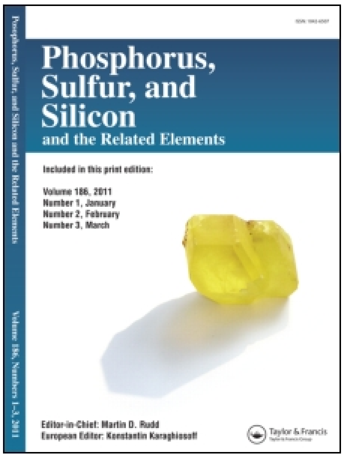

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Communication

FIRST SUCCESSFUL EXAMPLES OF 1,3-DIPOLAR CYCLOADDITION REACTION OF NITRONES WITH α,β-UNSATURATED PHOSPHONIUM SALTS

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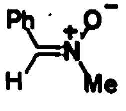
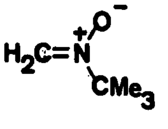
α,β-Unsaturated phosphonium salts, both of vinylic and acetylenic type of unsaturation, are shown to display dipolarophilic properties towards nitrones

Nitrones are 1,3-dipoles which attract a special attention.[1] They undergo a cycloaddition with a great variety of dipolarophiles, often with highly predictable and remarkable regioselectivity and stereoselectivity.[1,2,3] On the other hand, α,β-unsaturated phosphonium salts are good dipolarophiles in cycloaddition reactions.[4,5,6,7] However, only one example of an attempted reaction of a nitrone with cyclobutenyl phosphonium salt is available up to now.[5] We now demonstrate that α,β-unsaturated phosphonium salts are able to undergo the [3 + 2] cycloaddition reaction with a variety of nitrones.

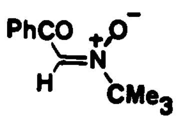
Thus, the reaction of a tenfold excess of a nitrone (**1a–e**) with (2-phenylethynyl)triphenylphosphonium bromide (**2a**) (chloroform, room temperature, 36 hours)



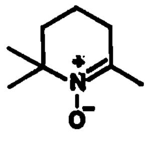
(1a)



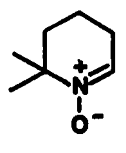
(1b)



(1c)



(1d)



(1e)

$Br^- \; Ph_3\overset{+}{P}-C{\equiv}C-Ph$

(2a)

$Ph_3\overset{+}{P}-CH{=}CH-R \; PF_6^-$

(2b) R = COPh

(2c) R = H

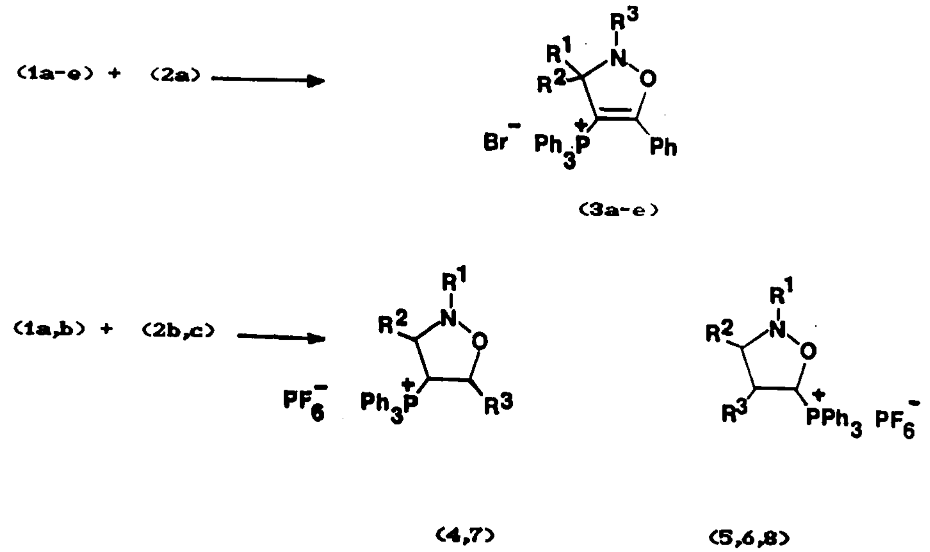
Scheme 1

led to the quantitative formation of a single (^{31}P n.m.r.) isoxazoline (**3a**) (entries 1–5). The formation of 4-phosphonio substituted isoxazolines rather than their 5-phosphonio isomers is expected from the analysis of the literature data concerning alkyne cycloadditions to nitrones.[1,2]

In the case of aliphatic nitrones (**1b–e**), equimolar amounts of the latter were sufficient to provide practical conversion rates. The reaction of nitrones with α,β-ethylenic phosphonium salts leads to cycloadducts when either none or a π-electron withdrawing β-substituent is present in the structure of the salt. However, the reaction is less regioselective and mixtures of products are usually obtained.

Thus, in presence of a twofold excess of benzylidene methylamine N-oxide (**1a**), the cycloaddition reaction of 2-benzoylvinyltriphenylphosphonium hexafluorophosphate (**2b**), carried out in melted mixture of reagents at 70°C is completed in six hours, leading to the mixture of two products (**4**) and (**5**) (^{31}P n.m.r.) in a 1:1 molar ratio (based on ^{1}H n.m.r., entries 6 and 7). This reaction, when carried out in chloroform solution, either in room or elevated temperature, gives rise to a complex mixture of products, some of them being no cycloadducts at all. The attempts undertaken to separate all the products remained unsuccessful.

Similarly, in the reaction of vinyltriphenylphosphonium hexafluorophosphate



Scheme 2

TABLE I

Cycloaddition of nitrones to unsaturated phosphonium salts

entry	Nitrone	Product	R^1	R^2	R^3	$\delta^{31}P$
1	**(1a)**	**(3a)**	Ph	H	Me	12.55
2	**(1b)**	**(3b)**	H	H	*t*Bu	14.08
3	**(1c)**	**(3c)**	PhCO	H	*t*Bu	14.45
4	**(1d)**	**(3d)**	Me	$—(CH_2)_3$	$—CMe_2—$	13.13
5	**(1e)**	**(3e)**	H	$—(CH_2)_3$	$—CMe_2—$	14.23
6	**(1a)**	**(4)**[a]	Me	Ph	PhCO	27.78
7		**(5)**[b]	Me	Ph	PhCO	19.81
8	**(1b)**	**(6)**	*t*Bu	H	H	24.34
9	**(1b)**	**(7)**[b]	*t*Bu	H	PhCO	29.43
10		**(8)**[b]	*t*Bu	H	PhCO	23.03

[a] 4 : 5 ratio = 50 : 50

[b] 7 : 8 ratio = 15 : 85

(2c) with **(1a)** in chloroform solution, a mixture of products is obtained. This may be due to a low reactivity of the nitrone **(1a)**, which imposes a prolonged reaction time, and the large excess of the nitrone, which may favour side-reactions. Indeed, the attempted reaction of **(2c)** with more reactive nitrone **(1b)** in chloroform (1:1 molar reagent ratio, room temperature, 12 hours) yields the single isoxazolidine **(6)** (entry 8). The reaction of **(2b)** with this nitrone under similar conditions affords two isoxazolidines in a molar ratio **(7)**:**(8)** equal 1:6 (based on ^{1}H n.m.r., entries 9 and 10). The latter results confirm the increased selectivity of faster cycloaddition reactions.

In all cases, the products were isolated by slow addition of the reaction mixture in chloroform to great excess of diethyl ether. Mixtures of salts were separated, when possible, by fractional crystallization. The structures assigned to the products are based on the analysis of the spectral data (IR, ^{1}H, ^{13}C n.m.r.). The stereochemistry of the cycloadducts could not always be established unequivocally and the study is in progress.

In summary, it has been demonstrated, that the 1,3-dipolar cycloaddition occurs readily and regioselectively with acetylenic-type α,β-unsaturated phosphonium salts, affording exclusively 4-phosphonio-substituted isoxazolines. Similar cycloadditions involving ethylenic-type unsaturated salts are less selective, and provide usually a mixture of regioisomeric 4- and 5-phosphonio-substituted isoxazolidines, which may be separated by fractional crystallization. The structure of the products generally confirms the predictions based on the literature data.[1-3] Both functionalized isoxazolidines and isoxazolines are of potential utility in organic synthesis.

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