Published on 01 January 1968. Downloaded by University of California - San Diego on 20/12/2016 11:43:39.

A Simple Method for the Carbonylation of Allylic Halides with Insertion of Acetylene

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A simple procedure for the preparation of methyl 2,5-dienoates from allyl halides, acetylene, carbon monoxide, and methanol at room temperature and atmospheric pressure, based on the formation in situ of the catalytic nickel complex from nickel chloride, is described. A manganese-iron alloy is used as reducing agent and thiourea is used as ligand for the formation of the complex. A mechanism involving a five-co-ordinated complex is proposed.

WE have previously 1,2 described the carbonylation of allylic halides with insertion of acetylene in the presence of nickel carbonyl or of a complex obtained by reducing nickel chloride with iron powder, in the presence of thiourea. We have further studied the last method in order to develop an efficient general procedure for the carbonylation of allylic halides to give methyl dienoates according to equation (1) (written for the simplest member of the series).

$$CH_{2}=CH_{2}\cdot CH_{2}CI + CH \equiv CH + CO + MeOH \longrightarrow CH_{2}=CH\cdot CH_{2}\cdot CH = CH\cdot CO_{2}Me + HCl \quad (1)$$
(I)

RESULTS AND DISCUSSION

Excellent results can be obtained if a sufficient concentration of the reactive intermediate is maintained in the reaction mixture by appropriately reducing nickel chloride in the presence of thiourea. The best reducing agents tried so far are powdered manganeseiron alloys containing more than 80% of manganese and no more than 1% of carbon. Commercial alloys containing 75-85% of manganese and 1-2% of carbon were also effective. In this way nickel chloride is reduced faster than by iron powder and can be used in a much smaller amount. Manganese alone can also be used, but its efficiency is decreased by its reactivity towards the solvent.

The reaction is carried out at room temperature and atmospheric pressure, simply by passing in acetylene and carbon monoxide while adding the allylic halide to a methanolic solution of nickel chloride and thiourea containing, in suspension, a powdered manganeseiron alloy and a neutralising agent for hydrogen chloride such as magnesium oxide. The necessary concentration of the catalyst is maintained by addition of small amounts of nickel chloride, thiourea, and manganese alloy.

Very small amounts of the ingredients which give rise to the catalytic intermediate are needed. Only ca. 1 g. of metallic nickel is required to produce 30 g. of methyl hexadienoate from allyl chloride, acetylene, and carbon monoxide according to equation (1).

Analogous allylic derivatives react similarly. Conversions are almost complete and yields are generally 70—80%. The products contain a *cis*-double bond conjugated with the carboxylic ester group.

The main by-products from allyl chloride are hexa-1,5-diene, but-3-enoate, 2-oxocyclopent-3-enylacetate 4-oxo-5-(2-oxocyclopent-3-enyl)valerate (II), (III), phenyl hexa-2,5-dienoate and S-allylisothiouronium chloride.



Based on the recently described³ beaviour of the five-co-ordinate halogeno(carbonyl)(triphenylphosphine)- π -allylnickel complexes and on the isolation of halogenobis(thiourea)- π -allylnickel and halogeno(thiourea)- π -allylnickel⁴ we suggest that the course of this reaction is determined by a five-co-ordinate nickel complex (ionised in methanol⁴) into which acetylene can be inserted as shown in the Scheme.

The complex (IV) can react with allyl chloride to give hexa-1,5-diene,5,6 with carbon monoxide to give but-3-enoate, and with thiourea to give S-allylisothiouronium chloride. These molecules are likely to occupy

¹ G. P. Chiusoli, Chimica e Industria, 1959, 41, 506.

² G. P. Chiusoli, S. Merzoni, and G. Mondelli, Chimica e Industria, 1964, 46, 743.

³ F. Guerrieri and G. P. Chiusoli, Chem. Comm., 1967, 781.

⁴ F. Guerrieri, Chem. Comm., 1968, 983.

⁵ G. P. Chiusoli and G. Cometti, Chimica e Industria, 1963, 45,

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the co-ordination site held in (V) by acetylene, before the reaction with the allyl group. At the stage (VI), cyclisation to a cyclopentenone ring, followed by uptake of carbon monoxide, yields (II). Cyclisation of (VI) to phenol and attack of the latter on another molecule of (VI) explains the formation of phenyl hexadienoate. Further reaction of the cyclopentenonylacetyl group derived from (VI) with acetylene and carbon monoxide, followed by hydrogenation of the double bond thus formed, gives (III).⁷

EXPERIMENTAL

A round-bottomed flask (5 l.) was equipped with a stirrer, a graduated dropping funnel, a hopper consisting of glass oxide (33 g.) were introduced, and then a solution of allyl chloride (126 g.), nickel chloride hexahydrate (10 g.), and thiourea (3 g.) in methanol (300 ml.), was added from the funnel during 5 hr.

After a few min. the absorption of gases began. More powdered alloy was added at hourly intervals (three portions of 2 g. and one of 4 g.). As soon as the absorption of gases had ended, the mixture, containing a small quantity of slurry, was filtered through a steel filter connected to a solid carbon dioxide trap, under nitrogen.

Methanol and volatile products were distilled off at atmospheric pressure and collected in a solid carbon dioxide trap. The residue was diluted with water (300 ml.), then acidified with sulphuric acid and extracted with ether and chloroform. The solvents were removed from the



tube (connected to the flask with a rubber tube sealed with a Mohr clip), a thermometer, a condenser cooled by ammonia, and an inlet tube for the gaseous mixture. The temperature was controlled by a water-bath. The composition of the gaseous mixture was adjusted with flowmeters. The rate of gas absorption was measured with flowmeters placed before and after the reaction flask.

Acetylene from calcium carbide and carbon monoxide from formic acid were used. The gaseous mixture of acetylene and carbon monoxide also contained oxygen (0.15%), nitrogen (2-3%), and carbon dioxide (0.5-1%).

Allyl chloride (Shell) was 98.5% pure. The powdered Mn-Fe alloy had the composition: Mn, 79; Fe, 16; C, 1.46; Si, 0.8; Ni, 0.2% (particle size 0.025-0.040 mm. diam.).

Gases were analysed by the Orsat method and by g.l.c. [dimethylsulpholan on Chromosorb W 30-60 mesh (20:80) (6 m.) at 25° , carrier hydrogen, on Perkin-Elmer 154 and F11 instruments.

The distillation fractions were analysed by g.l.c. on columns K and P; K: Carbowax 1500 on Chromosorb W 30-60 mesh (20:80) (2.5 m.), 60°, carrier helium; P: succinate polyester of diethylene glycol on Chromosorb W 80-100 mesh (15:85) (2 m.) 110°, carrier helium.

The purity of the products was also estimated by u.v., i.r., and n.m.r., spectroscopy.

Methyl Hexa-2,5-dienoate (I).—The apparatus was swept out with carbon monoxide and acetylene, and methanol (1.5 1.) was introduced into the flask. The well stirred solvent was saturated at 25° with carbon monoxideacetylene (average composition 53:47); this gaseous mixture was introduced during the reaction at such a rate as to keep the rate of flow out of the apparatus approximately constant (average effluent rate 2 1./hr.).

From the hopper, powdered alloy (10 g.), nickel chloride hexahydrate (10 g.), thiourea (1.5 g.), and magnesium

combined extracts, and the residue was distilled under reduced pressure in a column connected to a solid carbon dioxide trap. Methyl hexadienoate was collected at $47-50^{\circ}/13$ mm./, and the residue was flashed at 1 mm. and 50° .

The aqueous solution contained metallic chlorides and S-allylisothiouronium chloride. The latter was identified by transformation into nickel allyl sulphide.

The yield of methyl hexadienoate $(152 \cdot 3 \text{ g.})$ was $74 \cdot 5\%$, based on reacted allyl chloride. Recovered allyl chloride 0.25 g., hexa-1,5-diene $2 \cdot 2 \text{ g.}$, methyl but-3-enoate $2 \cdot 6 \text{ g.}$, residue $25 \cdot 5 \text{ g.}$

The methyl hexadienoate obtained showed the following composition on g.l.c. (column P): 2-cis-5 98.4, 2-trans-5 0.4, 3-trans-5 1.15%. Slight changes in these values were found, owing to changes in the distillation conditions.

From the distillation residue methyl 2-oxocyclopent-3-enylacetate $(60-65^{\circ}/0.1 \text{ mm.})$ (13 g.) could be obtained. Methyl 4-oxo-5-(2-oxocyclopent-3-enyl)valerate [b.p. 100-110° (bath)/0.001 mm.], phenyl hexa-2,5-dienoate, and unidentified products were left behind.

The same procedure has been employed successfully for other allylic halides. But-2-enyl chloride gives methyl hepta-2,5-dienoate (73.5%), and 2-methylallyl chloride gives methyl 5-methylhexa-2,5-dienoate (77.5%).

These preparations were carried out on a smaller scale (1/5) than that of methyl hexadienoate, with the proportion of thiourea used increased by 60%.

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

[8/892 Received, June 27th, 1968]

⁷ G. P. Chiusoli and L. Cassar, Angew. Chem. Internat. Edn., 1967, 6, 125.