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Selective Catalytic Methoxycarbonylmethylenation of the Triple Bond of Vinylacetylene with Methyl Diazoacetate

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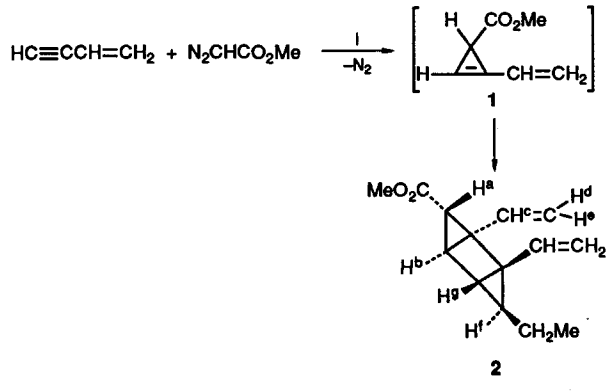
Selective $RH_2(OAc)_4$-promoted methoxycarbonylmethylenation of the triple bond of vinylacetylene with methyl diazoacetate results in methyl 1-vinylcyclopropene-3-carboxylate **1**, which [2+2]cyclodimerizes *in situ* to give dimethyl *trans*-1,2-divinyltricyclo[3.1.0.0^{2,4}]hexane-3,6-dicarboxylate **2**.

The possibility of selective cyclopropenation of the triple bond in conjugated enynes using alkyl diazoacetates has not been established until now. In the presence of Cu^{II} catalysts or $Rh_2(OAc)_4$, alkyl diazoacetates attack predominantly the double bond of enynes containing an internal triple bond, furnishing alkynylcyclopropanecarboxylate.[1] Cyclopropenation of the triple bond with a poor yield (< 19%) of the corresponding cyclopropene has only been achieved in the case of Cu-induced dediazotation of ethyl diazoacetate at 100 °C in the presence of *cis*-hex-2-en-4-yne.[2]

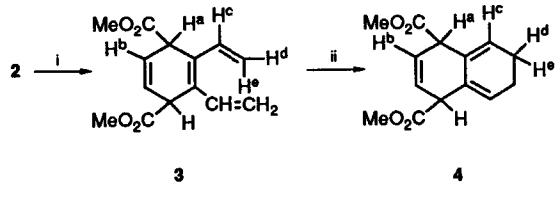
We have found that a 0.2 mol% $Rh_2(OAc)_4$-promoted reaction of methyl diazoacetate with a 2.5-fold excess of vinylacetylene in CH_2Cl_2 at 20 °C proceeds selectively, involving only the triple bond and resulting not in methyl 1-vinylcyclopropene-3-carboxylate **1** but in its [2+2]cyclodimer: dimethyl *trans*-1,2-divinyltricyclo[3.1.0.0^{2,4}]hexane-3,6-dicarboxylate **2**.

The previously unknown compound **2**† was isolated in 70% yield using column chromatography;‡ its structure was established on the basis of spectroscopic data.§



Scheme 1 *Reagents and conditions*: i, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C

† Heating compound **2** in toluene solution at 110 °C results in dimethyl 1,2-divinylcyclohexa-1,4-diene-3,6-dicarboxylate **3**, further Cope rearrangement of which yields dimethyl 1,4,6,7-tetrahydronaphthalene-1,4-dicarboxylate **4** (Scheme 2).



Scheme 2 *Reagents and conditions*: i, toluene, 110 °C; ii, Cope rearrangement

Spectroscopic data for **3**: ^{1}H NMR ($CDCl_3$, *J*/Hz) δ 6.95 (dd, 2H, H^c, J_{ce} = 17.5, J_{cd} = 11.5), 5.94 (d, 2H, H^b, J_{ab} = 1.5), 5.28 (dd, 2H, H^e, J_{ed} = 0.5), 5.24 (dd, 2H, H^d), 4.23 (d, 2H, H^a), 3.66 (s, 6H, OMe); ^{13}C NMR ($CDCl_3$) δ 171.82 (C=O), 132.57 (CH=), 129.38 (C), 123.85 (CH^b), 115.59 (CH_2=), 51.91 (OMe), 44.65 (CH^a).

For **4**: n_D^{20} 1.5363; IR ν/cm^{-1} 1736 (C=O); ^{1}H NMR ($CDCl_3$, *J*/Hz) δ 5.89 (d, 2H, H^b, J_{ab} = 2.25), 5.80 (m, 2H, H^c, J_{cd} = 1.25), 4.00 (dd, 2H, H^a), 3.72 (s, 6H, OMe), 2.15 (m, 4H, H^d and H^e); ^{13}C NMR ($CDCl_3$) δ 172.39 (C=O), 128.62 (C), 125.69 (CH^b), 123.69 (CH^c), 51.85 (OMe), 45.68 (CH^a), 22.11 (CH_2).

Thus, the significantly lower field shifts of the magnetically equivalent H^a and H^f protons in **3** (δ 2.69) in comparison with those of the cyclopropane ring protons in cyclopropanecarboxylates (δ 1.7–2.1) indicates an in-plane position of these protons with respect to the neighbouring cyclopropane rings that accords well with the chair conformation of the tricyclohexane fragment. The low value of the spin–spin coupling constant J_{ab} = 1.5 Hz indicates a *trans*-arrangement of the H^a and H^b protons and an *exo*-position of the CO_2Me groups. Caused by C–H-interaction of the H^a, H^b and H^g protons, the splitting of the ^{13}C(4)-atom signal in the doublet of triplets (δ 30.24, $^1J_{C-H^b}$ = 190 Hz, $^2J_{C-H^a} \approx 5$ Hz) in the full ^{13}C NMR spectrum of **2** indicates a vicinal arrangement of the vinyl groups and 'head-to-head'-type dimerization of **1**.¶

The unexpected change in the regioselectivity of the reaction of methyl diazoacetate with conjugated enynes in the case of vinylacetylene is likely to be caused by two factors: a large decrease in the nucleophilicity of the double bond and a high activity of Rh–carbene complexes in a CH_2Cl_2 medium towards terminal triple bonds. Thus, the use of this catalytic system promotes a high yield for the methoxycarbonylmethylenation of acetylene and methylacetylene under normal conditions.[9]

The absence of **1** in the reaction products is also unexpected. In fact, the 1,2-disubstituted analogue of **1**, ethyl 1-(1-propenyl)-2-methylcyclopropen-3-carboxylate, is stable up to 100 °C.[2] At the same time, easy [2+2]cyclodimerization of **1** has analogies in other classes of cyclopropenes and is, evidently, a particular property of monosubstituted alkenylcyclopropenes. Thus, 1-vinylcycloprop-3-ene is stable only below −100 °C; at higher temperatures it undergoes quantitative 'head-to-head' dimerization to the corresponding tricyclohexane.[4] Ethyl 1-phenylcyclopropene-3-carboxylate cyclodimerizes *in situ*,[5] while the cyclodimerization of 1,2-diphenylcyclopropene-3-carboxylates takes place only under sensitized photolysis.[6]

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‡ A hexane – diethyl ether mixture (5:1 v/v) was used for separation of the products.

§ *Spectroscopic data* for **2**: m.p. 100–105 °C; IR ν/cm^{-1} 1628 (C=C), 1720 (C=O); ^{1}H NMR ($CDCl_3$, *J*/Hz) δ 5.81 (dd, 2H, H^c, J_{cd} = 10.75, J_{ce} = 17.5), 5.41 (dd, 2H, H^e, J_{ed} = 1.9), 5.21 (dd, 2H, H^d), 3.68 (s, 6H, OMe), 2.69 (d, H^a and H^f, J_{ab} = 1.5), 2.27 (d, H^b and H^g); ^{13}C NMR ($CDCl_3$) δ 169.25 (C=O), 129.81 (CH=), 117.24 (CH_2=), 51.64 (OMe), 42.91 (CH^a), 40.70 (C), 30.24 (CH^b).

¶ Doublet–doublet splitting of this signal would be observed in the case of the opposite arrangement of the vinyl groups resulting in 'head-to-tail' dimerization.

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