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Synthetic Reactions by Complex Catalysts. XXXIII. Synthesis of Vinylcyclopropane Derivatives by Copper Isonitrile Complexes. Copper Vinylcarbenoid Intermediates

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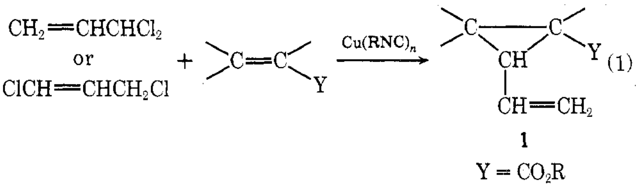
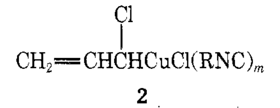
Several attempts[1] to prepare vinylcyclopropanes by means of vinylcarbenes generated from the corresponding diazo compounds and metal carbenoids have been made. Most of those attempts, however, have not given satisfactory results, because vinylcarbenes readily undergo intramolecular cyclization, leading to preferential formation of cyclopropenes.

Herein, we present a new and facile synthesis of vinylcyclopropane derivatives (**1**), utilizing copper carbenoid-isonitrile intermediates (**2**) which are formed by the reaction of allylidene dichloride or 1,3-dichloropropene with a Cu(0)-isonitrile complex (eq 1).



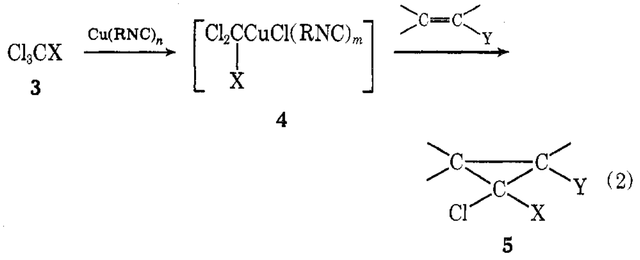


$CH_2{=}CH\overset{Cl}{\overset{|}{C}}HCuCl(RNC)_m$

2

In previous papers[2] we reported a synthetic method of cyclopropane ring formation in which a mixture of metallic copper and isonitrile was treated under nitrogen with a polyhalomethane derivative (**3**) to produce an organocopper-isonitrile complex (**4**), a copper carbenoid-isonitrile complex, which was then treated with an α,β-unsaturated carbonyl compound to produce the cyclopropane derivative **5** (eq 2). A reaction scheme involving conjugate addition and subsequent 1,3 elimination of copper halide was proposed.

Now, we find that employment of allylidene dichloride as the polyhalomethane component in the above reaction (eq 2) leads to the formation of vinyl-substituted cyclopropanes (**1**) in moderate yields. By heating a mixture of allylidene dichloride, diethyl fumarate, metallic copper, and an isonitrile in benzene at 80°, 1-vinyl-2,3-bis(ethoxycarbonyl)cyclopropane (67% yield) was produced, uncontaminated with stereoisomers, as judged by tlc. The reaction of allylidene dichloride with diethyl maleate produced the same vinylcyclopropane derivative. In addition, diethyl maleate and *cis*-1,2-bis(ethoxycarbonyl)cyclopropane were isomerized to the respective trans isomers by the copper-isonitrile system.[3] These findings may allow the assumption that the two ethoxycarbonyl groups on 1-vinyl-2,3-bis(ethoxycarbonyl)cyclopropane are oriented trans to each other. The nonequivalency of the two ethoxycarbonyl groups in the nmr spectrum is in accord with this assignment (see Experimental Section).



X = Ph, CO$_2$R, CN
Y = CO$_2$R, CN

In a similar way, the reactions of *trans*-cinnamylidene dichloride with diethyl fumarate or with diethyl maleate gave a single product, 1-(*trans*-styryl)-2,3-bis(ethoxycarbonyl)cyclopropane, in 77 and 43% yield, respectively, in which the two ester groups were assigned to be trans to each other from the above reasoning. On the other hand, the reaction of *trans*-cinnamylidene dichloride with methyl acrylate afforded a mixture of *cis*- and *trans*-1-(*trans*-styryl)-2-methoxycarbonylcyclopropane in 66% yield.

The reaction with *trans*-crotylidene dichloride produced the corresponding (*trans*-propenyl)cyclopropane derivative only in poor yield, probably owing to the instability of crotylidene dichloride under the reaction conditions. These results are summarized in Table I. The reactions of allylidene dichloride with other electron-deficient olefins by this procedure, however, afforded the corresponding vinylcyclopropane only in low yields and selectivities.

It is noteworthy that the reaction of 1,3-dichloropropene with α,β-unsaturated carbo esters gave the same products in almost the same yields as with allylidene dichloride (Table I). This result may be taken to suggest a common reaction intermediate. We wish to propose the 1-chloro-2-propenylcopper isonitrile complex **2** as the common intermediate. Probably, 3-chloro-2-propenylcopper isonitrile complex **6** is initially formed in the reaction of 1,3-dichloropropene with the copper isonitrile complex and then rearranges to **2**. Rapid 1,3 rearrangement of allylic organometallic compounds is well known.[4] A probable reaction scheme is shown below (eq 3).

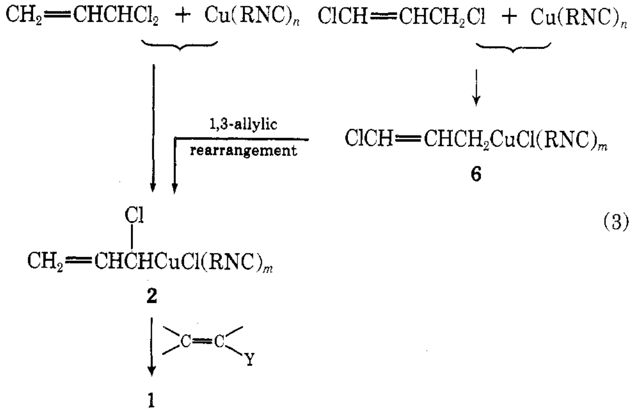
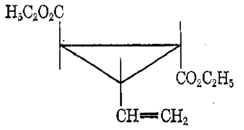
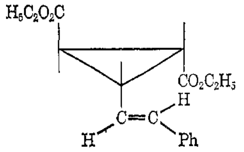
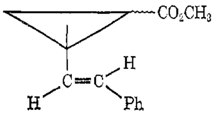
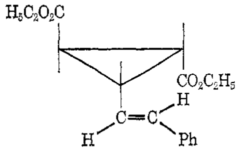
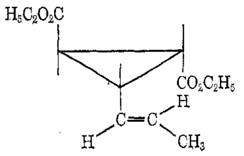
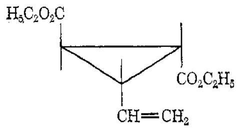
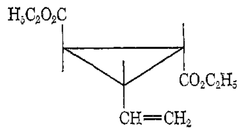
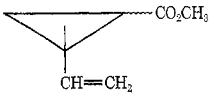


Table I
Synthesis of Vinylcyclopropane Derivatives

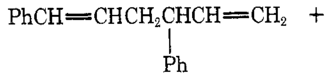
	Chloride (registry no.)	α,β-Unsaturated carbo ester (registry no.)	Product (%)[c]	Registry no.
i	$CH_2{=}CHCHCl_2$ (563-57-5)	*trans*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (623-91-6)	 1-i [a] (67)	51157-82-5
ii	$PhCH{=}CHCHCl_2$ (51157-80-3)	*trans*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$	 1-ii [b] (77)	51157-83-7
iii	$PhCH{=}CHCHCl_2$	$CH_2{=}CHCO_2CH_3$ (96-33-3)	 1-iii [b] (66)	51259-48-4[d] 51259-49-5[e]
iv	$PhCH{=}CHCHCl_2$	*cis*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (141-05-9)	 1-iv [b] (43)	
v	$CH_3CH{=}CHCHCl_2$ (51157-81-4)	*trans*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$	 1-v [a] (18)	51157-84-7
vi	$ClCH{=}CHCH_2Cl$ (542-75-6)	*trans*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$	 1-vi [a] (67)	
vii	$ClCH{=}CHCH_2Cl$	*cis*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$	 1-vii [a] (51)	
viii	$ClCH{=}CHCH_2Cl$	$CH_2{=}CHCO_2CH_3$	 1-viii [a] (48)	15186-44-4[d] 7119-58-6[e]

[a] *tert*-Butyl isocyanide was used. [b] Cyclohexyl isocyanide was used. [c] The yields of products are not necessarily optimum, since only one experiment has been done for each combination. All new compounds in the table gave satisfactory elemental analyses. [d] Cis isomer. [e] Trans isomer.

As to the nature of copper carbenoid-isonitrile complex **2**, it may be pertinent to describe that allyl chloride and cinnamyl chloride were quantitatively dimerized, even in the presence of a large excess of electron-deficient olefin, according to eq 4 and 5, respectively. For these dimerizations an allylic copper-isonitrile complex could be reasonably proposed as the reactive intermediate.

$$2CH_2{=}CHCH_2Cl \xrightarrow{Cu(RNC)_n} CH_2{=}CHCH_2CH_2CH{=}CH_2 \quad (4)$$

The formation of a *ca.* 1:1 mixture of 1,6-diphenyl-1,5-hexadiene and 1,4-diphenyl-1,5-hexadiene in the latter reaction indicates the 1,3-allylic rearrangement of allylcopper-isonitrile complex. Based upon these observations, it may be assumed that 3-chloro-2-propenylcopper-isonitrile complex **6** rearranges to copper carbenoid **2** before **6**



$$2PhCH{=}CHCH_2Cl \xrightarrow{Cu(RNC)_n} PhCH{=}CHCH_2\underset{\displaystyle Ph}{\underset{|}{C}H}CH{=}CH_2 + PhCH{=}CHCH_2CH_2CH{=}CHPh \quad (5)$$

Table II
Spectral Data

Vinylcyclopropane	Ir, cm^{-1} [a]	Nmr, τ[b]	Mass, *m/e*
1-i	>3000, 1726, 1638, 994, 912	3.87–4.96 (m, 3 H) 5.80 (two q, 4 H) 7.57–7.60 (m, 3 H) 8.73 (two t, 6 H)	212 (M$^+$)
1-ii	>3000, 1722, 1648, 967, 748, 692	2.78 (s, 5 H) 3.36 (d, *J* = 17 Hz, 1 H) 3.62–4.10 (m, 1 H) 5.86 (two q, 4 H) 7.26–7.65 (m, 3 H) 8.78 (two t, 6 H)	
1-iii	>3000, 1728, 1650, 960, 748, 693	2.72 (s, 5 H) 3.45 (d, *J* = 16 Hz, 1 H) 3.90–4.48 (m, 1 H) 6.32 (two s, 3 H) 7.60–9.12 (m, 4 H)	202 (M$^+$) 171 143
1-v	>3000, 1726, 1670, 968	3.86–4.87 (m, 2 H) 5.86 (two q, 4 H) 7.50–7.73 (m, 3 H) 8.34 (d, 3 H) 8.73 (two t, 6 H)	
1-viii	>3000, 1734, 1640, 995, 910	4.50–5.12 (m, 3 H) 6.30 (two s, 3 H) 7.67–9.18 (m, 4 H)	126 (M$^+$) 95 67

[a] Neat. [b] $CDCl_3$ solution (TMS reference).

undergoes the coupling reaction, and that 2 reacts with α,β-unsaturated carbo esters faster than with organic halides.

Experimental Section

All halides employed were prepared by the reaction of the corresponding aldehyde and PCl_5. 1,3-Dichloropropene and olefins were commercial reagents, purified by distillation after drying over molecular sieves.

Reaction of Allylidene Dichloride with Diethyl Fumarate in the Copper–Isonitrile System. Allylidene dichloride, 0.56 g (5 mmol), was added dropwise with stirring during 45 min to a mixture of metallic copper powder, 1.27 g (20 mg-atoms) (prepared by the reduction of $CuSO_4$ with zinc powder), *tert*-butyl isocyanide, 3.32 g (40 mmol), and diethyl fumarate, 1.72 g (10 mmol) in benzene (5 ml) at 80°, and the reaction mixture was heated for 12 hr. The mixture was triturated with ether, and the precipitated CuCl–isonitrile complex was removed by filtration. The filtrate was concentrated and distilled *in vacuo* to isolate 1-vinyl-*trans*-2,3-bis(ethoxycarbonyl)cyclopropane (67%), uncontaminated with its isomer as judged by tlc. The structure of the product was confirmed by spectral (Table II) and elemental analysis.

Reaction of *trans*-Cinnamylidene Dichloride with Methyl Acrylate in the Copper–Isonitrile System. *trans*-Cinnamylidene dichloride, 0.93 g (5 mmol), in benzene (3 ml) was added with stirring during 45 min to a mixture of metallic copper, 1.27 g (20 mg-atoms), *tert*-butyl isocyanide, 3.32 g (40 mmol), methyl acrylate, 0.86 g (10 mmol), and benzene (5 ml) at 80°. The reaction mixture was stirred at 80° for 12 hr. Work-up of the mixture according to the above procedure afforded a mixture of *cis*- and *trans*-1-(*trans*-styryl)-2-methoxycarbonylcyclopropane in 66% yield. Reactions of 1,3-dichloropropene with diethyl fumarate and methyl acrylate by copper–isonitrile system were carried out in similar ways.

Registry No.—*tert*-Butyl isocyanide, 7188-38-7; cyclohexyl isocyanide, 931-53-3; copper, 7440-50-8.

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Friedländer Synthesis and Rearrangement of 10-(*o*-Fluorophenyl)-1,4-ethanobenzo[*b*]-1,5-naphthyridines to Benzo[*b*]indolo[3,2,1-*d,e*]-1,5-naphthyridines

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The rearrangement of suitably functionalized 2-arylmethylene quinuclidines to tetrahydropyrido[1,2-*a*]indoles[1] provides ready access to this ring system and proved to be of great value in a recently completed total synthesis of dihydroeburnamenine.[2] An extension of this arrangement to a different category of quinuclidine derivatives is described in this note. The reactions involve nucleophilic attack on an aromatic ring by the quinuclidine nitrogen and are therefore favored by groups which can act as an electron sink in the formation of a Meisenheimer