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REACTION OF ETHYL α, β-UNSATURATED α- OR β-NITROCARBOXYLATES WITH SODIUM AZIDE

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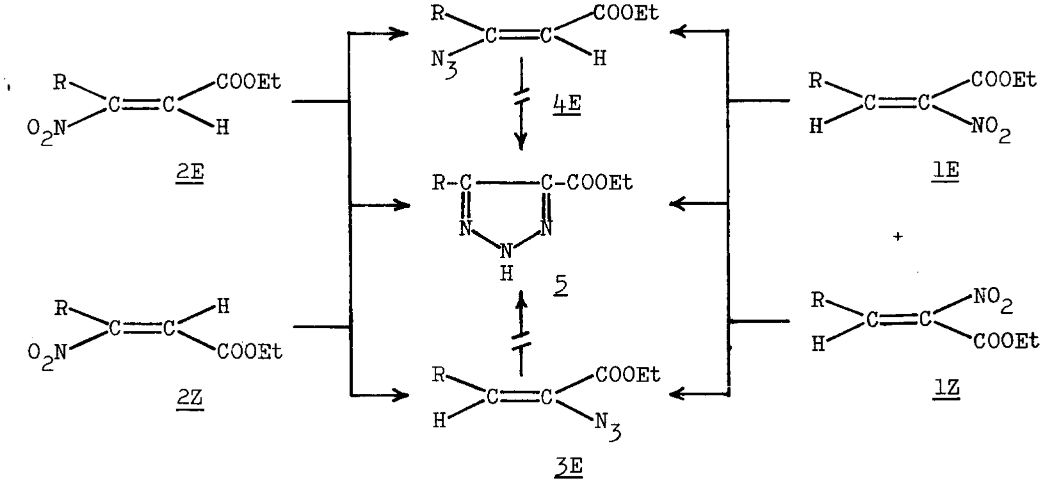
Although many literatures have been published on the synthesis and chemistry of azide compounds, the synthetic route to α,β-unsaturated α- and β-azidocarboxylic esters (3 and 4) has not been extended beyond the following methods: methyl α-azidocinnamates were synthesized by condensation of methyl azidoacetate and arylaldehydes$^{1)}$ and methyl α-azidopropenoate and methyl β-azidocinnamate by addition of iodo azide to the corresponding olefinic compound and successive elimination of hydrogen iodide,$^{2)}$ and β-azido-α-butenoate by addition of sodium azide to the corresponding allenic compound.$^{3)}$

On the other hand, it is known that the reaction of nitroolefin with sodium azide or hydrazoic acid gave the corresponding substitution product (triazole)$^{4,5)}$ or addition product (nitroazide),$^{6)}$ however, simple substitution of the nitro group with azide group was never reported.

In this paper, we wish to report the novel synthesis of 3, 4 or 4-ethoxycarbonyl-1,2,3-triazole derivatives (5) by the reaction of ethyl α,β-unsaturated α- or β-nitrocarboxylates (1 and 2) with sodium azide.

When mixture of E- and Z-isomer of 1 was treated with sodium azide in dry dimethylformamide at room temperature for 1 hr, compound 3, 4, and 5 as main product, were obtained. Compound 5 was obtained colorless crystals, and 3 and 4 were separated by chromatography on silica-gel column by elution with a mixture of petroleum ether and benzene (2 : 1) as pale yellow oils, respectively. While E- or Z-isomer of 2, under similar conditions, reacted with sodium azide to give

3, 4 as main product, and 5, at the almost same ratio, respectively. All products are confirmed to be one chemical species, respectively, by TLC and NMR. It is supposed that compounds 3 and 4 are stereochemically and thermodynamically stable E-conformer, because the products are considerably stable against to temperature and light.2) The structure of 3, 4 and 5 was chracterized with elementary and spectroscopic (IR and NMR) analyses and independent preparation of 3 and 4.



a; R=CH_3, b; R=C_2H_5, c; R=n-C_3H_7, d; R=i-C_3H_7, e; R=C_6H_5. Scheme 1

TABLE 1

Compond	Yield %		β-Ha)	Compound	Yield %		α-Ha)
	From 2	From 1	(δ)		From 2	From 1	(δ)
				4a	71.3	8.6	5.51
3b	6.5	8.6	6.18t	4b	41.4	5.1	5.48
3c	12.0	8.5	6.15t	4c	28.6	4.2	5.48
3d	13.5	21.5	6.02d	4d	31.0	—	5.48
3e	14.5	—	6.91s	4e	30.5	—	5.77

a) 100 MHz, measured in $CDCl_3$.

TABLE 2

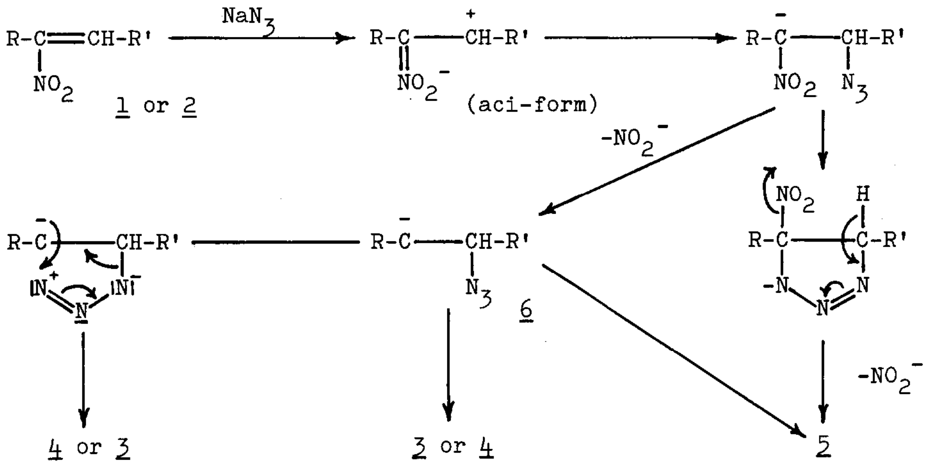
Compound	Yield %		mp °C[a]	-NH- (δ)[b]
	From 2	From 1		
5b	2.2	46.5	114 - 115	13.95
5c	12.7	55.8	83 - 84	14.38
5d	11.2	51.5	86 - 87	14.22
5e	27.0	58.5	48 - 49	12.23

a) Recrystallized from ethanol to give colorless prisms.
b) 100 MHz, measured in $CDCl_3$.

In the IR spectra, compound 3 and 4 showed the characteristic azide absorption of (2100 - 2120 cm^{-1}, strong) and of carbon-carbon double bond (1618 - 1630 cm^{-1}, middle), while compound 5 showed imino hydrogen (3080 - 3105 cm^{-1}, weak) and carbon-nitrogen double bond (1587 - 1588 cm^{-1}, strong). In the NMR spectra, vinyl proton of 4 in the α-position appeared at δ 5.48 - 5.77 region as singlet, while that of 3 in the β-position at δ 6.02 - 6.91 region, coupled variously with the protons in the γ-position. In compound 5, characteristic imino hydrogen signal was observed in lower magnetic field (δ 12.23 - 14.38) as broad singlet, as shown in Table 2.

To confirm the structure of 3 and 4, the reaction of ethyl E-3-chloro-2-propenoate with sodium azide and that of benzaldehyde with ethyl azidoacetate were successifully performed to afford 4b and 3e, respectively. However, attempted preparation of 3 from ethyl 2-bromo-2-propenoate and sodium azide and the conversion of 3 or 4 into 5 under several conditions were unsuccessful.

The latter fact indicates that nucleophilic attack of azide ion at the α- or β-position of aci-form of 1 or 2 was followed by elimination of nitro group to give 5 and carbene intermediate (6),[4] which subsequently stabilized to give olefinic azide or isomerized to the corresponding isomer by intramolecular addition -elimination of azide group as shown in Scheme 2. The compound 5 might be formed by either the concerted cyclization-elimination reaction of azide-nitro carbanion and cyclization of the carbene intermediate.



In the case of 1: R = ethoxycarbonyl group, R' = alkyl or phenyl group.

In the case of 2: R = alkyl or phenyl group, R' = ethoxycarbonyl group.

Scheme 2

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