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RHODIUM CATALYSED CYCLOPROPENATION OF ACETYLENES

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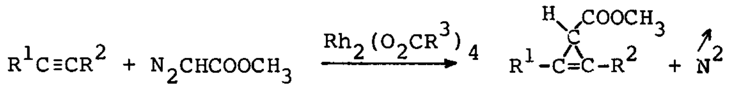
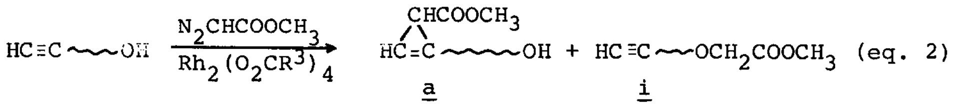
Cyclopropenes constitute a highly attractive class of strained molecules with interesting chemical properties and potential biological activity. Unfortunately, except in some rare cases, there is no straightforward general method for their synthesis. For example, the direct addition of carbenes to acetylenes does not give satisfactory yields with the ordinary copper-catalysed decomposition of diazocompounds, especially when monosubstituted acetylenes are concerned. (1)

In previous notes, we have already reported on the high efficiency of rhodium (II) carboxylates as catalysts for the cyclopropanation of alkenes (2) and insertion of carbenes into various X-H bonds. (3)

We will now report (Tables I, II) some characteristic results indicating the remarkable effectiveness of these rhodium carboxylates for the cyclopropenation (eq. 1), together with some observations concerning the control of the relative reactivities of a triple bond against an alcohol group in intramolecular competitions (eq. 2)



$$R^1C\equiv CR^2 + N_2CHCOOCH_3 \xrightarrow{Rh_2(O_2CR^3)_4} R^1\text{-}\overset{\overset{H\diagdown\ \diagup COOCH_3}{C}}{C{=}C}\text{-}R^2 + N^2\nearrow \qquad \text{(eq. 1)}$$



$$HC\equiv C\sim\sim OH \xrightarrow[Rh_2(O_2CR^3)_4]{N_2CHCOOCH_3} \underset{\underline{a}}{\overset{CHCOOCH_3}{HC{=}C}\sim\sim\sim OH} + \underset{\underline{i}}{HC\equiv C\sim\sim OCH_2COOCH_3} \qquad \text{(eq. 2)}$$

It is readily apparent (Table I) that *steric hindrance of the substituent* R^1 on the triple bond does not significantly influence the overall yield in cyclopropenes, whereas polar groups decrease it drastically (5, 6, 10). This is related to a lower stability of the corresponding cyclopropenes, at least in the case of (6) and (10) which rearrange easily.

An increase in the *electronegativity of the counter ions* of the catalyst also drastically lowers the yields (1, $R^3 = CF_3$); in particular, the latter system promotes the polymerization of the cyclopropenes.

The *regioselectivity* in the intramolecular competitions with various acetylenic alcohols (Table II) seems directed by a higher sensitivity to steric hindrance of the insertion reaction versus cyclopropenation; but it depends also markedly on the electronegativity of the R^3 group of the catalyst (Table III) : here again polymerization decreases the yield of the cyclopropene (23) when a CF_3 group is present.

The present results are best explained by a bimolecular carbenoïd mechanism, as the more nucleophilic functional group (OH) is preferentially attacked whereas the competition olefin-triple bond is poorly selective (8). These results agree in fact with our previous observations on competitive cyclopropanation and insertion reactions. (4)

Table I

Cyclopropenation of $R^1C\equiv CR^2$ (10 mmoles) by $N_2CHCOOCH_3$ (4 mmoles). Catalyst : 0,05 mmole. T : 25°C. No solvent.

	R^1	R^2	R^3(catalyst)	Yield (%)
(1)	n-C_4H_9	H	CH_3	84
	n-C_4H_9	H	$t_1C_4H_9$	70
	n-C_4H_9	H	CF_3	$0^{a)}$
(2)	t-C_4H_9	H	CH_3	86
(3)	Cyclohexyl	H	CH_3	80
(4)	C_6H_5	H	CH_3	$0^{a)}$
(5)	CH_3COOCH_2	H	CH_3	40
(6)	CH_3OCH_2	H	CH_3	$46^{b)}$
(7)	C_2H_5O	H	CH_3	$0^{c)}$
(8)	$CH_2=C(CH_3)$	$H^{d)}$	CH_3	$17 + 16^{e)}$
(9)	C_2H_5	C_2H_5	CH_3	68
(10)	CH_3OCH_2	CH_3OCH_2	CH_3	$38^{f)}$

a) polymers are present, formed from the reactive intermediate cyclopropene : in fact, 80 % of the phenylacetylene (calculated on the diazoester) are consumed after reaction.

b) rearranged quantitatively to $CH_3OCH_2-\Delta-COOCH_3$ in the presence of the catalyst.

c) the starting material polymerized at 10°C in the presence of the catalyst.

d) <u>inter</u>molecular competition between 1-hexyne and 1-octene gives 36 % cyclopropene and 16 % cyclopropane. (3)

e) the two cycloaddition products are detected by analytical GLC and spectroscopy (i.r. and n.m.r.) of the mixture but attempt to isolate them by preparative GLC gave essentially the dimers (mass spectroscopy : m/e = 276, expected for $C_8H_{10}O_2$: 138).

f) the allene $CH_2=C=C(CH_2OCH_3)CH(OCH_3)CO_2CH_3$ (yield : 8 %) probably formed by the propargylic rearrangement of an o-ylid intermediate, (6), is also detected.

<u>Table II</u>

Competitive intramolecular insertion-cyclopropenation of acetylenic alcohols (conditions: see Table I).

	Substrate	Total	Yield (7)		Ratio i/a
			Insertion	Addition	
(<u>11</u>)	propargyl alcohol	72	60	12	5,0[b)]
(<u>12</u>)	3-butyn-1-ol	69	50	19	2,6[b)]
(<u>13</u>)	1-pentyn-3-ol	75	54	21	2,6
(<u>14</u>)	3-methyl-1-pentyn-3-ol	73	37	36	1,0
(<u>15</u>)	1-ethynylcyclohexan-1-ol[a)]	22	10	12	0,8
(<u>16</u>)	4-methyl-1-pentyne-4-ol	54	25	29	0,9
(<u>17</u>)	ethanol +1-hexyne(1:1)	98	74	24	3,0[b)]

a) T = 50°C, b) comparison of these three values shows that the mutual intramolecular interaction between both groups disappear when they are separated by two C-atoms.

Table III

Influence of the catalyst on the competitive insertion-cyclopropenation reactions

	$Rh_2(O_2C\underline{R}^3)_4$	pKa of R^3COOH				$HC{\equiv}C-CH_2OH$		
			i	a	i/a	i	a	i/a
(<u>18</u>)	t - butyl	5,06	24	29	0,8	53	11	4,8
(<u>19</u>)	adamantyl	-	11	17	0,6	52	12	4,3
(<u>20</u>)	methyl	4,76	10	12	0,8	60	12	5
(<u>21</u>)	methoxy	3,53	16	14	1,1	-	-	-
(<u>22</u>)	menthoxy	-	-	-	-	59	4	14,7
(<u>23</u>)	trifluoromethyl	0,25	16	5	3,2	40	3	13,3

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5) The reported cyclopropenes have been identified from i.r. ($HC\overset{\Delta}{=}C$: 3200 cm^{-1}, 1800-1900 cm^{-1}), and n.m.r. spectra (: Ha : 6,2-6,4 ppm, Hb : 2 ppm (δ) J =2cps) and by comparison with reported data (M. Vidal, J.L. Pierre, P.Arnaud, Bull. Soc. Chim. Fr. 2864 (1969). M. Vidal, F. Massot, P. Arnaud, Compt. rend. Acad. Sc. (Paris) <u>268</u>c, 423, (1969).
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7) The reported products (<u>a</u> and <u>i</u>) have been identified after catalytic hydrogenation.

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