



yellow "zero-valent" complex **2**, R = allyl, in a trap cooled by liquid nitrogen.<sup>3</sup> Even higher yields (>80%) of this product can be obtained by the addition in portions of triethylenetetramine to the solutions of **1** and nickel bromide during the disproportionation reaction. Confirmation of the bis( $\pi$ -allyl) structure **2** for the volatile substance was obtained from the mass spectrum<sup>4</sup> and from the comparison of its nmr<sup>5,6</sup> spectrum with that of **2** derived from the reaction of allylmagnesium halide with nickel(II) halide.<sup>1</sup> The yellow "zero-valent" complex **2**, R = methallyl, was similarly obtained from **1**, R = methallyl, and identified by its mass<sup>7</sup> and nmr<sup>6,8</sup> spectra and also by its chemical properties, including (1) conversion to methallyl iodide with excess I<sub>2</sub>, (2) reaction with nickel bromide to form **1**, R = methallyl, and (3) reaction with allyl bromide in dimethylformamide to give a mixture of biallyl, allyl-methallyl, and bimethallyl by allylic coupling.<sup>2</sup>

The extension of this technique for the conversion of  $\pi$ -allylnickel(I) complexes of type **1** to bis( $\pi$ -allyl)-nickel(0) complexes is clearly limited by the requirement that the latter possess substantial volatility and therefore low molecular weight. The medium used is also critical. For example, only small amounts of **2**, R = allyl or methallyl, can be distilled from solutions of **1** in tetraglyme, presumably because the equilibrium is less favorable to disproportionation in that medium.<sup>9</sup> The transformation **1**  $\rightarrow$  **2** can be achieved much more generally by the use of a suitable reducing agent, e.g., zinc-copper couple. The allyl and methallyl complexes **2** can be obtained in >90% yield by reaction with an excess of zinc-copper couple<sup>10</sup> (granules) at 25° in hexamethylphosphoric amide or dimethylformamide at 0.01 mm by collection of the volatile product in a liquid nitrogen cooled trap. The nonvolatile bis( $\pi$ -allyl)nickel complexes **3-5** have been obtained (in yields of 60-80%) simply by reduction of the corresponding  $\pi$ -allylnickel(I) complexes using zinc-copper couple under 1 atm of argon and isolation by extraction with pentane after addition of a small amount of water.<sup>11</sup>

The complexes **3-5** were characterized by their chemical properties, including protonation to R-H with *p*-toluenesulfonic acid and allylic coupling *via* R-I to R-R using 1 equiv of I<sub>2</sub>, and by their reaction with CO which produced R-R from **3** and mixtures of R-R and RCOR from **4** and **5**.

(3) Some solvent codistills with **2**, the amount being smallest with hexamethylphosphoric amide, the least volatile of these solvents. Solvent-free **2** can be obtained by a redistillation of the product obtained using hexamethylphosphoric amide.

(4) See G. Wilke and B. Bogdanović, *Angew. Chem.*, **73**, 756 (1961).

(5) J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc.*, 423 (1967).

(6) H. Bönemann, B. Bogdanović, and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **6**, 804 (1967), report that solutions of bis( $\pi$ -allyl)-nickel contain two geometrical isomers in the ratio 3:1. In the present work a 2.5:1 ratio of these forms was found by nmr analysis in benzene as solvent.

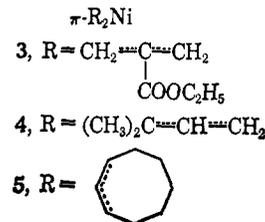
(7) The mass spectra of the complexes **2**, R = allyl, and **2**, R = methallyl, show molecular ion peaks corresponding to <sup>68</sup>Ni and <sup>60</sup>Ni isotopes in a ratio 2.5:1 as well as fragments corresponding to RNi<sup>+</sup>, RNiH<sup>+</sup>, and (RR - H)<sup>+</sup>.

(8) Two isomeric forms of **2**, R = methallyl, in the ratio 2.1:1 (in C<sub>6</sub>H<sub>6</sub>) were indicated by the nmr spectrum (*cf.* previously reported<sup>6</sup> ratio of 2.3:1).

(9) The most critical solvent interaction in controlling the position of equilibrium **1** is likely the coordination and solvation of nickel(II) bromide.

(10) E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).

(11) Because of the extreme sensitivity of the bis( $\pi$ -allyl)nickel complexes to oxygen, air must be rigorously excluded during these experimental operations.



The formation of nickel(0) complexes by reduction of  $\pi$ -allylnickel(I) halide complexes with zinc is apparently the result of the direct interaction of zinc with the nickel(I) complexes rather than the displacement of equilibrium **1** by reduction of nickel bromide by zinc. We have been able to demonstrate that nickel bromide is not reduced by zinc-copper couple in dimethylformamide under the conditions which allow the conversion of nickel(I) to nickel(0) complexes.

The synthetic route to bis( $\pi$ -allyl)nickel derivatives by the reduction of  $\pi$ -allylnickel(I) halide complexes is more convenient than the method<sup>1</sup> based on the reaction of an allylic Grignard reagent with a nickel halide and also allows the synthesis of complexes such as **3** which contain functional groups that would interfere with the Grignard synthesis. The intermediate  $\pi$ -allylnickel(I) complexes are easily obtained in high yield from the reaction of nickel carbonyl with an allylic halide.<sup>12-14</sup>

(12) E. J. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2755 (1967).

(13) In connection with the role of bis( $\pi$ -allyl)nickel compounds in allylic coupling reactions it has been observed that, although facile coupling occurs with allylic halides,<sup>2</sup> the reaction with *nonallylic* halides<sup>12</sup> such as iodobenzene or cyclohexyl iodide is much slower with the zero-valent complexes **2** than with the nickel(I) complexes **1**.

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### Stereoelectronic Factor in the Chloranil Dehydrogenation of Cannabinoids. Total Synthesis of *dl*-Cannabichromene<sup>1,2</sup>

Sir:

We wish to present evidence suggesting that the dehydrogenation of hydroaromatic compounds by chloranil can be added to the list of reactions in which stereo-electronic factors have been found to influence the course, stereochemistry, and rate. Among these are enolization, protonation and bromination of enols,<sup>4</sup> bimolecular eliminations,<sup>5</sup> oxidation of allylic alcohols by manganese dioxide,<sup>6</sup> dichlorodicyanoquinone,<sup>7</sup> and

(1) Hashish. XII. For part XI see R. Mechoulam, P. Braun, and Y. Gaoni, *J. Am. Chem. Soc.*, **89**, 4552 (1967).

(2) The term *cannabinoids* has been proposed<sup>3</sup> for the group of C<sub>21</sub> compounds typical of and present in *Cannabis sativa* L., as well as for their analogs and transformation products.

(3) R. Mechoulam and Y. Gaoni, *Fortschr. Chem. Organ. Naturstoffe*, **25**, 175 (1967).

(4) For example, E. J. Corey and R. A. Sneed, *J. Am. Chem. Soc.*, **78**, 6269 (1956), and earlier papers; R. Villotti, H. J. Ringold, and C. Djerassi, *ibid.*, **82**, 5693 (1960); S. K. Malhotra and H. J. Ringold, *ibid.*, **86**, 1997 (1964); *cf.* G. Stork and S. D. Darling, *ibid.*, **86**, 1761 (1964).

(5) For a recent summary see E. L. Eliel, N. L. Allinger, S. T. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 291.

(6) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961); G. Stork, *Alkaloids*, **6**, 223 (1960).