J. Org. Chem. 1993, 58, 1987-1988

1,2- and 1,3-Monoazabisylides as Novel Synthons

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Received December 21, 1992

Summary: The 1,2- and 1,3-monoazabisylides (**5** and **11**, respectively) were prepared in situ by the reactions of 1-[[(triphenylphosphorylidene)amino]methyl]benzotriazole (betmip, **2**) with diethyl phosphite anion and methylenetriphenylphosphorane, respectively, followed by treatment with butyllithium. The synthetic versatility of the new reagents **5** and **11** is illustrated by convenient methods for the preparation of isoquinoline, 2-azabutadienes, 2,3-diarylpyrroles, and 2-(3*H*)-benzazepine.

The Wittig and aza-Wittig reactions, for the preparation of alkenes and imines, respectively, are very important in organic chemistry.[1] One widely used application is the preparation of cyclic olefins by bis-Wittig reactions. This procedure has advantages over other available methods, particularly in the preparation of large rings. Unsaturated rings synthesized have ranged from 5 to 36 membered.[2] One bis-aza-Wittig reaction has been reported for the preparation of phthalazine from phthalic dicarboxaldehyde and triphenylphosphine–azine.[3] However, monoazabisylides which should be useful in heterocyclic synthesis have seldom been reported[4] and monoazabisylides (**1** with n = 0 or 1) are unknown. 1-[[(Triphenylphosphorylidene)amino]methyl]benzotriazole (betmip, **2**), a new reagent developed in our laboratory, has proved valuable in novel syntheses of primary amines,[5] trisubstituted imidazoles,[6] α-(arylidenamino)alkylamines[7] and carbodiimides, imines, isothiocyanates, aziridines, and secondary amines.[8] We now report the preparation from **2** of **5**, which is equivalent to a 1,2-monoazabisylide, and of the 1,3-monoazabisylide (**11**) and their use in the synthesis of isoquinoline, 2-azabutadiene, 4-aza-1,8-diphenyl-1,3,5,7-octatetrene, pyrroles, and 2-(3*H*)-benzazepine.

$$Ph_3P{=\!=}CH{-\!-}(CH_2)_n{-\!-}N{=\!=}PPh_3$$

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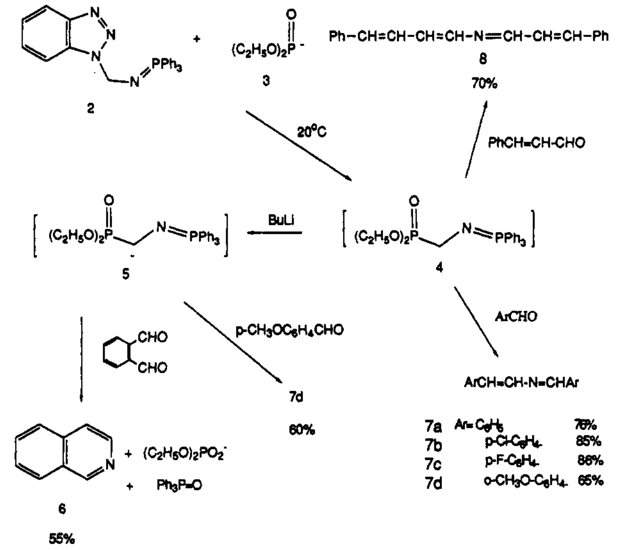
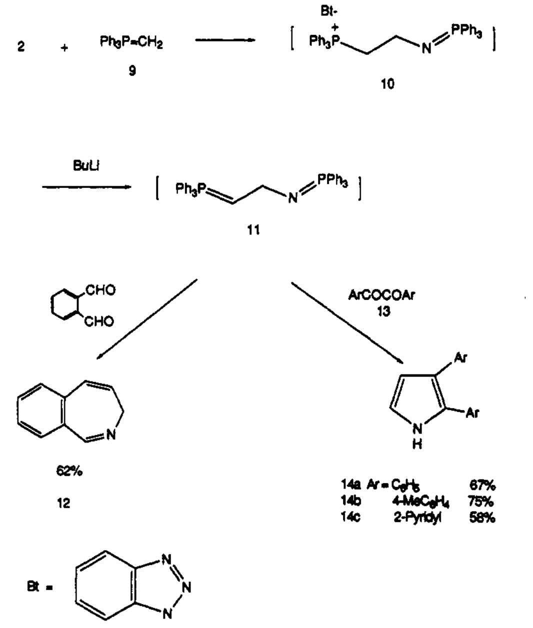
The benzotriazole group in betmip (**2**) is readily displaced by carbanions[7] and nitrogen anions.[5] We now find that with the anion **3** (from diethyl phosphite and butyllithium) at 20 °C it gives the intermediate **4** which with further butyllithium formed the bisylide **5**. The addition of phthalic dicarboxaldehyde gave isoquinoline **6** in 55% yield, as confirmed by comparison of the ^1H and ^{13}C NMR spectra with those of an authentic sample. Similarly, p-anisaldehyde gave 1,4-bis(4-methoxyphenyl)-2-azabutadienes (**7d**) in 60% yield. Intermediate **4**, without initial deprotonation, reacted with aryl aldehydes at room temperature to give the 2-azabutadienes **7a–d** and with cinnamaldehyde to give 4-aza-1,8-diphenyl-1,3,5,7-octatetrene (**8**) in 65–86% yields, Scheme I. The products were characterized by ^1H and ^{13}C NMR spectra and the new compounds **7b–d** and **8** by elemental analysis.

Scheme I



Scheme II



In a similar way, betmip (**2**) and methylenetriphenylphosphorane (**9**) gave the intermediate **10** over 10 h at room temperature. After deprotonation with butyllithium and stirring with phthalic dicarboxaldehyde at room

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0022-3263/93/1958-1987$04.00/0

temperature, 2(3*H*)-benzazepine (**12**) was isolated in 62% yield. By the same technique, the diaryl 1,2-diones **13** gave the 2,3-diarylpyrroles **14**, Scheme II. The new compounds all gave satisfactory elemental analyses or molecular fragments and showed the expected proton and carbon NMR spectra.

These results introduce new and convenient synthons for heterocyclic synthesis. The 1,2-monoazabisylide offers a new route to isoquinoline synthesis. The 1,3-monoazabisylide represents the first synthon for the conversion of 1,2-diketones to 2,3-disubstituted pyrroles and has enabled the first preparation of unsubstituted 2(3*H*)-benzazepine. We are continuing to apply these new monoazabisylides in heterocyclic synthesis.

Supplementary Material Available: Procedures and characterization data (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.