

A New Method for the Preparation of Conjugated Nitro Olefins

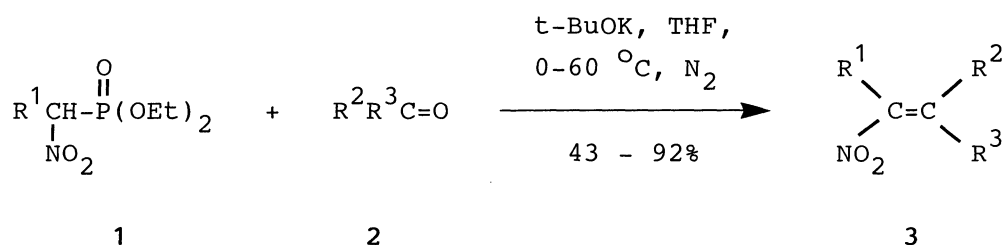
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Condensation of 1-nitroalkanephosphonates with carbonyl compounds affords a new and facile method for the preparation of conjugated nitro olefins.

Conjugated nitro olefins are versatile intermediates in organic synthesis.¹⁾ Owing to the powerful electron-withdrawing property of nitro group, conjugated nitro olefins serve not only as good dienophiles in the Diels-Alder reaction, but also as reactive acceptors in the Michael addition. The convertibility of the nitro group into a variety of functional groups such as carbonyl, oxime, hydroxyamine, amine, and hydrogen enhances the usefulness of the aliphatic nitroalkanes and nitroalkenes in synthetic organic chemistry.²⁾

In the present report, the author describes a new and convenient preparation of conjugated nitro olefins (3) by the condensation of 1-nitroalkanephosphonates (1) with carbonyl compounds (2).



The phosphonates 1 were prepared by Zon's method³⁾ using acid chlorides and triethyl phosphite as starting materials.⁴⁾ Condensation of 1 with 2 was carried out by stirring a mixture of the phosphonates 1 (1.0 equiv.), the carbonyl compounds 2 (1.2 equiv.) and potassium t-butoxide (1.3 equiv.) in THF at 0 °C to 60 °C under a nitrogen atmosphere. The results are summarized in Table 1. The reactions proceed under mild conditions to give 3 in high yields. Configurations of the products were assigned on the basis of ¹H NMR spectra by observing the signals of the vinylic protons of (*E*)-isomers which appear at lower field than those of

Table 1. Preparation of Conjugated Nitro Olefins 3

3	R ¹	R ²	R ³	Time/h	Yield/% ^{a)}	E/Z ^{b)}
a	CH ₃	Ph	H	5	92	100/ 0
b	C ₂ H ₅	Ph	H	5	86	95/ 5
c	CH ₃	CH ₃	H	5	90	100/ 0
d	C ₂ H ₅	CH ₃	H	5	83	100/ 0
e	Ph	CH ₃	H	5	75	88/12
f	c-C ₆ H ₁₁	Ph	H	5	79	74/26
g	CH ₃ O ₂ C(CH ₂) ₂	2-thienyl	H	5	91	92/ 8
h	c-C ₆ H ₁₁	2-furyl	H	5	68	69/31
i	CH ₃	PhCH=CH-	H	5	71	100/ 0
j	CH ₃	-(CH ₂) ₅ -		12	43	-

a) Isolated yields. b) Determined on ¹H NMR analysis.

(Z)-isomers because of the anisotropic effect of the nitro group.⁵⁾ It is to be noted that a conjugated nitro diene (3i) can be prepared in 71% yield and that a nitro olefin (3j) can be also obtained from cyclohexanone in a practical yield (43%) without the formation of allylic nitro compounds.⁶⁾

In practice, the present procedure provides a useful synthetic approach to a wide range of conjugated nitro olefins because various kinds of acid chlorides and carbonyl compounds are available as starting materials.

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References

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- 4) Isolated yields of 1a-e overall from the corresponding acid chlorides: 1a (R¹ = CH₃); 48%, 1b (R¹ = C₂H₅); 65%, 1c (R¹ = Ph); 61%, 1d (R¹ = c-C₆H₁₁); 58%, 1e (R¹ = CH₃O₂C(CH₂)₂-); 51%.
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