 (2)
C7	0.2399 (8)	0.7666 (5)	0.3244 (2)
C8	0.4080 (10)	0.8569 (6)	0.3373 (2)
C9	0.5222 (12)	0.9122 (7)	0.2940 (3)
C10	0.4678 (12)	0.8810 (7)	0.2378 (3)
C11	0.3038 (11)	0.7910 (6)	0.2248 (2)
C12	0.1911 (9)	0.7367 (5)	0.2678 (2)
C13	0.1217 (8)	0.6952 (5)	0.3713 (2)
C14	0.1007 (8)	0.7865 (5)	0.4240 (2)
HC2	0.511 (6)	0.645 (4)	0.412 (2)
HC3	0.665 (6)	0.434 (4)	0.452 (2)
HC5	0.145 (6)	0.235 (4)	0.388 (2)
HC6	−0.047 (6)	0.442 (4)	0.366 (2)
HC8	0.438 (6)	0.899 (4)	0.383 (2)
HC9	0.604 (6)	1.005 (4)	0.304 (2)
HC10	0.548 (6)	0.927 (4)	0.205 (2)
HC11	0.286 (6)	0.769 (4)	0.183 (2)
HC13	−0.041 (6)	0.679 (4)	0.358 (2)
HC14	0.229 (6)	0.811 (4)	0.439 (2)

comes in the rotation of the remaining *p*-chlorophenyl ring of each compound: the deviations from the "butterfly" angle are 24, 47, and 33° for I, II, and III, respectively. In I, the 24° rotation decreases repulsion between (a) the C14 hydrogen and the nearby ortho hydrogen on the *p*-chlorophenyl ring, and (b) the chlorine on the *o*-chlorophenyl ring and the other ortho hydrogen on the *p*-chlorophenyl ring. In II and III, a chlorine replaces the hydrogen on C14, and further rotation is required to minimize the energy. Thus, the conformation of the antitumor agent I in this crystal differs somewhat from those of the crystalline insecticides II and III.[2] The slight differences observed may be responsible for the difference in activity, but unfortunately neither activity is as yet well understood.[2,8]

Figure 4 shows the packing diagram for I. The only intermolecular distances less than 3.5 Å are 3.353 (Cl3–Cl5) and 3.434 Å (Cl1–Cl4).

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Registry No.—*o,p′*-DDD, 53-19-0.

Supplementary Material Available. Tables of temperature factors, bond distances and angles involving hydrogens, and torsion angles (3 pages). Ordering information is given on any current masthead page.

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An Improved Synthesis of Dichloromethylenetriphenylphosphorane

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The phosphorus ylide, dichloromethylenetriphenylphosphorane (II), has been shown to be of good synthetic utility in the Wittig method of converting aldehydes,[1-3] ketones,[1,2] keto esters,[3] and acyl cyanides[4,5] to the corresponding 1,1-dichloroethylene derivatives.

Methods previously reported for the preparation of II include (a) the reaction of potassium *tert*-butoxide with chloroform in the presence of triphenylphosphine,[1] (b) the reaction of triphenylphosphine with $PhHgCCl_2X$, where X = Cl or Br,[6] and (c) the reaction of triphenylphosphine with carbon tetrachloride.[2] The last procedure offers several advantages, among which are simplicity and cost of the starting materials. It does have the disadvantage of being rather slow, i.e., several days at 0°. This time may be shortened by heating the reaction mixture to reflux; however, by-prod-

Table I
Conversion of Acyl Cyanides to 2-Substituted 3,3-Dichloroacrylonitriles

	$Cl_2C{=}CRCN$, % yield	
RCOCN, R	CCl_4[a] method	CCl_3Br[b]
Ia, CH_3	61	90
Ib, CH_3CH_2	45[c]	82
Ic, $(CH_3)_2CH$	40[c]	87
Id, $(CH_3)_3C$	48	91
Ie, p-ClC_6H_4	20	43
If, p-$CH_3OC_6H_4$	60	85

[a] The CCl_4, triphenylphosphine procedure is reported in ref 4 and 5. [b] Yield based on pure distilled or recrystallized product. [c] Yield based on VPC analysis of crude distillate.

ucts and lower yields result whenever more sensitive carbonyl components are added.[4,5]

We now wish to report on an improved method for the preparation of II and some reactions of II with acyl and aroyl cyanides. It has been found that the substitution of bromotrichloromethane for carbon tetrachloride allows the Wittig reagent II to be formed much faster and the concurrent reaction with the carbonyl component is significantly improved with higher yields and virtually no by-product formation. Gas chromatographic analysis of the crude reaction mixture does not show any of the bromochloroethylene derivative.

Although this procedure should be applicable toward the conversion of other carbonyl containing compounds to the dichlorovinyl group ($=CCl_2$) we have studied the carbonyl of acyl cyanides so that yields may be directly compared with our previous work.

$$2Ph_3P + Cl_3CBr \rightarrow Ph_3P{=}CCl_2 + Ph_3PBrCl$$

$$RCOCN + Ph_3P{=}CCl_2 \rightarrow Ph_3PO + Cl_2C{=}CRCN$$

In a typical reaction, excess dry bromotrichloromethane was added to 1.0 equiv of triphenylphosphine in sufficient dry benzene to produce a convenient volume. The mixture was stirred under a dry nitrogen atmosphere at 0° for 15–30 min, then 0.5 equiv of the acyl cyanide, Ia–f, was added and the mixture stirred at 0° for 2–4 hr. An immediate shift of the nitrile band as well as appearance of a strong $=CCl_2$ band in the 920–940-cm^{-1} region was observed[7]. After approximately 30 min, large quantities of triphenylphosphine oxide began to precipitate from the reaction mixture. After 1–2 hr, the carbonyl stretching band was almost totally gone. Stirring the mixture for a longer period of time had little effect on the yield. In cases using aliphatic acyl cyanides, the reaction mixture was rapidly warmed and benzene, excess bromotrichloromethane, and liquid products were removed under vacuum. Unlike our previous report,[4] the 2-alkyl-3,3-dichloroacrylonitriles were virtually free of impurities and easily purified by simple distillation to give yields of 82–91% (Table I). With aroyl cyanides, the benzene and excess bromotrichloromethane was stripped from the reaction mixture and crude products extracted with boiling ligroin and the crude products recrystallized from anhydrous methanol to give yields of 43–85%.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. Boiling points and melting points are uncorrected. Infrared spectra were performed on a Beckman IR-8 and calibrated at 1601.0 cm^{-1} with polystyrene film. Commercial triphenylphosphine was used without purification. The bromotrichloromethane and benzene were purified by atmospheric distillation, using only the center cuts.

Acyl Cyanides. The acyl cyanides used in this study were prepared according to procedures reported previously.[4,5]

Reaction of II with Aliphatic Acyl Cyanides. General Procedure. A mixture of triphenylphosphine (0.15 mol) and 80 ml of dry benzene was cooled in an ice bath and then 40 g of bromotrichloromethane was added. The mixture was stirred at 0° for 30 min and then 0.075 mol of the aliphatic acyl cyanide (Ia–d) was added rapidly. After maintaining the reaction at 0° for approximately 3 hr it was heated under vacuum (25–30 mm) to yield benzene, the excess bromotrichloromethane, and crude product. A second distillation of the crude product gave pure 2-alkyl-3,3-dichloroacrylonitriles with physical properties and ir spectra identical with those reported previously.[5]

Reaction of II with Aryl Acyl Cyanides. General Procedure. In a manner similar to that described above, the aryl acyl cyanide (Ie,f) was added rapidly to a mixture of benzene, triphenylphosphine, and bromotrichloromethane at 0°. After 3 hr, the mixture was vacuum stripped to remove the benzene and excess bromotrichloromethane. The solid residue was extracted three times with 100-ml portions of boiling ligroin. The combined extracts were cooled to remove most of the triphenylphosphine oxide. Concentration and cooling the extracts gave a crude product which was recrystallized twice from anhydrous methanol. The pure 2-aryl-3,3-dichloroacrylonitriles displayed physical properties and ir spectra identical with those reported previously.[4]

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Registry No.—Ia, 631-57-2; Ib, 4390-78-7; Ic, 42867-39-0; Id, 42867-40-3; Ie, 13014-48-7; If, 14271-83-1; II, 6779-08-4; triphenylphosphine, 603-35-0; bromotrichloromethane, 75-62-7; 2-methyl-3,3-dichloroacrylonitrile, 31413-58-8; 2-ethyl-3,3-dichloroacrylonitrile, 42791-06-0; 2-isopropyl-3,3-dichloroacrylonitrile, 42867-43-6; 2-*tert*-butyl-3,3-dichloroacrylonitrile, 42867-44-7; 2-(*p*-chlorophenyl)-3,3-dichloroacrylonitrile, 37447-52-2; 2-(*p*-methoxyphenyl)-3,3-dichloroacrylonitrile, 37447-53-3.

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Synthesis of Some New Hindered Biaryls

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Our studies of the effects of chemical structure on molecular orbital energy levels and electron distributions[1-5] and associated electrical properties[6] have concerned themselves primarily with planar aromatic systems. Some such systems are subject to steric effects or nonbonded interactions which can lead to deviations from coplanarity and hence deviations from anticipated behavior. The biphenyl system is one whose susceptibility to these effects is well known.[7] The target structures **1–5** were designed with a view toward providing (1) a high rotational barrier about the biphenyl bond and (2) systems with an electron-rich ring and an electron-poor ring as well as ones with both rings electron poor or rich.