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Reactions of Allenes III. Reactivities of Allenes in Comparison with Acetylenes and Olefins

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The reactivities of allenes in comparison with acetylenes and olefins were discussed on their carboxylation, polymerization, and epoxidation reactions. No reaction of allene examined here proceeded more smoothly than that of olefin or acetylene, that is, allene had an intermediate reactivity between acetylene and olefin. The merits to use allene as a raw material for synthetic purposes seem almost defined to the reactions of 1, 2 bifunctional additions and ring formations.

INTRODUCTION

It may be thought that allene $CH_2=C=CH_2$, having a peculiar chemical structure, is an interesting raw material for various synthetic chemicals. The authors have been examined its carboxylation, polymerization, and epoxidation reaction for several years. In this paper** the results of these reactions were described, and in addition, the comparison of reactivities of methylacetylene, allene, and propylene was also discussed.

In view of its reactivity and/or selectivity, however, we found allene is not yet a favourable synthetic material for these reactions at least.

EXPERIMENTAL

Nickel carbonyl, allene, and other gaseous materials were obtained commercially. Solvents were purified by the conventional methods. Other reagents were prepared according to literatures.

Carboxylation reactions[1~4] were carried out in magnet-rotating type stainless steel autoclaves at the specified conditions. Carbon monoxide was supplied continuously at a constant pressure. The products were analyzed by the gas-liquid chromatography (GLC).

Polymerization[5] was performed similarly in an autoclave in the atomosphere of nitrogen. The yield of polymer was obtained from the weight of residue remained after evaporating the solvent under the reduced pressure.

Epoxidation was performed in a glass vessel under atomospheric pressure. The extinction of the peracid was followed by the iodometry, and the product was examined by GLC of the reaction mixture and the i. r. spectrum of the

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** A part of experimental results was already published in the separate papers.[1~5] solvent-removed material.

RESULTS AND DISCUSSION

Allene consists of two sp^2 hybridized carbons and a sp hybridized carbon, which shows it is a compound having both characteristics of olefin and acetylene. The extened Hückel[6] calculations show atomic bond populations of carbon-carbon bonds of ethylene, allene, and acetylene are 1.259, 1.368, and 1.948, respectively. These figures suggest allene has the intermediate characters between olefins and acetylenes. Next, atomic populations for these hydrocarbons are as follows. These figures, in turn, suggest that with a proper selection of reaction conditions,

$$\underset{4.244}{H_2C{=}CH_2} \qquad \underset{3.818}{CH_2}{=}\underset{4.397}{C}{=}CH_2 \qquad \underset{4.162}{HC{\equiv}CH}$$

allenes might be more reactive than acetylenes and olefins.

The results obtained here support the former situation. The latter situation is observed for the reaction of allene with some transition metals such as palladium.[7~9]

Carboxylation reaction. The reactivities of hydrocarbons for carboxylation must be compared by the rate of the reaction. The rate equation for carboxylation by nickel carbonyl was designated as follows:[2] $r=k$ (Cat) (H.C) (Acid)/$(P_{co})^n$, where (Cat) shows the catalyst concentration; (H. C), the reactant concentration; (Acid), the water and acid concentration; and P_{co} shows the carbon monoxide pressure charged in the vessel ($n=2$ or higher). To compare the reactivity of allene with that of methylacetylene in Table 1, the rate value of allene must be multiplied by 4, that equals 52, which is comparable to or a little smaller than that of methylacetylene. The reactivity of propylene was so low that the catalyst decomposed before the reaction mixture reached the specified temperature (Run 3). The products in Run 4 was due to mere esterification of the added acid.

The results for C_6 hydrocarbons are shown in Table 2. The difference in reactivity between allene and acetylene became pronounced, and 1, 2-hexadiene was not carboxylated virtually at the conditions at which 1-hexyne reacted smoothly. By the existence of some amount of methyl acetylene, the hexadiene gave products a little. 1-Hexene barely gave some products only in the presence of a large amount of acid and water. The low reactivities of alkyl substituted hydrocarbons would result from steric and inductive effects of substituents, which accords with the product distribution from hexadiene. The decreases in the reactivities of each unsaturated hydrocarbons would have made the difference between acetylene and allene pronounced.

Concerning the selectivity for the main reaction which was observed from the product distribution, allene was far less selective for carboxylation than acetylene. Under proper conditions, methylacetylene gave carboxylation products in a 92.1 % yield based on the acetylene[2] used, and propylene gave a 97.5 % yield of acids based on the olefin[4] consumed. Allene, however, gave only a 63.4 % yield of carboxylated products.[1] The lower selectivity of allene would be a main handicap for its use as a synthetic raw material. The accompanying material

Table 1. Comparison of Allene, Methylacetylene, and Propylene for the Carboxylation Reaction.[a]

Run No.	Hydrocarbon (g)		Methanol (ml)	Nickel Carbonyl (g)	H_2O (ml)	CO (atm)	Temp (°C)	Time (hr)	Initial[b] Rate	Products[c] MMA (%)	MAA (%)	MC (%)	HB (g)	Rd (g)
1	methylacetylene	8.1	70	2.0	10	12	180	2.7	56	56.5	11.6	6.5	—	1.4
2	allene	8.2	140	2.0	20	12	180	5.5	13	38.1	9.7	trace	1.1	3.6
3	propylene	2.3	80	2.0	20	10	250	—	—			ester 0		
4[d]	propylene	12.0	45	2.0	8	32	280–290	6.0	—			ester 12(%)		

a) The reaction was carried out in the presence of 0.05-0.1 g hydroquinone in a 300 ml (1, 2) and 200 ml (3, 4) autoclaves.
b) Adsorption of CO/hr in per cent.
c) MMA; methyl methacrylate, MAA; methacrylic acid, MC; methylcrotonate, HB; high boiling material, Rd; tar. All yields were calculated based on the hydrocarbons charged.
d) Isobutyric acid (2 ml) was added.

Table 2. Comparison of C_6 Hydrocarbons for the Carboxylation Reaction.[a]

Run No.	Hydrocarbon (g)	Solvent (ml)	Nickel Carbonyl (g)	CO (atm)	Temp (°C)	Time (hr)	Product[b]			
5	1-hexyne 6.0	n-BuOH 50 AcOH 3 H_2O 2	2.0	10	150	2.2	A_1 55.1	A_2 6.2	E_1 21.6	E_2 6.8
6	1, 2-hexadiene 12.6	MeOH 50 AcOH 3 H_2O 2	2.0	10	190	4.7	MMH 3.2	MBP 0.5	HBM (g) —	Polymer[d] ○
7[c]	1, 2-hexadiene 6.0	MeOH 50 AcOH 3 H_2O 2	2.0	10	150	3.5	MMH 12.0	MBP 2.6	HBM (g) 5.3	Polymer[d] ×
8	1-hexene 10.0	THF 25 H_2O 25 i-BA[f] 10	3.6	15	190–200	7.0	acid[e] 12			

a) The reaction was carried out in the presence of 0.1 g hydroquinone in a 200 ml autoclave.
b) A_1; α-butylacrylic acid, A_2; β-butylacrylic acid, E_1; n-butyl α-butylacrylate, E_2; n-butyl β-butylacrylate, MMH; methy 2-methyl-1-hexenoate, MBP; methyl 2-butylpropenoate, HBM; high boiling material. Yields were per cent based on hydrocarbons used unless otherwise specified.
c) Methylacetylene was added (3.0 g). d) Presence or absence of a solid precipitate; ○: present, ×: absent.
e) Acid was determined by titration. f) Isobutyric acid.

here was tar or/and solid polymer. The latter was obtained in a large amout especially when the carboxylation did not proceed smoothly. The polymer obtained in large quantities in Run 6 disappeared when methylacetylene was added and the carboxylation reaction became more smooth (Run 7). Without methylacetylene, much polymer was obtained also at 150°C[1] using 3 g of hexadiene. The reactivity of methylacetylene for polymerization was, as described later, not inferior to allene. Therefore, it might be considered that the inhibition of polymerization by methylacetylene appears not to arise from the result of such a mere saturation of coordination site on the metal as was suggested for inhibition of polymerization by carbon monoxide.[5] These results suggest that both carboxylation and polymerization, which proceed on the metal catalyst, would not include the same intermediate.

Considering the coordination of the three C_3 hydrocarbons examined here to nickel(0), π^* levels of hydrocarbons (in e. v.) become lower in the following order,[10,11]

$$\begin{gathered} CH_3CH{=}CH_2\ 2.7 \ll CH_2{=}C{=}CH\text{-}C_2H_5\ 4.1 < \\ CH_2{=}C{=}CH_2\ 4.5 \leqq CH_3C{\equiv}CH\ 4.9 \end{gathered}$$

which shows the increasing ability to accept π back bonding. Alkyl substituted allene has the higher π^* level than allene. As zero valent nickel has a relatively small ionization potential compared with other group VIII metals,[12] it seems easy for nickel(0) to donate the electron back to the ligand. These discussions leaded us to speculate that, in the intermediate (or transitional) metal complex coordinated with these hydrocarbons, nickel would have a relatively higher oxidation state in the complex of acetylene, and under the same conditions, have a lower oxidation state in that of propylene. From the results in Runs 6 and 7, it was assumed that, for carboxylation, a more highly oxidized nickel would be needed than that for polymerization. The oxidation state effective for carboxylation would be reached easily with methylacetylene, but it becomes more difficult with allene, and most difficult with propylene. The above explanation was well in accordance with the experimental results. Also it is consistent with the results of the kinetic study for the carboxylation reaction of methylacetylene that the rate determining step might be the reaction of a hydrocarbon with an organometallic compound. The results described above are summarized as follows; a) the reactivities of the three C_3 unsaturated hydrocarbons for carboxylation reaction were decreasing in the order, methylacetylene≳allene≫propylene, b) a side reaction (polymerization) was pronounced for allene relatively to propylene and methylacetylene.

Table 3. Polymerization with $NiBr_2\ (P\phi)_3)_2$(a) Cat.; 0.2 mmole, Benzene; 30 ml, N_2

Hydrocarbon (g)		Temp (°C)	Time (hr)	Conversion (%)
methylacetylene	3.5	75	6.0	31
allene	3.4	75	6.0	11
propylene	8.0	100	6.0	0

a) The reaction was carried out in a 200 ml autoclave with rotation of 150 rpm.

Polymerization. Comparison of the three C_3 hydrocarbons for polymerization by the catalysis of $NiBr_2(P\phi_3)_2$ was attempted. The results were summarized in Table 3.

Methylacetylene and allene polymerized smoothly at a relatively low temperature, but propylene did not polymerize even at 100°C. In this case the catalyst was a complex of highly oxidized nickel(II), and the discussions described in the preceding section does not hold good. It was suggested from the experiments using the catalysts with various halogen atoms$^{5),10)}$ and mirror formation experiments$^{5)}$ that the active species for the polymerization contained nickel in a considerably low oxidation state. The reduction might proceed *via* metal-halogen cleavage and subsequent formation of metal-haloalkenyl or -haloalkyl bond and this was inferred from the existence of halogen in the polymer.$^{5),13)}$ Then the difference between the metal-carbon bonds becomes important. A σ-alkenyl or a π-allyl complex is a more stable than a σ-alkyl complex, owing to the ability of ligands to accept back donation. The low reactivity of propylene would be attributable to this instability.

Epoxidation. Epoxidation of allene with perbenzoic acid was attempted and the reaction conditions are listed in Table 4.

Table 4. Reaction Conditions of Allene and Perbenzoic Acid.

Perbenzoic acid (g)	Solvent (ml)	Allene (g)	Temp (°C)	Time
49.2	Bz 950	10.8	15	137 hr
16.0	Bz 100	12.5	5	3 day
14.5	Bz 100	3.9	0	20 hr
19.4	$CHCl_3$ 150	11.0	5	4 day
23.0*	$CHCl_3$ 120	9.0	3	4 day

* contained 0.15 g of iodine.

Although ethylene$^{14)}$ and propylene$^{15)}$ were epoxidized easily at a relatively low temperature, allene did not react under such conditions as described above. No product was detected by GLC (20 % PEG 6000, 2.5 m at 85°C and 30 % DOP, 4 m, at 85°C) and the solid obtained by evaporation of solvents showed the same i. r. adsorptions as those of perbenzoic acid. The reaction is considered to proceed *via* electrophilic attack by peracid oxygen to the substrate, and the results show that allene is less reactive than propylene for such a reaction.

As has been discussed, it is difficult that higher reactivity and/or selectivity is obtained for allene than for methylacetylene or propylene in the reaction catalyzed by metal complexes or such electrophilic reaction as epoxidation, and this imposes a heavy burden upon the use of allene as a synthetic raw material. In spite of these defects the specific structure of cumulated double bonds would attract the ceaseless attention of synthetic chemists. In other words, the superiority of methylacetylene to allene is undeniable for usual Markownikoff type additions even with an intervention of a step of rearrangement from allene to methylacetylene. But the additions of bifunctional groups (the simplest reaction might be halogenation) or 1, 2- and 1, 4-cyclic addition reactions remain to be investigated.*

In addition, allene produces various stable complexes by the reactions with transition metals,⁽⁷~⁹⁾ which shows that it may be possible to isolate the intermediate or a complex which gives some informations on the intermediate for the reaction catalyzed by transition metals. This might suggest a possible feature of allene chemistry.

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* The Diels Alder reaction of allene with isoprene gave mainly metha directing products.⁽¹⁶⁾