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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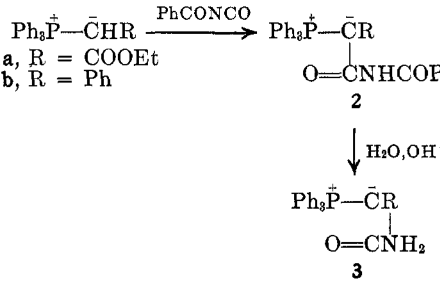
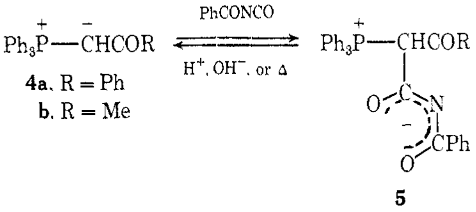
Wittig-type reactions or formation of stable ylides have been observed in the reactions between phosphonium ylides and heterocumulenes,[1–5] but reactions of ylides with acyl isocyanate have not been reported. It is well known that isocyanates having a carbonyl group adjacent to the cumulative double 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.



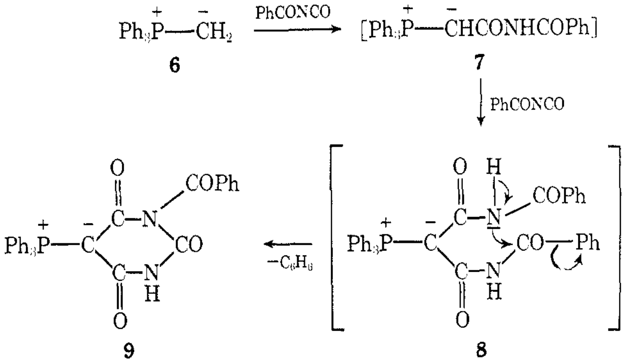
The nmr and ir spectra of the ylide **2a** showed N-H peaks at δ 12.67 ppm and 3200 cm^{-1}, respectively. The ylide **2a** was hydrolyzed easily to the ylide **3a**. Similar reactions were observed for phenylmethylenetriphenylphosphorane (**1b**).

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.

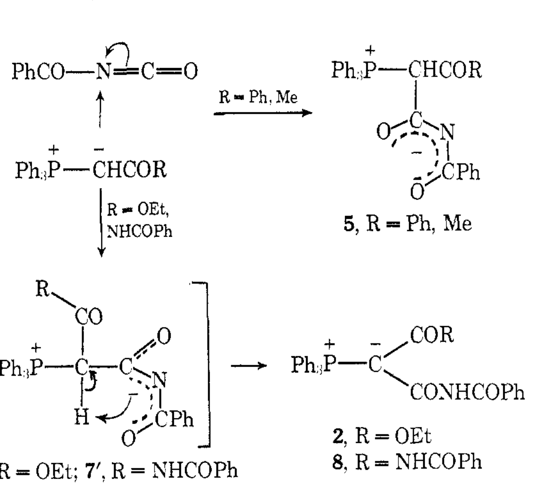


The reaction type for methylenetriphenylphosphorane (**6**) was similar to that of the ylide **1**. Benzoyl isocyanate (2 mol) was added to the ylide **6** with prototropic shifts, and the adduct **8** cyclized immediately to the ylide **9** (Scheme I). From the fact that the adduct **7** was not isolated, 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 byproduct 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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that of the betaine **5**,[9] and thus the former give stable ylides and the latter gives a betaine.

Possibly the high acidity of the betaine in the case of the ylide **1b** is due to a resonance effect of the phenyl group.

Experimental Section

Materials.—Benzoyl isocyanate was prepared according to the procedure of Speziale:[10] bp 99–101° (20 mm); ir 2240 cm^{-1} (NCO).

The ylides **1a**,[11] **4a**,[12] and **4b**[12] were prepared according to the known procedures. The physical properties were identical with reported data.

Reaction of the Ylide 1a.—Benzoyl isocyanate (0.02 mol) dissolved in 3 ml of benzene was added dropwise to 0.02 mol of the ylide **1a** dissolved in 200 ml of benzene under a nitrogen stream. The mixture was stirred at 50° for 3 hr. The resulting precipitate was filtered off and recrystallized with methanol to give 6.0 g (93%) of the ylide **2a**: mp 195–196.5°; ir (Nujol) 3200 (NH), 1700, 1640, 1600 cm^{-1} (CO); nmr ($CDCl_3$) δ 0.52 (t, 3, $J = 7.1$ Hz, CH_3), 3.73 (q, 2, $J = 7.1$ Hz, CH_2), 12.62 (s, 1, NH); mol wt (vpo, $CHCl_3$) 498 (calcd 496).

Anal. Calcd for $C_{30}H_{26}O_4NP$: C, 72.72; H, 5.29; N, 2.83. Found: C, 72.95; H, 5.35; N, 2.86.

Hydrolysis of the Ylide 2a.—The ylide **2a** (1.5 g) was dissolved in 50 ml of EtOH, and a small quantity of NaOH was added. The mixture was refluxed for 10 hr, concentrated, extracted (benzene), and recrystallized (MeOH) to give 0.7 g (60%) of the ylide **3a**: mp 192–193°; ir ($CHCl_3$) 3560, 3360 (NH), 1620, 1600 cm^{-1} (CO); nmr ($CDCl_3$) δ 0.52 (t, 3, $J = 7.5$ Hz, CH_3), 3.69 (q, 2, $J = 7.5$ Hz, CH_2); mass spectrum (70 eV) m/e 391 (M^+, calcd 391), 347 ($Ph_3P{=}CCOOEt^+$), 319 ($Ph_3P{=}CHCOO^+$).

Anal. Calcd for $C_{23}H_{22}O_3NP$: C, 70.58; H, 5.66; N, 3.58. Found: C, 70.92; H, 5.81; N, 3.49.

Reaction of the Ylide 1b.—The mixture of 0.04 mol of phenyllithium, 0.03 mol of benzyltriphenylphosphonium chloride, and 150 ml of ether was stirred for 8 hr at room temperature under a nitrogen stream.[13] Benzoyl isocyanate (0.03 mol) was added dropwise, and stirring was continued for 7 hr. The reaction mixture was concentrated and recrystallized (benzene–methanol) to give 15.0 g (73%) of the ylide **2b**: mp 176.5–178°; ir ($CHCl_3$) 3440 (NH), 1690, 1610 cm^{-1} (CO); nmr ($CDCl_3$) δ 8.12 (b, NH, disappeared by D_2O addition); mass spectrum (70 eV) m/e 499 (M^+, calcd 499), 379 ($Ph_3P{=}C(Ph)CO^+$), 351 ($Ph_3P{=}CPh^+$).

Anal. Calcd for $C_{33}H_{26}O_2NP$: C, 79.34; H, 5.25; N, 2.80. Found: C, 79.69; H, 5.24; N, 2.64.

Reaction of the Ylide 4a.—Benzoyl isocyanate (0.02 mol) was added dropwise to 0.02 mol of the ylide **4a** dissolved in 100 ml of toluene, and the mixture was stirred for 3 hr at 60° under a nitrogen stream. The resulting precipitate was recrystallized (MeOH–Et_2O) to give 9.5 g (90%) of the betaine **5a**: mp 169–170°; ir ($CHCl_3$) 1700, 1640, 1580 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.68 (s, 1, CH); mass spectrum (70 eV) m/e 380 ($Ph_3P{=}CHCOPh^+$), 147 ($PhCONCO^+$).

Anal. Calcd for $C_{34}H_{26}O_3NP$: C, 77.41; H, 4.98; N, 2.67. Found: C, 77.12; H, 4.92; N, 2.65.

Decomposition of the Betaine 5a. A.—The betaine **5a** (2.5 g) was heated at 180° for 15 min under reduced pressure (20 mm). Benzoyl isocyanate was trapped as benzamide. The residue was chromatographed (Al_2O_3, benzene) to give 1.55 g (86%) of the ylide **4a**.

B.—The ethanol solution of the betaine **5a** was refluxed for 7 hr in the presence of a small quantity of HBr. The ylide **4a** was recovered quantitatively.

Reaction of the Ylide 4b.—The ylide **4b** reacted with benzoyl isocyanate in the same manner as the ylide **4a** to give the betaine **5b**: yield 85%; mp 196.5–197.5° (recrystallized from MeOH–Et_2O); ir (Nujol) 1700, 1620, 1540 cm^{-1} (CO); mass spectrum (70 eV) m/e 318 ($Ph_3P{=}CHCOMe^+$), 147 ($PhCONCO^+$).

Anal. Calcd for $C_{29}H_{24}O_3NP$: C, 74.83; H, 5.20; N, 3.01. Found: C, 74.58; H, 4.94; N, 3.01.

Decomposition of the Betaine 5b.—The ethanol solution of the betaine **5b** was refluxed for 8 hr in the presence of a small quantity of NaOH. The ylide **4b** was recovered quantitatively by extraction with benzene.

Reaction of the Ylide 6.—The mixture of 0.01 mol of methyltriphenylphosphonium bromide, 0.01 mol of NaH, and 200 ml of THF was stirred for 8 hr.[14] After separation of the insoluble solid, 0.02 mol of benzoyl isocyanate was added dropwise, and stirring was continued for 7 hr at room temperature under a nitrogen stream. The reaction mixture was concentrated and extracted (benzene). Insoluble solid was recrystallized (MeOH–benzene) to give 2.2 g (43%) of the ylide **9**: mp 282–283°; ir (Nujol) 3420 (NH), 1750, 1700, 1640, 1600 cm^{-1} (CO); mass spectrum (70 eV) m/e 492 (M^+, calcd 492), 449 ($M^+ - HNCO$), 431 ($M^+ - CONHCO$), 147 ($PhCONCO^+$).

Anal. Calcd for $C_{29}H_{21}O_4N_2P$: C, 70.53; H, 4.30; N, 5.69. Found: C, 70.52; H, 4.26; N, 5.61.

The extract with benzene was recrystallized (benzene–hexane) to give 0.5 g (19%) of the triazine **10**: mp 239–240°; ir (Nujol) 1520 cm^{-1}, identical with that of the authentic sample;[15] mass spectrum (70 eV) m/e 309 (M^+, calcd 309).

Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.50; H, 4.59; N, 13.56.

Registry No.—**2a**, 29411-29-8; **2b**, 29411-30-1; **3a**, 29520-63-6; **5a**, 29411-31-2; **5b**, 29250-64-7; **9**, 29411-32-3; benzoyl isocyanate, 4461-33-0.

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Spontaneous Ring Enlargement during the Free-Radical Bromination of 2-Benzyl-1,3,3-trimethyl- and 2-Benzyl-3,3-dimethylbicyclo[2.2.1]heptanol-2

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Previous publications[1] have reported a simple method by which one may effect a ring expansion, namely, through the decomposition of the magnesium salts of halohydrins with appropriate structures (eq 1). New examples[1b,d] (eq 2) were cited of the previously reported[2] anomalous migration (in the norbornyl system) of the *less*-substituted C-2–C-3 bond instead of the *more*-substituted C-1–C-2 bond to an incipient electron-deficient center.[3] The latter occurs even though the transition state proceeds through the less favorable boat conformation (eq 2) in preference to the chair conformation. It is apparent that one must consider some factor(s) opposing both electronic and boat form interactions in the transition state. Sauers[2] offered a rationale by proposing a third factor. The factor is

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