Novel Reaction of Ethyl Diazoacetate with π-Allylnickel Bromide

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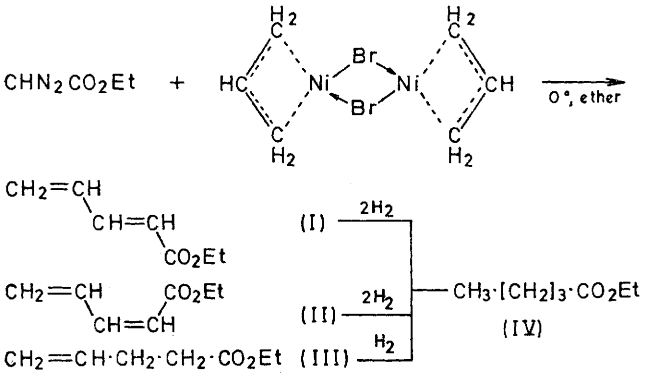
Summary Reaction of ethyl diazoacetate with π-allylnickel bromide gives ethyl β-vinylacrylate.

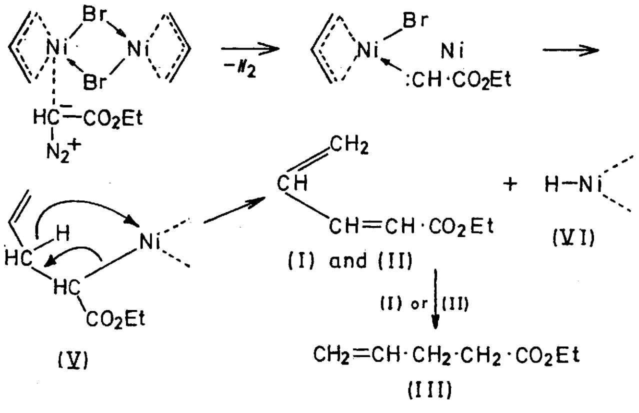
THERE have been several reports on the reaction of diazo-compounds in the presence of π-allyl metal complexes.[1] However, these complexes, as well as metals,[2] metal halides,[3] and organometallic compounds,[4] have only acted as catalysts for the decomposition of diazo-compounds.

We now report that ethyl diazoacetate reacts with the ligand of π-allylnickel bromide, affording mainly butadiene derivatives.



SCHEME 1

Dropwise addition of ethyl diazoacetate to an excess of π-allylnickel bromide[5] in ether at 0° under nitrogen led to the immediate and quantitative evolution of nitrogen, and the colour of the solution changed from red to dark brown. After the evolution of nitrogen had ceased, the reaction mixture was filtered in air.† Concentration and distillation of the filtrate, followed by preparative g.l.c. separation gave three products (I) 69%; (II) 19%; and (III) 8%, together with unidentified material. The structure of (I) was confirmed as ethyl *trans*-β-vinylacrylate by its analytical and spectral data, and further by comparison with an authentic sample;[6] n_D^{20} 1·4770; i.r. (neat) 1740 (C=O), 1640 (C=C), and 1600 cm.$^{-1}$ (C=C); n.m.r. J_{45} 15 Hz. (Table); analysis satisfactory for $C_7H_{10}O_2$. Hydrogenation of (I) with palladium black resulted in the uptake of two equivalents of hydrogen, and gave ethyl n-pentanoate (IV). The elemental analysis of (II) indicated that it is an isomer of (I); n_D^{20} 1·4750; i.r. (neat) 1715 (C=O), 1635



SCHEME 2

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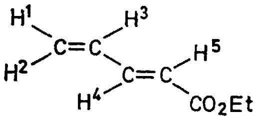
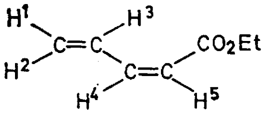
† The dark brown residue changed slowly to green in air. This is being investigated.

(C=C), and 1590 cm.$^{-1}$ (C=C); n.m.r. J_{45} 9·75 Hz (Table). From these data, (II) was assigned as ethyl *cis*-β-vinylacrylate. Reduction of (II) with palladium black also afforded (IV) with the absorption of two equivalents of hydrogen. Compound (III) was identified as ethyl pent-4-enoate[7] in the same manner; n_D^{20} 1·4159; i.r. (neat) 1740 (C=O) and 1642 cm.$^{-1}$ (C=C); n.m.r. (in CCl_4) τ 8·76 (triplet 3H), 7·68 (doublet 4H), 5·95 (quadriplet 2H), 5·08 (multiplet 1H), 5·05 (m 1H), and 4·23 (m 1H); analysis satisfactory for $C_7H_{12}O_2$.

N.m.r. spectra of ethyl trans-*β-vinylacrylate* (I) *and ethyl* cis-*β-vinylacrylate* (II)

	Chemical shift (τ) and coupling const (Hz)				
	1-H	2-H	3-H	4-H	5-H
 (I)	4·66	4·54	3·66	2·94	4·28
	J_{12} (1·5), J_{13} = J_{34} (9·75), J_{23} (16·5), J_{45} (15)				
 (II)	4·46	4·47	2·31	3·45	4·23
	J_{12} (0·75), J_{13} = J_{34} = J_{45} (9·75), J_{23} (16·5)				

A possible mechanistic rationalization of this reaction would involve the insertion‡ of the carbene into the C–Ni bond (V), followed by the formation of nickel hydride (VI) which would reduce ethyl β-vinylacrylate to produce (III).

The similar reaction of ethyl diazoacetate with π-allylpalladium chloride was also investigated; however, even at 25° the Pd complex was recovered, and only diethyl fumarate and diethyl maleate were obtained.[9]

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‡ It is well known that carbon monoxide, which has formally a bivalent carbon, inserts into a C–Ni bond.[8]

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