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Coupling of Allylic Halides by Nickel Carbonyl

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Representative allylic chlorides have been coupled in excellent yields by nickel carbonyl in methanol as solvent. The diene hydrocarbons produced are richer in straight-chain (terminally coupled) product than those generally produced by metal coupling reactions, but isomeric allylic chlorides yield identical mixtures of isomeric dienes. The experimental facts indicate that the mechanism of the nickel carbonyl coupling reaction may involve free allyl or substituted allyl radicals.

Nickel carbonyl reacts with an allylic halide in a Wurtz-type reaction[1] producing in excellent yields mixtures of diene hydrocarbons related to the original halide by allylic rearrangement (reaction 1). In this respect nickel carbonyl is similar to metals which have been used for coupling—through organometallics. The hydrocarbons produced by coupling of allylic halides by nickel carbonyl contain somewhat more straight-chain or terminally coupled products than those generally produced by metallic coupling agents.[2] Thus, as herein described, 1-chloro-2-butene and 3-chloro-1-butene produced 78 ± 2% 2,6-octadiene and 22% 3-methyl-1,5-heptadiene in yields of 74 and 81%, respectively. None of the doubly branched product, 3,4-dimethyl-1,5-hexadiene, was found. Similarly, 1-chloro-5-methoxy-2-pentene and 3-chloro-5-methoxy-1-pentene coupled with nickel carbonyl to produce 79–82% yields of dimethoxydecadienes which consisted principally of 1,10-dimethoxy-3,7-decadiene. 1-Chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene (the isoprene hydrochlorides) coupled in 81 and 70% yields, respectively, and the hydrocarbon mixtures contained about 65% 2,7-dimethyl-2,6-octadiene and 35% 3,3,6-trimethyl-1,5-heptadiene. None of the bitertiary product, 3,3,4,4-tetramethyl-1,5-hexadiene, could be found.

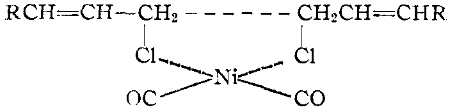
$$\left.\begin{array}{l}\mathrm{2RCH{=}CH{-}CH_2Cl}\\ \quad\text{or}\\ \mathrm{2RCHCl{-}CH{=}CH_2}\end{array}\right\} + \mathrm{Ni(CO)_4} \longrightarrow$$

$$\left\{\begin{array}{c}\mathrm{RCH{=}CH{-}CH_2{-}CH_2{-}CH{=}CHR}\\ +\\ \mathrm{RCH{=}CH{-}CH_2{-}CHR{-}CH{=}CH_2}\end{array}\right. \qquad (1)$$

$$+ \mathrm{NiCl_2} + 4\mathrm{CO}$$

The mechanisms of coupling of allylic derivatives by metals or of reactions of allylic derivatives with organometallics appear, in general, to involve resonating ion intermediates,[3] transient coördinate intermediates,[4,5] or radicals,[5] all of which allow allylic rearrangement.

From available data it is difficult to decide on one of these mechanisms for coupling by nickel carbonyl. The coupling reaction of nickel carbonyl differs from the organometallic coupling in one important respect, namely, that alcohols may be used as solvents; yet no appreciable amount of reaction with the solvent occurs. For this reason and by analogies with other metal carbonyl reactions, we are inclined to believe that the reaction mechanism does not involve ionic intermediates, *e.g.*, carbonium ions or carbanions, as have been proposed for organometallic coupling reactions,[5a] since these ions should react with the solvent sphere and produce at least by-product amounts of ethers or monoölefins, respectively. A complex intermediate of the type I involving rearrangement of either starting allylic chloride isomer, facilitated by nickel carbonyl or nickel chloride, prior to reaction, appears unlikely. Thus, in an experiment intentionally carried to only 25% conversion of the starting 3-chloro-1-butene, unreacted chlorobutene was recovered as a mixture containing 80% 3-chloro-1-butene and 20% 1-chloro-2-butene, instead of the equilibrium mixture or a mixture identical with the composition of the coupled products. Furthermore, compared qualitatively to the speed of the coupling reaction, rearrangement of the allylic halide was much slower.



I

A free-radical mechanism seems most plausible. Identical mixtures of biallylic hydrocarbons would be expected from either allylic chloride since the allylic forms become indistinguishable in the free-radical R′·, possibly formed by equation 2.

$$\mathrm{R'Cl} + \mathrm{Ni(CO)_4} \longrightarrow \mathrm{R'\cdot} + \mathrm{\cdot NiCl} + 4\ \mathrm{CO}$$

Formation of radicals through organonickel halides seems unlikely in hydroxylic media.[6] The clean-cut character of this nickel carbonyl coupling is not incompatible with a free-radical mechanism. Analogous reactions indicate that coupling is characteristic of free-radicals in solution.[7] Coupling of radicals formed by equation 2 should be kinetically distinguishable from coupling through I; a kinetic study by gasometric methods is in progress.

Precautions in Handling Nickel Carbonyl.—This low-boiling liquid is extremly poisonous and

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(1) Belgian Patent 448,884 (1943), *C. A.*, **41**, 6576 (1947), describes the preparation of bimethallyl (2,5-dimethyl,1,5-hexadiene) from β-methallyl chloride.

(2) A. L. Henne and H. H. Chanan, THIS JOURNAL, **66**, 392 (1944); **63**, 3474 (1941); W. G. Young, J. D. Roberts and H. Wax, *ibid.*, **67**, 841 (1945).

(3) K. W. Wilson, J. D. Roberts and W. G. Young, *ibid.*, **71**, 2019 (1949); S. J. Cristol, J. R. Douglass, W. C. Overhultz and J. S. Meek, 117th National Meeting, A. C. S. abstr., p. 91.

(4) R. T. Arnold and S. Searles, THIS JOURNAL, **71**, 2021 (1949).

(5) (a) A. A. Morton and others, *ibid.*, **64**, 2240 (1942); (b) H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1009; (c) M. S. Kharasch, D. W. Lewis and W. B. Reynolds, THIS JOURNAL, **65**, 498 (1943), and other papers.

(6) The character of organonickel compounds is not known. None is listed, for example, by E. Krause and A. V. Grosse, "Die Chemie der Metallorganische Verbindungen," Borntraeger, Berlin, 1937.

(7) E. G. E. Hawkins, *Nature*, **166**, 69 (1950), showed that coupling was the major reaction of radicals produced by ferrous sulfate reduction of methylcyclopentane hydroperoxide. A. F. Bickel and W. A. Waters, *Rec. Trav. Chim.*, **69**, 1490 (1950), showed that fragments from decomposition of azobisisobutyronitrile undergo coupling predominantly.

inflammable. It was found expedient to weigh the liquid nickel carbonyl directly from Matheson Co. one pound cylinders, under a blanket of carbon monoxide, into a dropping funnel surrounded by ice in a beaker, which rested on the balance pan. This method avoided spontaneous flashing which frequently occurs when nickel carbonyl is exposed to air. Nickel carbonyl should be handled only in well-ventilated hoods and with adequate body protection.

Experimental

Coupling was carried out essentially according to reference 1 which describes the preparation of bimethallyl from methallyl chloride and nickel carbonyl in methanol. Solvent effects were scouted briefly, and coupling was found to occur in methanol and ether but not in petroleum ether.

Butenyl chlorides and isoprene hydrochlorides were prepared by low temperature addition of hydrogen chloride to butadiene and isoprene, respectively, and separation of the isomers by fractional distillation through a 3-foot Fenske column packed with glass helices. Methoxypentenyl chlorides were prepared by adding monochloromethyl ether to butadiene.[8] The physical properties of the samples used in coupling experiments are given in Table I and those of the hydrocarbon products isolated from coupling experiments in Table II.

TABLE I

PHYSICAL CONSTANTS OF ALLYLIC HALIDES STUDIED

Compound	B.p., °C.	Press., mm.	n_D
3-Chloro-1-butene	63	Atm.	1.4143(23.5°)
1-Chloro-2-butene	82	Atm.	1.4330(23.5°)
3-Chloro-3-methyl-1-butene	38–41	190	1.4189(21°)
1-Chloro-3-methyl-2-butene	71	200	1.4470(25°)
1-Chloro-5-methoxy-2-pentene	81–83	35	1.4498(28°)
3-Chloro-5-methoxy-1-pentene	60–62	39	1.4354(26°)

TABLE II

PHYSICAL CONSTANTS OF HYDROCARBONS ISOLATED[a]

	B.p., °C.		$n^{20}D$	
	This paper[b]	Reported[2]	This paper	Reported[2]
3-Methyl-1,5-heptadiene	112.5	111	1.4230[c]	1.4240
2,6-Octadiene	125	124.5	1.4300[d]	1.4336
3,3,6-Trimethyl-1,5-heptadiene	148–150	149.7	1.4368–1.4405	1.4391
2,7-Dimethyl-2,6-octadiene	162–164	168.6	1.4516–1.4556	1.4478

[a] The dimethoxydecadienes were not separated. See text. [b] Uncorrected. [c] 22.5°. [d] 23°.

Coupling of 1-Chloro-2-butene (Crotyl Chloride).—To a solution of 223 g. of 1-chloro-2-butene (2.5 moles) and 250 ml. of methanol, stirred at 25°, was added 260 g. of nickel carbonyl (1.5 moles, a 20% excess of calculated) over six hours, and the resulting solution stirred overnight. The off-gas was passed through cold traps and a hot (150°) tube, to decompose any entrained nickel carbonyl, and the resulting carbon monoxide metered. A total of 95.5 l. of gas was given off. The cold trap material was returned to the pot, giving another 3 l. off-gas: total yield of carbon monoxide 98.5 l. (4.0 moles, 80% yield, based upon 1-chloro-2-butene).

The reaction mixture was diluted with 500 ml. of water, and the hydrocarbon layer was separated, washed with water, dried over calcium chloride and analyzed by careful fractional distillation at 60–90/1 reflux ratio through a 4-ft. Podbielniak Hypercal column. Only 3-methyl-1,5-heptadiene (crotylmethylvinylcarbinyl), 30 ml. (22 ± 2% of total coupled products), and 2,6-octadiene (dicrotyl), 108 ml. (78 ± 2%), were found: yield of coupled products 138 ml., 103 g. (74%). The pot residue and column drainings from the Podbielniak were distilled through a modified Vigreux column to separate remaining 2,6-octadiene, b.p. 124–125°, $n^{26}D$ 1.4290, and this material is included in yield figures shown. Higher boiling products amounted to 11 ml.

No 3,4-dimethyl-1,5-hexadiene (di-methylvinylcarbinyl) was found as a coupled product of either butenyl chloride.

When 3-chloro-1-butene (methylvinylcarbinyl chloride) was coupled, only a 5% excess of nickel carbonyl was employed. The hydrocarbon mixture isolated was found to contain 79 ± 2% 2,6-octadiene and 21 ± 2% 3-methyl-1,5-heptadiene. In another experiment, 25% of the stoichiometric amount of nickel carbonyl was employed, and the products were fractionated through an all-glass still. The recovered halide was 80% 3-chloro-1-butene and 20% 1-chloro-2-butene. This shows that the reaction mixture is capable of effecting allylic rearrangement of the reacting halide.

The butenyl chlorides failed to couple with Raney nickel in boiling ether.

Coupling of Isoprene Hydrochlorides.—Coupling of 3-chloro-3-methyl-1-butene and of 1-chloro-3-methyl-2-butene were carried out as described above but, prior to Podbielniak precision analysis, the hydrocarbon products were vacuum distilled (70–80° at 60 mm.) to remove higher boiling by-products and nickel deposit which may have formed from any unreacted nickel carbonyl during isolation and distillation. The hydrocarbon mixture from 1-chloro-3-methyl-2-butene contained 62% 2,7-dimethyl-2,6-octadiene and 38% 3,3,6-trimethyl-1,5-heptadiene, while that from 3-chloro-3-methyl-1-butene contained 67 and 33% of the two hydrocarbons, respectively. The physical constants of these isolated products do not agree precisely with those reported.[2] Since we have no fragmental oxidative data, and infrared scanning proved uninformative in the absence of reference standards, we are unable to explain these discrepancies. However, for this reason we believe that the 5% spread in product compositions is not significant. No 3,3,4,4-tetramethyl-1,5-hexadiene was found among coupled products from either isoprene hydrochloride.

Coupling of Chloromethoxypentenes.—1-Chloro-5-methoxy-2-pentene and 3-chloro-5-methoxy-1-pentene were both coupled with nickel carbonyl as described above for butenyl chlorides. The dimethoxydecadienes formed were separated, distilled through a Vigreux column (b.p. 138–142° at 25 mm., $n^{25}D$ 1.4513), and scanned in the infrared to estimate the amounts of 1,10-dimethoxy-3,7-decadiene and branched-chain products present. The infrared absorption curves were identical and showed a large peak at 10.35 microns, but only very slight peaks at 10.90, 10.03 and 6.04 microns; therefore it was concluded that the major constituent of both samples of dimethoxydecadienes was 1,10-dimethoxy-3,7-decadiene. This was confirmed by hydrogenation of a sample over palladium catalyst, and oxidation of the resulting 1,10-dimethoxydecane with nitric acid to sebacic acid, m.p. (bar) 131–132°, in excellent over-all yield.

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[8] A. N. Pudovik and B. A. Arbusov, *C. A.*, **42**, 6311 (1948); W. S. Emerson, G. F. Deebel and R. I. Longley, *J. Org. Chem.*, **14**, 696 (1949).