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REARRANGEMENT, COUPLING AND CARBOXYLATION OF THE ALLYLIC GROUP ON NICKEL COMPLEXES

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In a preceding paper (1) we reported some results on the allylic rearrangement accompanying the coupling and carboxylation reactions of ^{14}C labelled allyl bromide $\underset{3}{CH_2}=\underset{2}{CH}-{}^{14}\underset{1}{CH_2}Br$ (2) in nickel complexes.

From the coupling reaction (3) we obtained 1,5-hexadiene $\underset{1}{CH_2}=\underset{2}{CH}\underset{3}{CH_2}\underset{4}{CH_2}\underset{5}{CH}=\underset{6}{CH_2}$ having the radioactivity of both the allylic groups equally distributed between the terminal carbon atoms ($^{14}C_1 = {}^{14}C_3 = {}^{14}C_4 = {}^{14}C_6 = 25\%$, complete rearrange-

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1) M. Dubini, G.P. Chiusoli and F. Montino, *Chimica e Industria (Milan)* - in press.

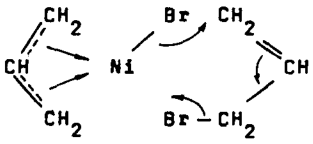
2) R.H. Nystrom and J.C. Leak, *J.Am.Chem.Soc.* **75**, 3039 (1953) Isotopic distribution $^{14}C_1 = 92\%$; $^{14}C_3 = 8\%$.

3) I.D. Webb and G.T. Borcherdt, *J.Am.Chem.Soc.* **73**, 2654 (1951).

ment). In the carboxylation reaction (4) with acetylene and carbon monoxide, leading to 2,5-hexadienoic acid $\underset{6}{C}H_2{=}\underset{5}{C}H\underset{4}{C}H_2\underset{3}{C}H{=}\underset{2}{C}H\underset{1}{C}OOH$, we noted the same behaviour of the allylic group.

The unreacted allyl bromide recovered from the reactions was also found to be rearranged to a 50 to 50 mixture of $^{14}CH_2{=}CH{-}CH_2Br$ and $CH_2{=}CH\,^{14}CH_2Br$. The rearrangement was shown to be catalytic. Nickel carbonyl, bis π -allylnickel bromide (5) and iron-reduced nickel bromide proved to be effective in promoting this rearrangement.

It was then concluded that an allylnickel bromide might be responsible for the observed rearrangement, probably acting in the following way :



All nickel monohalides stabilized by coordination with

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4) G.P. Chiusoli, *Chimica e Industria (Milan)*, **41**, 503, 506, 512, 762 (1959); *Angew. Chem.* **70**, 74 (1960); G.P. Chiusoli and S. Merzoni, *Chimica e Industria* **43**, 256, 259 (1961); **45**, 6 (1963); *Z. Naturforschg.* **17b**, 850 (1962); G.P. Chiusoli, G. Bottaccio and A. Cameroni, *Chimica e Industria* **44**, 131 (1962).

5) E.O. Fischer and G. Bürger, *Z. Naturforschg.* **16b**, 77 (1961); *Ber.* **94**, 2409 (1961).

a suitable ligand are also likely to be effective.

Additional information on the behaviour of the allylic group is given in the present work.

New data were collected from the study of the coupling reaction of allyl acetate with nickel carbonyl, recently described by Bauld (6). Operating with ^{14}C allyl acetate $CH_2=CH\ ^{14}CH_2OCOCH_3$ (7) in tetrahydrofuran or dioxane at 60-80°C and using the same technique as in our preceding work (ozonization of hexadiene and allyl acetate after gas-chromatographic separation and isolation of the metone derivative of formaldehyde) we established that unreacted allyl acetate was not rearranged even with a 1:1 molar ratio of allyl acetate to nickel carbonyl. On the other hand, the hexadiene-forming allylic groups showed a partial rearrangement ($^{14}C_1 + {}^{14}C_6 = 38\%$).

A similar result was obtained with ^{14}C allyl acetate, acetylene and carbon monoxide (1:1 ratio), nickel carbonyl and methanol at 130°C and 50 atm. The unreacted allyl acetate was shown to be partially rearranged ($^{14}C_3 = 10\%$) whereas the allylic group of the methyl 2,5-hexadienoate formed proved to be completely rearranged ($^{14}C_6 = 50\%$).

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6) N.L. Bauld, <u>Tetrahedron Letters</u> No. 19, 859 (1962).

7) Prepared from $^{14}C_1$ allyl alcohol and acetic anhydride. Isotopic distribution : $^{14}C_1 = 99\%$; $^{14}C_3 = 1\%$).

Carrying out the coupling reaction on ^{14}C allyl p-toluensulfonate and nickel carbonyl dissolved in tetrahydrofuran at room temperature (the reactivity of allyl p-toluensulfonate being higher than that of allyl acetate), the hexadiene-forming allylic groups were found to be partially rearranged ($^{14}C_1$ + $^{14}C_6$ = 40%); the unreacted allyl p-toluensulfonate showed only a small rearrangement ($^{14}C_3$ = 12%, estimated value (8)).

It can be concluded from these results that the coupling and the carboxylation reactions occur independently of the rearrangement of the unreacted allylic compound.

The complete rearrangement observed in the hexadienoic ester is consistent with the formation of π -allylic complexes as intermediates in the carboxylation reaction (1), since from the alternative hypothesis of rapidly rearranging σ -allylic intermediates rearrangement of unreacted allyl acetate would be expected. Actually, a rearrangement of only 10% was observed, in spite of the high temperature and the use of methanol as solvent.

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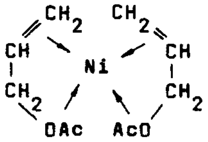
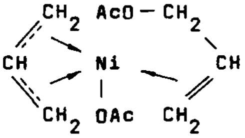
8) In order to obtain a product easily separated and purified as needed for ozonization, the unreacted p-toluensulfonate was transformed with NaBr in allyl bromide (2). This latter showed a $^{14}C_3$ = 20% rearrangement, which is inclusive of that occurring during the reaction between p-toluensulfonate and sodium bromide.

If this is correct, a π -allylic bond should also be formed in the coupling reaction. Yet, the partial rearrangement found in the hexadiene formed suggests that the two allylic halves do not give a symmetrical intermediate according to the following scheme :



Since one of the two molecules should form a π -allylic bond as shown for the hexadienoic ester, fission of the C-O bond in the other should occur to some extent without rearrangement, during the reaction with the π -allylnickel half. In other words, to account for the uncomplete rearrangement observed, <u>a non symmetric transition state should be postulated</u>, as already noted on stereochemical grounds for the coupling reaction of halocrotonic esters and nitriles (9) :



We thank Prof. A. Quilico for his interest in this work.

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9) G.P. Chiusoli and G. Cometti, Chimica e Industria 45, 404 (1963).