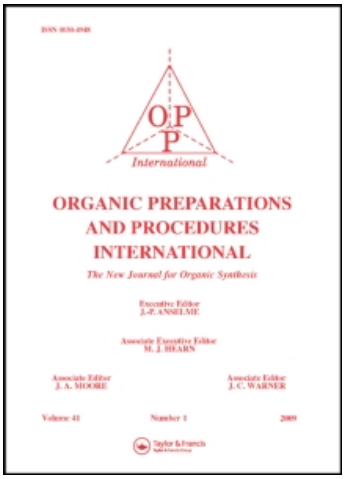

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E. A. Shapiro[a]; A. V. Kalinin[a]; O. M. Nefedov[a]
[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, RUSSIA

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OPPI BRIEFS

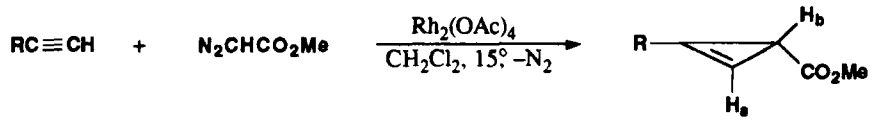
METHYL CYCLOPROPENE-3-CARBOXYLATES BY DIRECT CATALYTIC CYCLOPROPENATION OF ACETYLENES WITH METHYL DIAZOACETATE

Submitted by (12/05/91)

E. A. Shapiro, A. V. Kalinin and O. M. Nefedov*

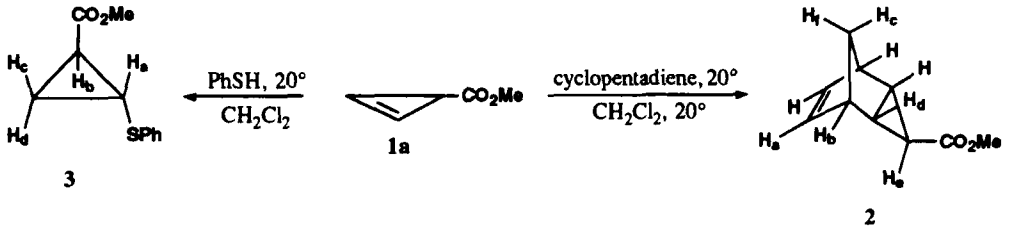
N. D. Zelinsky Institute of Organic Chemistry
Russian Academy of Sciences
Leninsky Prospect, 47, 117913, Moscow B-334, RUSSIA

Cyclopropene-3-carboxylates are promising reagents for organic synthesis.[1] The simplest way for their preparation is rhodium(II) acetate-promoted cyclopropenation of corresponding alkynes with alkyl diazoacetates.[2] Nevertheless, there is no information about the use this method for preparation of the first members of the homologous family of cyclopropene-3-carboxylates, *e. g.* methyl cyclopropene-3-carboxylate (**1a**) and methyl 1-methylcyclopropene-3-carboxylate (**1b**). Multi-stage procedures[3,4] and heterogeneous catalytic processes in a flow reactor[5] with yields of 10-30% have been only described for acetylene and methylacetylene (MA). We now report a convenient procedure for the synthesis of **1a** and **1b** based on direct catalytic cyclopropenation of acetylene and MA with methyl diazoacetate (MDA) in the medium of CH_2Cl_2 at 15-20°; MDA deazotation was induced by 0.2 mol. % $Rh_2(OAc)_4$.



a) R = H b) R = Me **1**

Ester **1a** is unstable under normal conditions and its formation in the reaction of MDA with acetylene was confirmed by chemical transformations. Thus, the immediate treatment of crude reaction mixture with cyclopentadiene at 20-25° yields methyl tricyclo[3.2.1.$0^{2,4}$]oct-6-en-3-carboxylate



3 **1a** 2

(2).[6] Thiophenol adds to the endocyclic multiple bond of **1a** (CH_2Cl_2, 20°)[7] affording methyl *trans*-2-phenylthiocyclopropanecarboxylate (**3**) in 40% yield. The transoid configuration of the substituents in **3** was established by the spin-spin coupling constant (4.0 Hz). The more stable **1b** was isolated by vacuum distillation. The yields of **1b** are affected by the reagent ratio and type of solvent. Thus, in CH_2Cl_2 the reaction of MA with an equimolar quantity of MA leads to a 32% yield of **1b**. A 2-fold excess of MA increased the yield to 68%. The maximum yield of **1b** (75%) was obtained using a 2.5-fold excess of MA. Further increase of the MDA excess (up to 4 to 5-fold) caused the yield to decrease to 45-50%. In $CHCl_3$ the reaction of MDA with MA did occur as well, but the yield of **1b** did not exceed 55%.

The formation of **1a** from MDA and acetylene occurs only in the presence of CH_2Cl_2. In other solvents studied (hexane, ether, benzene), MDA in the presence of $Rh_2(OAc)_4$ is deazotated as well, but **1a** is not formed. In our opinion, the decisive influence of CH_2Cl_2 on the success of the cyclopropenation of the simplest alkynes is due to the ability of this solvent to induce the formation of the alkyne-$Rh_2(OAc)_4$ complex which in turn promotes the cyclopropenation of the alkyne. In fact, saturation of a suspension of the catalyst in CH_2Cl_2 with acetylene or MA results in intensely colored solutions. Visible spectra of these solutions display an absorption band at λ_{max} value of 640 nm, which was earlier established for the $\pi^*_{Rh\text{-}Rh} \rightarrow \sigma^*_{Rh\text{-}Rh}$ transition in $Rh_2(OCOC_3F_7)_4$-olefin complexes.[8] MDA addition induces the intensification of the color of reaction mixture, the rest of the $Rh_2(OAc)_4$ being dissolved completely. At the same time, most of the catalyst remains undissolved in acetylene-hexane or acetylene-benzene mixtures; there are no corresponding absorption bands in the visible spectra and the color of the mixtures do not change significantly during MDA addition.

EXPERIMENTAL SECTION

The ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Jeol FX-90Q insrument, using TMS as an internal standard, and the IR spectra were recorded in $CDCl_3$ with a Bruker IFS-113V Spectrometer. The visible spectra were measured on Specord M400 insrument. The mass spectra were taken at 70 eV on a quadrupole chromatomass-spectrometer, Finigan INCOS-50. For GLC-analysis an OV-1501 column (0,25 mm x 30 m) was used. A solvent system of hexane-ether 6:1 (v/v) and silica gel L 40/100 were used for product isolation.

Methyl 1-Methylcyclopropene-3-carboxylate (1b).- Liquid MA (4.4 g, 0.11 mole) was added to a cooled (-40°) suspension of $Rh_2(OAc)_4$ (0.044 g, 0.1 mmole) in 100 mL of CH_2Cl_2 (dried over P_2O_5). The mixture was heated to 15° with efficient stirring for 10 min, and the resulting intensely emerald color solution of the catalytic complex was treated with a solution of MDA (5 g, 0.05 mole) in 20 mL of CH_2Cl_2 for 5-6 hrs, evaporated MA being returned to the reaction mixture with a condenser, cooled by a CO_2-acetone mixture at -40°. After N_2 evolution ended, the mixture was stirred for 30 min; the solvent and volatile material were removed *in vacuo*; and the residue was distilled under reduced pressure to give **1b** (4.2 g, 75%), bp. 55°/20mm, lit.[3] 64°/30mm. ^1H NMR (90 MHz): δ 6.33 (m, 1H, H_a, J_{ab} = 1.53Hz), 3.66 (s, 3H, OCH_3), 2.15 (d, 3H, CH_3, J = 1.22Hz), 2.12 (d, 1H, H_b).

Methyl Tricyclo[3.2.1.0^{2,4}]oct-6-en-3-carboxylate (2).- The reaction of MDA with acetylene was carried out by treatment (ca. 40 min) of a solution of the catalytic complex [from 5 mg, (0.011 mmole) of $Rh_2(OAc)_4$] in 20 mL CH_2Cl_2 with a solution of MDA (0.5 g, 5 mmoles) in 20 mL CH_2Cl_2, simultaneous saturation of the reaction mixture with acetylene having been accomplished. The reaction mixture, containing **1a**, was stirred for 10 min and was used immediately for further transformations. Thus, treatment with cyclopentadiene (2 g, 30.3 mmoles) at 20°, following the known[6] procedure of isolation, furnished **2** (0.33 g, 40%), n_D^{20} 1.4939, lit.[6] 1.4930. ^{1}H NMR (90 MHz): δ 5.75 (t, 2H, H_a, J_{ab} = 2Hz), 3.52 (s, 3H, OCH_3), 2.87 (broad s, 2H, H_b), 1.97 (m, 2H, H_c), 1.82 (m, 1H, H_d), 1.60 (m, 1H, H_e, J_{de}= 7.0Hz), 1.45 (t, 1H, H_f, J_{cf} = 2.3Hz). ^{13}C NMR (22.5 MHz): δ 171.90 (C=O), 131.60 (C=C), 64.15 (CH_2), 51.26 (OCH_3), 42.92 (CH_b), 31.11 (CH_d), 22.93 (CH_e).

Methyl *trans*-2-Phenylthiocyclopropanecarboxylate (3).- A solution of thiophenol (0.55 g, 5 mmoles) in 2 mL of CH_2Cl_2 was added over 30 min to the reaction mixture containing **1a** (from 5 mmoles of MDA). The mixture was stirred for 2 hrs at 20°, concentrated to a volume of 5 mL, and finally diluted with 10 mL of pentane. The solution was filtered through silica gel (ca. 3 cm^3), and filtrate was evaporated *in vacuo*. The residue contained two compounds (GC-MS) with the same molecular ions (m/z 208) in 99.8:0.2 ratio. The major one, the *trans* isomer of **3**, was isolated (0.39 g, 38%) by column chromatography on silica gel, n_D^{20} 1.5634. IR (neat): 1741 (C=O). ^{1}H NMR (90 MHz): δ 7.28 (m, 5H, aromatic H), 3.72 (s, 3H, OCH_3), 2.79 (1H, H_a, J_{ab} = 4.0Hz, J_{ac} = 8.5Hz, J_{ad} = 6.0Hz), 1.91 (1H, H_b, J_{bc} = 5.5, J_{bd} = 9.0Hz), 1.64 (1H, H_c, J_{cd} = 4.9), 1.26 (1H, H_d). ^{13}C NMR (22.5 MHz): δ 172.55 (C=O), 136.69, 128.89, 127.43, and 125.80 (C_6H_5), 51.96 (OCH_3), 23.90 (CH_b), 22.44 (CH_a), 17.24 (CH_2). MS [m/z, (I,%)]: 208 (76) [M], 177 (23) [M-OMe], 176 (32) [M-MeOH], 149 (94) [M-COOMe], 109 (48) [PhS], 99 (100) [M-SPh].

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.44; H, 5.81; S, 15.39. Found: C, 63.52; H, 5.94; S, 15.98

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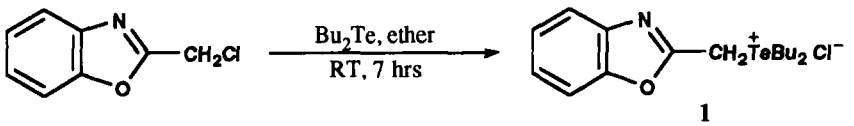
A FACILE SYNTHESIS OF 2-(2'-SUBSTITUTED VINYL)BENZOXAZOLES

Submitted by (08/09/92) Jian-Guo Shao, Qi Zhong*, Hai-Ping Liao, Chang-Qing Liu and Jing-Feng Zhou

Department of Chemistry, Yangzhou Teachers College
Yangzhou, Jiangsu, P. R. CHINA

2-(2'-Substituted vinyl)benzoxazoles belong to a versatile class of compounds.[1] The synthesis of these compounds *via* telluronium salt has not been reported. Recently, we described a convenient method for preparing α,β-unsaturated nitriles, ketones, esters, amides and substituted cyclopropanes.[2-5] We now report the facile synthesis of 2-(2'-substituted vinyl)benzoxazoles. 2-Benzoxazolylmethyldibutyltelluronium chloride (**1**), easily prepared (79%) by the reaction of dibutyl telluride with



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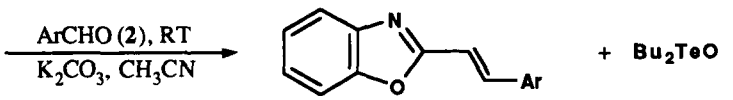

3

a) Ar = C_6H_5 b) Ar = *p*-$CH_3OC_6H_4$ c) Ar = *p*-ClC_6H_4
d) Ar = *p*-FC_6H_4 e) Ar = *p*-$NO_2C_6H_4$ f) Ar = *p*-$CH_3C_6H_4$ g) Ar = 2-furfuryl

2-chloromethylbenzoxazole in ether at room temperature, reacted with aromatic aldehydes **2a-e** in acetonitrile containing trace amounts of formamide in the presence of potassium carbonate to afford 2-(2'-substituted vinyl)benzoxazoles **3**. The IR and ^1H NMR spectra indicated all the products to be the E-isomers. These compounds E-2-(2'-substituted vinyl)benzoxazoles could be obtained with high stereoselectivity in a one-pot reaction directly from 2-chloromethylbenzoxazole, the aldehydes (**2a-g**) and dibutyl telluride at reflux in acetonitrile under neutral conditions.