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. 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. Oxime, hydroxyamine, amine, and hydrogen enhances the usefulness of the aliphatic nitroalkanes and nitroalkenes in synthetic organic chemistry.

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 method 3) 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 $^{\circ}$ C to 60 $^{\circ}$ 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 1 H NMR spectra by observing the signals of the vinylic protons of (E)-isomers which appear at lower field than those of

3	R ¹	R ²	R ³	Time/h	Yield/% ^{a)}	E/Z^{b})
a	CH ₃	Ph	Н	5	92	100/ 0
b	С ₂ Н ₅	Ph	Н	5	86	95/ 5
С	CH ₃	CH ₃	Н	5	90	100/ 0
đ	С ₂ Н ₅	CH ₃	Н	5	83	100/ 0
е	Ph	CH ₃	Н	5	75	88/12
f	^{C-C} 6 ^H 11	Ph	Н	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	Н	5	68	69/31
i	CH ₃	PhCH=CH-	Н	5	71	100/ 0
j	CH ₃	-(CH ₂) ₅ -		12	43	-

Table 1. Preparation of Conjugated Nitro Olefins 3

(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 (R^1 = CH_3); 48%, 1b (R^1 = C_2H_5); 65%, 1c (R^1 = Ph); 61%, 1d (R^1 = C_2H_1); 58%, 1e (R^1 = $CH_3O_2C(CH_2)_2$ -); 51%.
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a) Isolated yields. b) Determined on ¹H NMR analysis.