

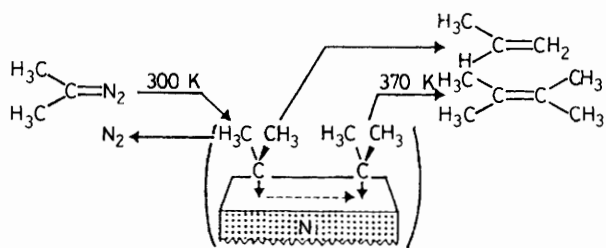
## Stereoselective Formation of Maleic Acid Diester from Two Diazo Acetic Acid Esters on a Raney Nickel Surface. Evidence for Dipod-chemisorbed Carbenes<sup>1</sup>

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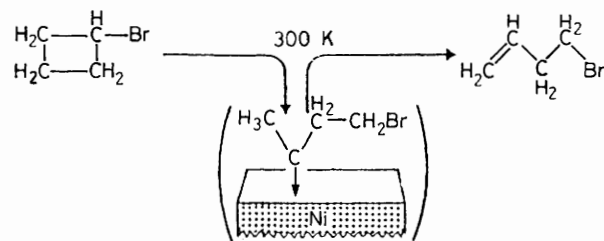
The N<sub>2</sub> elimination from diazo acetic acid esters, heterogeneously catalysed by Raney Nickel, yields as chemisorbed main product up to 93% maleic acid diester, *cis*-stereoselectivity is observed and additional methyl/ethyl ester crossing experiments provide evidence for dipod-chemisorbed surface carbene intermediates.

For the Fischer–Tropsch synthesis of hydrocarbons from CO + H<sub>2</sub> mixtures, a methylene propagation mechanism is generally accepted,<sup>2</sup> based largely on its decisive support by the 'classical' reactions of diazomethane on Fe, Ru, Co, Ni, Pd, and Cu catalysts.<sup>3</sup> For our investigations aimed at novel heterogeneous processes and using photoelectron (PE)-spectroscopic real-time analysis to identify the temperature-dependent products in the gas flow passing a heated reactor,<sup>4</sup> *inter alia*, Raney nickel<sup>5</sup> was selected as a highly active solid.<sup>6,7</sup> The experiments performed<sup>6</sup> suggest the formation of carbene intermediates chemisorbed on the Raney nickel surface. For example, diazopropane (caution: explosive) catalytically splits off N<sub>2</sub> at only 300 K, *i.e.*, 250 K below its thermal gas phase fragmentation temperature, and on warming to 370 K both propene and tetramethylethylene are chemisorbed (Scheme 1).<sup>7b</sup>

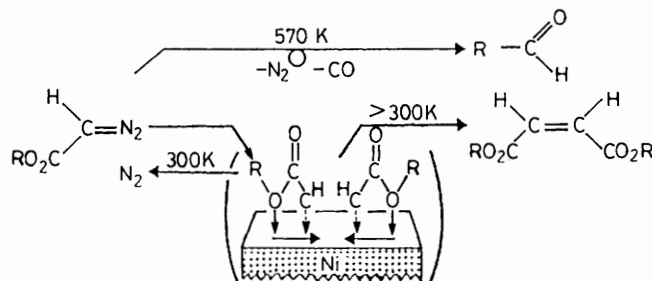


Scheme 1

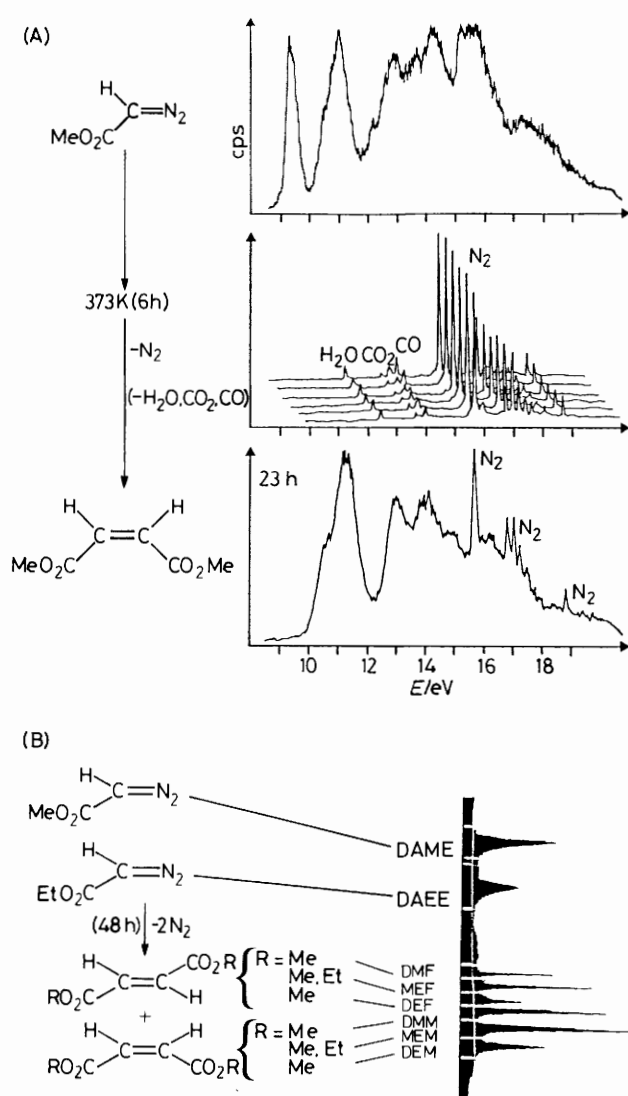
The reaction products are best rationalized by a surface intermediate [(CH<sub>3</sub>)<sub>2</sub>C··Ni] and its competing reaction pathways of H migration and dimerisation. Analogously, the rather unexpected ring opening of bromocyclobutane at room temperature yielding quantitatively 4-bromobut-1-ene,<sup>7c</sup> is in



Scheme 2



Scheme 3

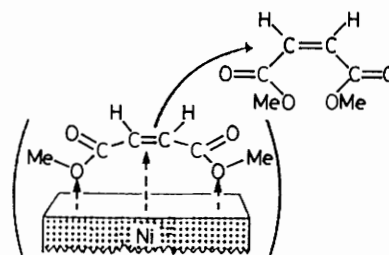


**Figure 1.** The reaction of two diazo acetic acid methyl esters with Raney Ni at 373 K to the corresponding maleic and fumaric diesters: (A) He(I) PE spectra of  $\text{MeO}_2\text{CCHC}=\text{N}_2$ , its continuous  $\text{N}_2$  elimination on passing the Raney Ni zone {accompanied by minor amounts of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$  due to the  $[\text{Al}(\text{O})\text{OH}]$  surface component resulting from the Ni/Al alloy + KOH preparation}, and of the eventually chemisorbed dimethyl maleate. (B) GC of the reaction products from a 1:1 mixture of diazo acetic acid methyl ester (DAME) and ethyl ester (DAEE) formed at Raney Ni and cool trapped, proving each 1:2:1 component ratios of dimethyl (DMF); methyl/ethyl (MEF); diethyl (DEF) fumaric acid esters and dimethyl (DMM); methyl/ethyl (MEM); diethyl (DEM) maleic acid esters (*cf.* text).

accord with a carbene intermediate at the nickel surface (Scheme 2).

Here, we report on the stereoselective formation of maleic acid diester from two diazo acetic esters on Raney nickel slightly above room temperature (Scheme 3).<sup>6,8</sup>

In contrast, the thermal  $\text{N}_2$  elimination in the gas phase ( $P = 10$  Pa) needs considerably higher temperatures *e.g.*, for the methyl ester above 570 K, and produces, presumably *via* a Wolff rearrangement<sup>9</sup> to the corresponding methoxy ketene,<sup>9</sup> exclusively  $\text{CO}$  and acetaldehyde. As concerns the heterogeneously catalysed reaction, a representative experiment<sup>6</sup> at 373 K oven temperature (Figure 1) demonstrates that the



**Scheme 4**

saturation of the Raney nickel surface with carbene fragments remaining after the PE spectroscopically controlled  $\text{N}_2$  elimination needs between 6 and 20 h, depending on the surface area,<sup>†</sup> the length of the catalyst zone, and its temperature. Towards the end, only the ionisation patterns [Figure 1(A)] of  $\text{N}_2$  and of the ethylene dicarboxylic acid esters are detected PE spectroscopically, and additional GC MS analysis<sup>†</sup> proves both the total conversion of  $\text{MeO}_2\text{CCHC}=\text{N}_2$  and the stereoselective formation of up to 93% of the *Z* isomer. To further substantiate the dimerisation pathway *via* chemisorbed carbalkoxy carbenes moving on the Ni metal surface with low activation barriers,<sup>3</sup> in an additional crossing experiment a 1:1:1 vapour mixture of diazo acetic acid methyl and ethyl esters was passed for 38 h over a regenerated<sup>†</sup> Raney nickel. After this time, the PE spectroscopic band patterns of the diazo compounds become visible again and the GC MS analysis of the cool-trapped products [Figure 1(B)] clearly proves the expected ratio of each approximately 25:50:25 dimethyl, methyl/ethyl, and diethyl maleates and fumarates. Detailed studies<sup>6</sup> using Raney nickel contacts with different Ni contents or surface areas<sup>†</sup> and varying the reaction conditions reveal only small differences in yields and in *Z*:*E* isomer ratios of the resulting ethylene dicarboxylic acid esters,  $\text{RO}_2\text{C}-\text{CH}=\text{CH}-\text{COR}$ . However, in all experiments,<sup>6</sup> the thermodynamically less favoured maleic acid diester is formed stereoselectively in yields between 72 and 93%.<sup>†</sup>

How can the heterogeneously catalysed stereoselective formation of maleic acid dimethylester from  $\text{MeO}_2\text{CCHC}=\text{N}_2$  at Raney Ni be rationalized? Raney Ni consists of macroparticles containing Ni metal crystallites of about 1000 pm average diameters, which exhibit (100), (110) as well as (111) surface area regions.<sup>5</sup> Presumably, physisorbed diazo compounds split off  $\text{N}_2$  already at room temperature<sup>3,6,7</sup> [Figure 1(A)] to become chemisorbed as respective carbenes, *i.e.*, more than 250 K below the temperature required for their thermal fragmentation into  $\text{N}_2$ ,  $\text{CO}$ , and acetaldehyde

<sup>†</sup> Details of the Raney nickel preparation from a 50% Ni/50% Al alloy (DEGUSSA) by reaction with aqueous KOH below 343 K under Ar, controlled by the  $\text{H}_2$  volume generated, its transfer in a reaction tube strictly excluding air, followed by 12 h drying at 10 Pa and 3 h activation in a  $\text{H}_2$  flow at 620 K, are reported in ref 7c. Ni contents varied between 61% Ni (B.E.T. surface area  $14 \text{ m}^2 \text{ g}^{-1}$ ) and 85% (pyrophoric, B.E.T. surface area  $50 \text{ m}^2 \text{ g}^{-1}$ ). The Raney Ni catalyst can be regenerated in an  $\text{H}_2$  flow at 620 K within about 3 h, losing little of its activity and selectivity. The heterogeneous reactions with  $\text{RO}_2\text{CCHC}=\text{N}_2$  have been carried out in a building block apparatus (*cf.* ref. 4), consisting of the sample trap, of the heated flow reactor, as well as of a set of cooling traps with bypass lines and is connected directly to a PE spectrometer Perkin Elmer 16. Additional GC MS analysis of the cool-trapped products has been performed using a Varian 1700/MAT CH7 combination. Reactions at the pyrophoric Raney Ni shows some peculiarities, *e.g.*, GC MS analysis proves up to 33% hydrogenation to the saturated succinic acid diesters.

(Scheme 3). The presence of Ni surface carbalkoxy carbenes [ $\text{RO}_2\text{CHC} \rightarrow \text{Ni}$ ] and their mobility under the reaction conditions is proven by the diazo acetic acid methyl + ethyl esters 'crossing' experiment, which approximately yields the predicted 1 : 2 : 1 ratio for the dimethyl : methyl/ethyl : diethyl esters of the ethylene dicarbonic acids [Figure 1 (B)] formed via surface dimerisation<sup>3,7</sup> (cf. Schemes 1 and 3). In addition, known chemisorption enthalpies on Ni (110) surfaces, which amount to only 242 kJ/mol for  $\text{H}_2\text{C}=\text{CH}_2$  but *e.g.*, to 448 kJ/mol<sup>10</sup> for oxygen, suggest that the stereoselectivity is generated in the final chemidesorption step with the  $\pi_{\text{CC}}$  bond lifting off first from the metal surface (Scheme 4).

The more strongly bound carbalkoxy oxygens follow consecutively. Such a stepwise chemidesorption, which is also observed *e.g.*, in the catalytic decomposition of  $\text{RO}_2\text{CHC}=\text{N}_2$  on Re metal,<sup>11</sup> provides evidence that carbalkoxy carbenes are 'dipod' chemisorbed at both their C and O surface coordination centres. If so, other appropriate surface molecular species attached differently at different sites could also form stereoselectively the thermodynamically less stable isomer in a heterogeneously catalysed reaction.

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