extent into the benzene layer and there carry out the normal Wittig reaction. In support of this viewpoint,

$$\mathrm{Ar(R)CHO} + \mathrm{Ph_3\overset{+}{P}{-}\overset{-}{C}HCN} \xrightarrow[\text{heat}]{\text{benzene}} \mathrm{Ar(R)CH{=}CHCN} + \mathrm{OPPh_3}$$

independent reaction of II with benzaldehyde in hot benzene produced cinnamonitrile in the same yield and stereoisomeric composition of the two-phase reaction using I.[9]

Experimental Section

Melting and boiling points are uncorrected. The former were taken in capillary tubes in a Mel-Temp apparatus. Infrared spectra (in μ) were taken on a Perkin-Elmer Model 221 instrument. Nuclear magnetic resonance spectra (in δ units, parts per million, with TMS as internal reference) were determined on a Varian A-60A spectrometer in CCl_4 unless stated otherwise. Only significant spectral data are given. Microanalyses are by Micro-Tech Laboratories, Skokie, Ill. Aldehydes used were commercial samples purified immediately before use by distillation or recrystallization. Petroleum ether (bp 30–60°) was used throughout the work.

Cyanomethylidenebis(triphenylphosphonium) Dibromide (I).—Triphenylphosphine (Aldrich, 577 g, 2.2 mol) in benzene (1500 ml) was treated dropwise with dibromoacetonitrile[10] (218.6 g, 1.1 mol) at 30° with vigorous stirring. Salt I began to precipitate after 30 min. After 18 hr of further reaction at 45° the benzene was decanted and replaced by an equal volume of petroleum ether. The mixture was stirred 30 min and filtered to give I as a white solid: 673.4 g (93.4%); mp 268–269°; λ (KBr) 4.40 (CN); δ (DMSO) 8.30 s (CH), 7.75 m (Ar H).

Anal. Calcd for $C_{38}H_{31}NBr_2P_2$: C, 63.11; H, 4.28; Br, 22.10. Found: C, 63.14; H, 4.68; Br (Volhard determination by authors), 22.25, 22.46.

Cyanomethylenetriphenylphosphorane (II).—Sodium hydroxide (8 g, 0.2 mol) in water (100 ml) was added dropwise to a solution of I (72.31 g, 0.1 mol) in water (500 ml) at 25° with stirring. The crystalline precipitate of II was collected and recrystallized from benzene–ether: 26.7 g (88.8%); mp 196–197° (lit.[9] mp 186°); λ (KBr) 4.65 (CN); δ ($CDCl_3$) 7.7 m (CH and Ar H).

Anal. Calcd for $C_{20}H_{16}NP$: C, 79.75; H, 5.31. Found: C, 80.08; H, 5.30.

General Procedure for Use of I.—The appropriate aldehyde (75 mmol), salt I (54.2 g, 75 mmol), benzene (125 ml), and aqueous sodium hydroxide (10%, 50 ml) were refluxed (*ca.* 69°) for 18 hr (overnight). The layers were separated and the aqueous phase was extracted with petroleum ether. The extract together with further petroleum ether (100 ml) was added to the benzene layer. Triphenylphosphine oxide precipitated[11] and was separated [quantitative yield, mp and mmp (with authentic material) 155°]. The organic material was dried (Na_2SO_4) and evaporated and the residue distilled to afford the nitrile products. In the case of *p*-nitrocinnamonitrile, addition of the petroleum ether (200 ml) caused it to precipitate also. Separation from the phosphine oxide was achieved with hot toluene from which the nitrile could be recovered after filtration and chilling.

Cyclohexanone was recovered in 90.5% yield when subjected to this procedure. Ylide II with benzaldehyde in benzene (overnight reflux) gave the same results as use of I in the procedure above.

Properties of Nitriles. Cinnamonitrile: 8.2 g; bp 132–134° (12 mm) [lit.[12] bp 134–136° (12 mm)]; δ 7.37 sharp m (Ar H), 7.26 d, 5.80 d (trans HC═CH), 7.05 d, 5.40 d (cis HC═CH).

***p*-Nitrocinnamonitrile:** 10.5 g; mp 200–202° (lit.[13] mp 200°); δ ($CDCl_3$) 8.17 d, 7.52 d (Ar H, AA′BB′, J = 8 Hz), 7.40 d, 5.95 d (trans HC═CH).

***p*-Isopropylcinnamonitrile:** 9.4 g; bp 166–168° (16 mm); δ 7.6–6.8 m (Ar H), 7.20 d, 5.67 d (trans HC═CH), 7.10 d, 5.21 d (cis HC═CH), 2.83 septet (CH, J = 7 Hz), 1.21 d (CH_3CCH_3, J = 7 Hz).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.64. Found: C, 84.19; H, 7.61.

***p*-Methoxycinnamonitrile:** 8.7 g; bp 165–170° (18 mm); mp 64° (lit.[9] mp 63°); δ 7.22 d, 6.75 d (Ar H, AA′BB′, J = 8 Hz), 7.12 d, 5.53 d (trans HC═CH), 3.72 s (OCH_3).

γ-Hexylcinnamylideneacetonitrile: 14 g; bp 214–216° (15 mm); δ 7.4–6.9 m (Ar H), 6.7 m (Ar CH═C), 5.48 m, 5.22 m (HC═CH),[14] 2.2 m, 1.3 m, 0.92 m (aliphatic H's).

Anal. Calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.83. Found: C, 85.00; H, 8.79.

Furfurylideneacetonitrile: 3.4 g; bp 95–97° (11 mm) [lit.[15] bp 70° (6 mm)]; δ 7.8–6.5 series of sharp multiplets (furan ring H's and downfield portions of HC═CH), 5.83 d (upfield portion of trans HC═CH), 5.35 d (upfield portion of cis HC═CH).

2(3)-Nonenenitrile: 7.6 g; bp 98–100° (10 mm) [lit.[16] bp 99–100° (10 mm)]; δ 7.0–6.4 m, 5.5 m, 5.25 m (HC═CH),[14] 3.1 m (═CH_2CN of Δ^3 isomer), 2.5–0.90 m (aliphatic H's). Integration data indicated 18% Δ^3 isomer.

5-Methyl-2(3)-hexenenitrile: 5.4 g; bp 168–170° (750 mm); δ 6.7–6.18 m, 5.84 m, 5.22–5.05 m (HC═CH),[14] 2.97 m (═CH_2CN of Δ^3 isomer), 2.4–0.80 m (aliphatic H's). Integration data indicated 25% Δ^3 isomer.

Anal. Calcd for $C_7H_{11}N$: C, 77.02; H, 10.14. Found: C, 77.06; H, 10.10.

4-Ethyl-3-octenenitrile: 7.4 g; bp 226–228° (752 mm); δ 5.10 t (═CH, J = 7 Hz), 2.97 d (═CCH_2CN, J = 7 Hz), 2.3–0.60 m (aliphatic H's). Integration data indicated only the unconjugated nitrile.

Anal. Calcd for $C_{10}H_{17}N$: C, 79.41; H, 11.31. Found: C, 79.35; H, 11.50.

In the aromatic cases, λ (CN) = 4.50–4.55 μ, whereas in the aliphatic cases λ (CN) = 4.48 μ. Where determined, J_{trans} for HC═CH was 16–17 Hz, whereas J_{cis} was 12–14 Hz.

Registry No.—I, 29127-76-2; II, 29127-77-3; *cis*-cinnamonitrile, 24840-05-9; *trans*-cinnamonitrile, 1885-38-7; *trans*-*p*-nitrocinnamonitrile, 29246-70-6; *cis*-*p*-isopropylcinnamonitrile, 29246-71-7; *trans*-*p*-isopropylcinnamonitrile, 29246-72-8; *trans*-*p*-methoxycinnamonitirle, 14482-11-2; γ-hexylcinnamylideneacetonitrile, 29127-81-9; *cis*-furfurylideneacetonitrile, 6137-73-1; *trans*-furfurylideneacetonitrile, 6125-63-9; 2-nonenenitrile, 29127-83-1; 3-nonenenitrile, 29246-75-1; 5-methyl-2-hexenenitrile, 29127-84-2; 5-methyl-3-hexenenitrile, 29246-76-2; 4-ethyl-3-octenenitrile, 29127-85-3.

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[9] Using II otherwise prepared, G. Schiemenz and H. Englehard, *Chem. Ber.*, **94**, 578 (1961), previously prepared cinnamonitrile in this way.

[10] J. W. Wilt and J. L. Diebold, *Org. Syn.*, **38**, 16 (1958).

[11] In aliphatic cases this precipitation was slower and was completed in several hours at 25°.

[12] "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967–1968, p C-254.

[13] S. Novikov and G. Shvekhgeimer, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2061 (1960).

[14] Stereochemistry was unassigned due to complexity of the spectrum.

[15] A Sugihara, *Yakugaku Zasschi*, **86**, 527 (1966); *Chem. Abstr.*, **65**, 12193c (1966).

[16] K. v. Auwers, T. Meissner, O. Seydel, and H. Wissebach, *Justus Liebigs Ann. Chem.*, **432**, 46 (1923).

Reactions of Hydroxymethylferrocene. III. Ethers: Reaction with Grignard Reagents

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Grignard and Ritz have reported the cleavage of phenyl ethers by alkylmagnesium halides to give a

TABLE I

EXPERIMENTAL RESULTS

$$C_5H_5FeC_5H_4CHROR' + R''MgX \longrightarrow C_5H_5FeC_5H_4CHRR''$$

Product	R	R'	R''	X	$n^{20}D$ or mp, °C		Yield, %
					Found	Lit.	
IIa[a]	H	CH_3	CH_3	Br	1.6017	1.6011[b]	90
IIb	H	CH_3	$CH{=}CH_2$	Cl	1.5983	1.5990[c]	66[d]
IIc	H	CH_3	$CH_2CH{=}CH_2$	Br	1.5939	1.5940[c]	60
IId	H	CH_3	C_6H_5	Br	72–73	73–74[e]	85
IIe	CH_3	CH_3	C_6H_5	Br	1.6277[f]	1.6270[g]	80
IId	H	$CH_2CH{=}CH_2$	C_6H_5	Br	72–73	73–74[e]	57
IId	H	$CH(CH_3)_2$	C_6H_5	Br	73–74	73–74[e]	67

[a] C and H analyses (±0.3) for compounds IIa–IIe were also obtained as part of the characterization. [b] E. L. DeYoung, *J. Org. Chem.*, 26, 1312 (1961). [c] Reference 11. [d] 84% yield without solvent. [e] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, 22, 903 (1957). [f] Measured at 25°. [g] G. L. K. Hoh, W. E. McEwen, and J. Kleinberg, *J. Amer. Chem. Soc.*, 83, 3949 (1961).

variety of low-molecular-weight hydrocarbon products.[1] Several examples of cleavage of allyl ethers by Grignard reagents have been reported.[2-5] Hill has studied the cleavage of vinyl ethers,[6-8] while Mann and Stewart have described cleavage of benzyl ethers by alkyl and arylmagnesium halides.[9]

We now report the cleavage of ethers of hydroxymethylferrocene by Grignard reagents to yield the corresponding substituted alkylferrocene compounds in good yields. Heretofore the cleavage of ethers by Grignard reagents has found preparative use primarily in the dealkylation of protected aromatic hydroxyl groups which could not be cleaved conveniently with hydrogen bromide, hydrogen iodide, or alkali.[10] The reaction presently described appears to have broad use in the synthesis of α-substituted ferrocenylmethyl compounds from ferrocenylmethyl ethers, as well as certain α,α-disubstituted compounds which are not easily accessable otherwise. Generally, alkylferrocenes are prepared by acylation followed by reduction Nesmeyanov has obtained alkylferrocenes in 30–60%. yields by treatment of ferrocenylmethyl quaternary ammonium salts with Grignard reagents.[11] Indications are that Grignard reagents of all types will react with methyl ferrocenylmethyl ether to give the substituted products in 60–90% yields as shown.

$$C_5H_5FeC_5H_4CHROR' + R''MgX \longrightarrow C_5H_5FeC_5H_4CHRR''$$

Ia, $R = H$; $R' = CH_3$ — II a, $R = H$; $R'' = CH_3$

b, $R = CH_3$; $R' = CH_3$ — b, $R = H$; $R'' = CH{=}CH_2$

c, $R = H$; $R'' = CH_2CH{=}CH_2$

d, $R = H$; $R'' = C_6H_5$

e, $R = CH_3$; $R'' = C_6H_5$

Ethylferrocene was prepared in 90% yield by the reaction of methylmagnesium bromide with methoxymethylferrocene. Similarly, allylferrocene, 4-ferrocenyl-1-butene, and benzylferrocene were prepared from methoxymethylferrocene and vinylmagnesium chloride, allylmagnesium bromide, and phenylmagnesium bromide, respectively. In general, the reaction is done by addition of a benzene solution of the alkyl ferrocenylmethyl ether to a solution of the Grignard reagent in benzene. While the reaction of vinylmagnesium chloride with methoxymethylferrocene in benzene gave a 66% yield of allylferrocene (Table I), when the reaction was done without solvent the yield was 84%.

One particularly attractive feature of the method is the fact that pure products are obtained without crystallization, distillation, or chromatography. Another point worth noting is the unusual stability of compounds prepared in this way. The decomposition of ethylferrocene and other short-chain liquid alkylferrocenes is a well-known phenomenon recognized in these laboratories as well as elsewhere.[12,13] However, ethylferrocene prepared by treatment of methylmagnesium bromide with methoxymethylferrocene is stable at room temperature in the presence of light and air for several months. Although the thermodynamic stability is independent of the method of synthesis, factors influencing stability of specific samples may vary considerably. Low-molecular-weight liquid alkylferrocenes prepared by acylation–reduction continue to be unstable after rigorous purification while those prepared by the Grignard method are stable with no purification. Further experiments to explore this point are in progress.

Experimental Section

Melting points are uncorrected and were obtained by use of a Büchi apparatus. The experimental procedure is illustrated for the preparation of ethyl ferrocene, and a summary of experimental results is shown in Table I.

Ethylferrocene (IIa).—A solution of methylmagnesium bromide (4 ml, 3 *M* in ethyl ether, 0.012 mol) was placed in a 25-ml pear-shaped three-neck flask fitted with a nitrogen inlet tube, reflux condenser, and stirrer. The ether was replaced by adding sodium-dried benzene and distilling off the ethyl ether. A solution of methoxymethylferrocene (2.30 g, 0.01 mol in 5 ml of dry benzene) was added dropwise during 0.5 hr to the Grignard reagent at 70°. Mild refluxing occurred. Benzene (5 ml) was added and the mixture was cooled and filtered. The filtrate was washed with water and dried ($MgSO_4$). Solvent was removed under vacuum leaving pure ethylferrocene (1.93 g, 90% yield). In reactions in which phenylmagnesium bromide is used, heating

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[1] V. Grignard and J. Ritz, *Bull. Soc. Chim. Fr.*, **3**, 1181 (1936); *Chem. Abstr.*, **30**, 5952 (1936).

[2] A. Luttringhaus, G. Wagner-v. Saaf, E. Sucker, and G. Borth, *Justus Liebigs Ann. Chem.*, **557**, 46 (1945); *Chem. Abstr.*, **40**, 5418 (1946).

[3] C. M. Hill, L. Haynes, D. E. Simmons, and M. E. Hill, *J. Amer. Chem. Soc.*, **75**, 5408 (1953).

[4] C. M. Hill, D. E. Simmons, and M. E. Hill, *ibid.*, **77**, 3889 (1955).

[5] C. M. Hill, L. Haynes, D. E. Simmons, and M. E. Hill, *ibid.*, **80**, 3623 (1958).

[6] C. M. Hill, R. A. Walker, and M. E. Hill, *ibid.*, **73**, 1663 (1951).

[7] C. M. Hill, G. W. Senter, L. Haynes, and M. E. Hill, *ibid.*, **76**, 4538 (1954).

[8] C. M. Hill, R. Woodberry, D. E. Simmons, M. E. Hill, and L. Haynes, *ibid.*, **80**, 4602 (1958).

[9] F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 4127 (1954).

[10] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, p 1029.

[11] A. N. Nesmeyanor, E. G. Perevalova, and L. S. Shilovtseva, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1982 (1961); *Chem. Abstr.*, **56**, 10185 (1962).

[12] M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 1016 (1957).

[13] A. N. Nesmeyanov and N. A. Vol'kenau, *Dokl. Akad. Nauk SSSR*, **107**, 262 (1956); *Chem. Abstr.*, **50**, 15519 (1956).

the final product under vacuum is necessary to remove biphenyl which is a by-product.

Allyferrocene (IIb).—A solution of vinylmagnesium chloride (0.012 mol in 6 ml of tetrahydrofuran) was added dropwise during 30 min to methoxymethylferrocene (2.3 g, 0.01 mol) at 100–120° under nitrogen with occasional stirring. Heating was continued for 2 hr. The reaction mixture was allowed to cool, taken up in ether, and filtered. The filtrate was washed with water, dried over $MgSO_4$, and filtered. Removal of solvent gave 1.9 g of analytically pure allylferrocene (84%).

Registry No.—Ia, 12153-89-8; Ib, 12512-90-2; I ($R = H$; $R' = CH_2CH{=}CH_2$), 12512-91-3; I [$R = H$; $R' = CH(CH_3)_2$], 12300-26-4.

The Chemistry of Cumulated Double-Bond Compounds. XII. The Reaction of Phosphonium Ylides with Benzoyl Isocyanate

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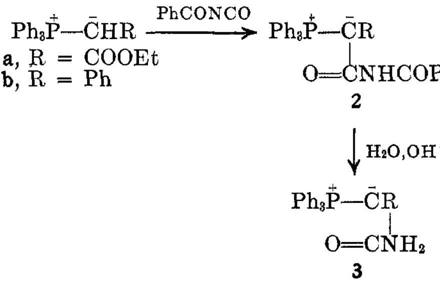
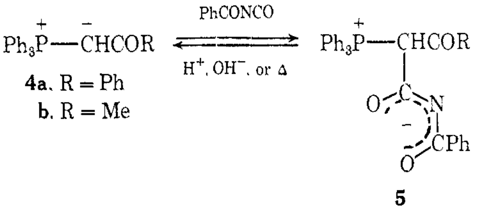
Wittig-type reactions or formation of stable ylides have been observed in the reactions between phosphonium ylides and heterocumulenes,[1–5] but reactions of ylides with acyl isocyanate have not been reported. It is well known that isocyanates having a carbonyl group adjacent to the cumulative double bonds may react as 1,4-dipolar reagents in cycloaddition reactions.[6] In this paper, reactions of phosphonium ylides with benzoyl isocyanate were studied.

The reaction of carbethoxymethylenetriphenylphosphorane (**1a**) with benzoyl isocyanate gave the stable ylide **2a** in good yield.



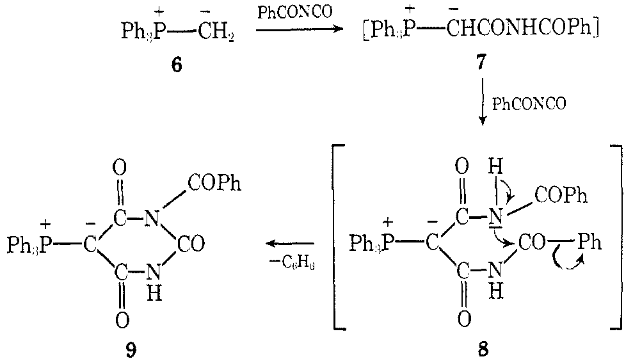
The nmr and ir spectra of the ylide **2a** showed N–H peaks at δ 12.67 ppm and 3200 cm^{-1}, respectively. The ylide **2a** was hydrolyzed easily to the ylide **3a**. Similar reactions were observed for phenylmethylenetriphenylphosphorane (**1b**).

In the reaction of the ylide **4** with an acyl group adjacent to the ylide carbon, the betaine **5** was obtained in high yield. The ir spectrum indicated no peak near 3200 cm^{-1}. The signal of the methine proton was observed at δ 1.68 ppm in the nmr spectrum of the betaine **5a**. The betaine **5** was easily decomposed to the starting ylide **4** and benzoyl isocyanate. Thus, in this reaction, a prototropic shift was not observed.

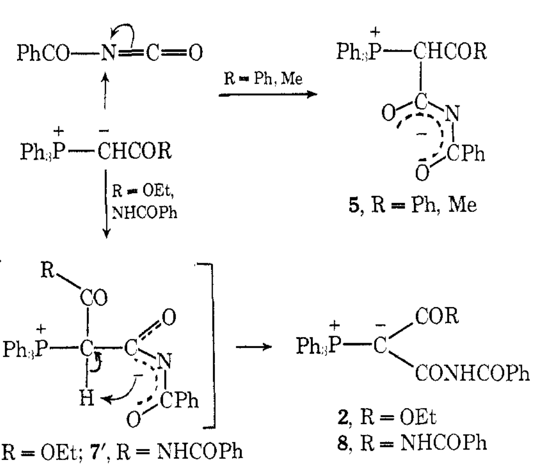


The reaction type for methylenetriphenylphosphorane (**6**) was similar to that of the ylide **1**. Benzoyl isocyanate (2 mol) was added to the ylide **6** with prototropic shifts, and the adduct **8** cyclized immediately to the ylide **9** (Scheme I). From the fact that the adduct **7** was not isolated, it seemed that the addition rate of the adduct **7** was very fast. 2,4,6-Triphenyl-1,3,5-triazine (**10**) was obtained as a by-product in this reaction.

SCHEME I



In conclusion, the reaction between benzoyl isocyanate and an ylide which has a hydrogen atom on the ylide carbon gives a betaine in the initial step. The ease of the prototropic shifts can be correlated with the substituent constants,[7,8] σ_m and σ^+, of the substituent adjacent to the carbonyl group. It is apparent that the acidity of the betaine **1a′** or **7′** is higher than



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(1) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 132.

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