REACTIONS OF DIAZOALKANES WITH UNSATURATED COMPOUNDS.

7. CATALYTIC CYCLOPROPANATION OF 1-ALKOXY-, 1-ACETOXY-, AND 1-(TRIMETHYLSILYLOXY)BUTA-1,3-DIENES WITH DIAZOMETHANE*

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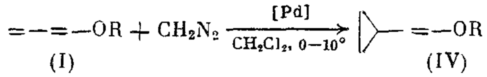
Cyclopropanation of 1-butadienyl ethers or esters with diazomethane proceeds selectively in the presence of $(PhCN)_2PdCl_2$, as opposed to CuCl, at the less polar terminal double bond in these dienes when the molar proportions of reactants and catalyst are 1:(1.3-2):(0.002-0.005) to give the 2-cyclopropylvinyl ethers or esters in yields of 80-85%.

The extensive use of diazomethane in the synthesis of cyclopropanes from the corresponding olefins is largely attributable to the use of palladium compounds as deazotization catalysts, resulting in high efficiency and regioselectivity of cyclopropanation, for example of intracyclic C=C bonds [2-4] and terminal olefins [3-5]. Diazomethane in the presence of palladium compounds also readily cyclopropanates mono- and disubstituted double bonds in unsaturated compounds with functional groups (OH, NR_2, COR, COOR) [6-8].

Developing methods for the selective cyclopropanation of polyunsaturated compounds with functional substituents at the double bond, we have now examined the reactions of diazomethane with 1-alkoxy- (I), 1-acetoxy- (II), and 1-(trimethylsilyloxy)buta-1,3-dienes (III). The experiments were carried out at 0-10°C by passing a 1.3-2 molar amount of diazomethane at an average rate of ~0.03 mole/hour (as a gaseous mixture with nitrogen) into a solution of the freshly distilled unsaturated compound and 0.2-0.5 mole% of $(PhCN)_2PdCl_2$ in dichloromethane. The reaction of diazomethane with 1-methoxy- (Ia) or 1-ethoxybutadiene (Ib) containing, respectively, ~86 and 94% of the E-isomers and ~12 and 5% of the Z-isomers gave overall yields of 80-85% of the (2-alkoxyvinyl)cyclopropanes (IV) with approximately the same proportions of E- and Z-isomers as the starting dienes.



(I) (IV)

~1 : 1,3 80—85%

H = Me (a), Et (b).

The PMR spectrum (250 MHz) of the mixture obtained by reacting (Ia) with a twofold excess of diazomethane in CD_2Cl_2 in the presence of $(PhCN)_2PdCl_2$ showed signals for the E- and Z-isomers (IVa) (overall yields ~90%), together with small amounts of the starting diene (Ia) (mainly the E-isomer), but none for the product of the cyclopropanation of the disubstituted double bond in (Ia).

The structures of the cyclopropane ethers (IV) followed conclusively from their PMR spectra (Table 1), which contained characteristic low-field signals for the protons of the 1,2-disubstituted double bond. The coupling constants of the olefinic protons were approximately the same as in the corresponding butadienyl ethers.

It is noteworthy that earlier syntheses of the ethers (IV) were complex and gave low yields [9, 10].

The cyclopropanation of (Ia) with diazomethane in the presence of CuCl, as opposed to $(PhCN)_2PdCl_2$, is nonselective, giving the ether (V) in addition to (IVa), together with the product of the double cyclopropanation (VI). In order to maintain the activity of the cat-

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*For previous communication, see [1].

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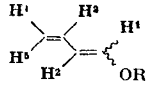
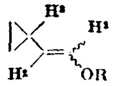
TABLE 1. PMR Spectra of Butadienyl (I)-(III) and 2-Cyclopropylvinyl Ethers and Esters (IV), (VII), (VIII) (in $CDCl_3$, δ, ppm; J, Hz).

										
compound	R	H^1 ($J_{1,2}$)	H^2 ($J_{2,3}$)	H ($J_{3,4} + J_{3,5}$)	compound	R	H^1 ($J_{1,2}$)	H^2 ($J_{2,3}$)	H^3	remaining protons
E-(Ia)	Me	6,62 br.d (12,6)	5,55 br.d.d (11,0)	6,22 d.d.d. (10,6 , 17,4)	*E*-(IVa)	Me	6,38 br.d. (13,0)	4,48 d.d (7,7)	1,24 m	3,48 s (OCH_3); 0,6 and 0,25 m (CH_2CH_2)
Z-(Ib)	Me	5,90 m (6,4)	5,08 *	6,67 m (10,5 , 17,5)	*Z*-(IVa)	Me	5,91 br.d (6,4)	3,87 d.d (9,9)	*	3,61 s (OCH_3); 0,7 and 0,28 m (CH_2CH_2)
E-(Ib)	Et	6,56 br.d (12,6)	5,52 d.d (11,0)	6,18 d.d.d (10,5 , 17,5)	*E*-(IVb)	Et	6,28 d (12,8)	4,46 d.d (7,4)	1,20 m	3,64 q (OCH_2, $J = 7,0$); 1,21 t (CH_3, $J = 7,0$); 0,58 and 0,22 m (CH_2CH_2)
E-(II)	Ac	7,38 br.d (12,7)	6,02 d.d (11,4)	6,24 d.d.d (10,8 , 17.3)	*E*-(VII)	Ac	7.03 d (13,0)	4.92 d.d (8,2)	1,20 m	2,02 s (CH_3); 0,7 and 0,35 m (CH_2CH_2)
Z-(II)	Ac	7,04 m (6,7)	5,49 m (11,3)	6,69 m (10,8, 17.5)	*Z*-(VII)	Ac	6,90 d (6,6)	4,12 d.d (10,1)	1,7 m	2,10 s (CH_3); 0,7 and 0,35 m (CH_2CH_2)
E-(III)	$SiMe_3$	6,56 br.d (12,2)	5,69 d.d (11,2)	6,23 d.d.d (10,4 , 17,4)	*E*-(VIII)	$SiMe_3$	6,31 br.d (12,4)	4,67 d.d (8,4)	1,20 m	0,6 and 0,18 m (CH_2CH_2); 0,16 s ($SiMe_3$)
Z-(III)	$SiMe_3$	6,19 m (6,3)	5,22 br.d.d. (11,1)	6,71 m (11,0 , 17,5)	*Z*-(VIII)	$SiMe_3$	6,18 br.d (6,2)	3,98 d.d (9,8)	1,22 m	0,68 and 0,15 m (CH_2CH_2); 0,20 s ($SiMe_3$)

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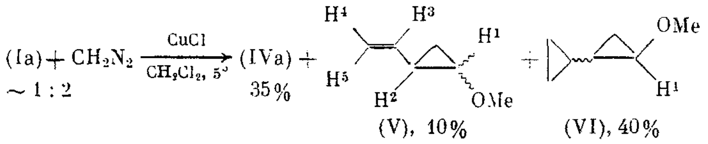
*Signals overlap other group protons.

TABLE 2. Bond Lengths (R, Å), π-Bond Order (BO), and Electronic Charge Distribution (q in electron charges) on Carbon Atoms in the Butadienyl Moiety in (I)-(III) Obtained by the MNDO Method.

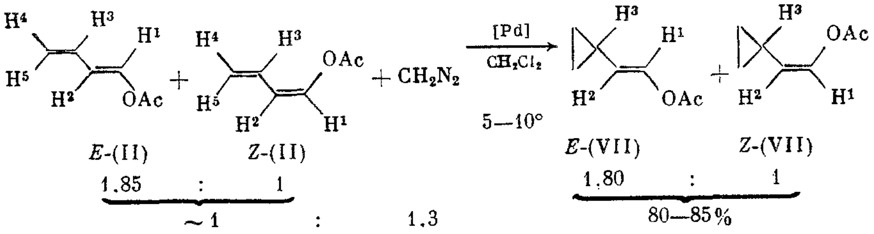
Alkyl butadienyl-ether $RO{-}C^1{=}C^2{-}C^3{=}C^4$	q_1	q_2	q_3	q_4	R_{1-2}	R_{3-4}	$\pi BO_{1,2}$	$\pi BO_{3,4}$
E-(Ia)	0,089	−0,118	−0,064	−0,060	1,360	1,345	0,922	0,963
Z-(Ia)	0,090	−0,116	−0,050	−0,071	1,359	1,345	0,921	0,960
E-(Ib)	0,092	−0,121	−0,063	−0,062	1,360	1,344	0,922	0,964
Z-(Ib)	0,093	−0,119	−0,052	−0,068	1,359	1,345	0,920	0,963
E-(II)	0,092	−0,097	−0,060	−0,061	1,360	1,345	0,931	0,963
Z-(II)	0,094	−0,096	−0,060	−0,058	1,359	1,345	0,930	0,964
E-(III)	0,163	−0,167	−0,048	−0,080	1,364	1,345	0,906	0,968
Z-(III)	0,165	−0,166	−0,031	−0,092	1,359	1,346	0,906	0,963

alyst and to increase the extent of conversion of the starting ether to the cyclopropanes, it was necessary to add the diazomethane slowly at such a rate that the mixture remained almost colorless.

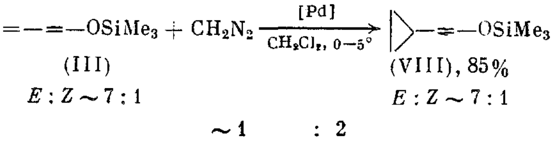


Compounds (IVa)-(VI) were isolated as the mixed cis- and trans-isomers by preparative GLC (SE-30, 80°C), giving nearly complete separation of the components which were characterized by their PMR spectra. It is noteworthy that, in contrast to the experiments with the palladium catalyst, when the (Ia) had an E:Z ratio of ~7:1, the ether (IVa) obtained as a mixture of E- and Z-isomers was enriched in the E-isomer (~9:1) and the ether (V) was obtained as a mixture of the trans- and cis-isomers in a ratio of ~4:1. Since no isomerization of the products formed occurs under the reaction conditions the results obtained must clearly be due to slight differences in the rates of cyclopropanation over the Cu catalyst of the structurally similar double bonds in the E- and Z-isomers of the diene (Ia).

The reaction of diazomethane with acetoxybutadiene (II) (E:Z isomer ratio 63:34) in the presence of $(PhCN)_2PdCl_2$ proceeds, as in the cyclopropanation of (I), exclusively at the terminal C=C bond, the 2-cyclopropylvinyl acetates (VII) being obtained in overall yields of 80-85% and with approximately the same ratio of E to Z-isomers as in the starting (II). The isomeric composition of the esters (VII) was determined from the PMR spectra, the signals for the olefinic protons with the greater coupling constants being regarded as due to the E-isomers. It is noteworthy that, as in the starting dienes, the signals for the olefinic protons H^1 and H^2 in the Z-isomers are seen at higher field and, for H^3, at lower field than the signals for these protons in the E-isomers (Table 1).



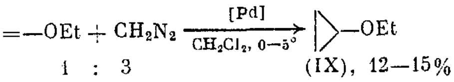
The reaction of diazomethane with 1-(trimethysilyloxy)butadiene (III) in the presence of $(PhCN)_2PdCl_2$ results exclusively in the cyclopropanation of the terminal double bond. When a twofold excess of diazomethane is used, the conversion of the diene (III) into the corresponding E- and Z-(2-trimethysilyloxyvinyl)cyclopropanes (VIII) reaches 85%.



The PMR spectra of the silyl ethers (VIII) are given in Table 1, their structures also following conclusively from the signals for the olefinic protons.

Cyclopropanation of 1-butadienyl ethers with diazomethane in the presence of this palladium catalyst therefore provides a further example of the regioselective cyclopropanation of terminal double bonds [4, 5, 7, 11] and provides a convenient and efficient method for the synthesis of 2-cyclopropyl vinyl ethers, which can be not only alkyl but also trimethysilyl ethers or esters which have not previously been reported.

In contrast to alkyl 1-butadienyl ethers, the reaction of diazomethane with vinyl ethyl ethers (VEE) in the presence of $(PhCN)_2PdCl_2$ results in rapid loss of the activity of the catalyst, so that the diazomethane mostly decomposes with the formation of ethylene and cyclopropane. Significant amounts of the cyclopropyl ethyl ether (IX) were obtained only when the catalyst was added to a mixture of the VEE and diazomethane, although here also the diazomethane was mostly converted into ethylene and cyclopropane.



These results show that the efficiency of cyclopropanation of the double bond in VEE, although it is only monosubstituted, is much lower than with the diene ethers (I) and 1-alkenes, for which the yields of the cyclopropanes under comparable conditions are 50-80% [1, 5].

In order to explain this behavior and to compare the effects of the substituent OR on the double bond in the butadienyl grouping, a theoretical examination of these compounds was carried out using the MNDO quantum chemical method [12]. As will be seen from Table 2, a feature of the electronic structure of the dienes (I)-(III) is the nonequivalence of the double bonds $C^1{=}C^2$ and $C^3{=}C^4$. The $C^1{=}C^2$ bond is subject to strong influence by the electron donating OR substituent, causing a marked shift in π-electrons toward the β-carbon atom (compare the charges on C^1 and C^2) and is even more polar than the $C^1{=}C^2$ bond in VEE, the charges on C^1 and C^2 of which are +0.063 and −0.124, respectively ($R_{C=C}$ = 1.349 Å). The charges on C^3 and C^4 show that the polarity of the terminal double bond in the diene ethers (I)-(III) is much lower, i.e., it has much greater charge symmetry than the $C^1{=}C^2$ bonds in vinyl ethers.

The nonequivalence of the $C^3{=}C^4$ and $C^1{=}C^2$ bonds in the diene ethers (I)-(III) is also shown by their geometry, the latter tending to be longer than the terminal double bond, due to a reduction in the π-constituent bond orders ($\pi BO_{1,2}$, Table 2).

These differences in the double bonds in the dienes (I)-(III) are also apparent on cyclopropanation. For instance, the extent of the polarization of the double bond is likely to have a marked effect on its complexation with palladium and will ultimately play a decisive part in determining the regioselectivity of cyclopropanation of the double bonds. The formation of cyclopropanes at the $C^3{=}C^4$ bonds in dienes (I)-(III) is in good agreement with their lower polarity and relatively high πBO values. On the other hand, the absence of significant amounts of the products of cyclopropanation of (I)-(III) at the disubstituted double bond, together with the low yield of the ether (IX) in the case of VEE, is due to the considerable polarization of these double bonds.

EXPERIMENTAL

The reaction mixtures were analyzed by GLC on an LKhM-8MD chromatograph with a flame ionization detector and I-02 integrator (300 × 0.3 cm column with 5% SP-2100 on Chromatone N-AW-DMCS, carrier gas helium, 30 ml/min). Preparative separation was affected on an LKhP-7I chromatograph (column 150 × 1.2 cm with 5% SE-30 on Chromatone N-AW-DMCS, 0.25-0.36 mm; carrier gas argon, 240 ml/min). PMR spectra were recorded on a Bruker WM-250 (250 MHz) instrument for 5-10% solutions in $CDCl_3$ for the reaction mixtures) using 0.1% TMS as internal standard. Gas chromatography—mass spectrometry was carried out on a Varian MAT-111 instrument. Quantum chemical calculations for (I)-(III) and VEE were carried out with full optimization of the geometric parameters, using the program of Dewar and Thiel [13].

1-Methoxybutadiene (Ia) (bp 92-94°C, E:Z isomer ratio ~86:12) was obtained by liquid phase pyrolysis of 1,1,3-trimethoxybutadiene, as in [14]. Similarly, from crotonaldehyde diethyl acetal there was obtained 1-ethoxybutadiene [10] (Ib), bp 64-65°C (150 mm), E:Z isomer ratio ~94:5. 1-Acetoxybutadiene (II) (E:Z ~ 63:34) was obtained from crotonaldehyde and acetic anhydride as in [15], bp 63-64°C (40 mm). 1-Trimethylsilyloxybutadiene (III), (E:Z ~ 85:12) was synthesized as in [16], bp 58-61°C (50 mm). Diazomethane was generated by gradual addition of nitrosomethylurea to 50% KOH solution, as in [17].

Cyclopropanation of 1-Butadienyl Ethers (I)-(III). Into a solution of 0.02 mole of the diene ether in 5 ml of dichloromethane was passed at 0-10°C diazomethane, diluted with nitrogen (1:4-5) at an average rate of 0.03 mole/h. After 2-3 min, 20-30 mg of $(PhCN)_2PdCl_2$ in 1 ml of dichloromethane was added and passage of diazomethane continued (total amount of nitrosomethylurea, 4.2 g). The molar ratio diene:diazomethane under these conditions was ~1:1.3. The reaction mixture was then fractionated to isolate the 2-cyclopropylvinyl ethers in yields of 80-85%. Their PMR spectra are given in Table 1.

1-Methoxy-2-cyclopropylethylene (IVa). E:Z ~ 86:12, bp 56-58°C (100 mm). Mass spectrum (m/z): 98 M^+, 97 $[M-H]^+$, 83 $[M-CH_3]^+$, 67 $[C_5H_7]^+$.

1-Ethoxy-2-cyclopropylethylene (IVb). E:Z ~ 93:5, bp 68-70°C (100 mm). Mass spectrum (m/z): 112 M^+, 111 $[M-H]^+$, 97 $[M-CH_3]^+$, 83 $[M-C_2H_5]^+$.

1-Acetoxy-2-cyclopropylethylene (VII). E:Z ~ 62:34, bp 71-73°C (40 mm). Mass spectrum (m/z): 126 M^+, 125 $[M-H]^+$, 111 $[M-CH_3]^+$, 83 $[M-COCH_3].^+$

1-Trimethylsilyloxy-2-cyclopropylethylene (VIII). E:Z ~ 84:12, bp 63-65°C (40 mm). Mass spectrum (m/z): 156 M^+, 155 $[M-H]^+$, 141 $[M-CH_3]^+$,113, 83 $[C_5H_7O].^+$

Cyclopropanation of (Ia) in the Presence of CuCl. Into a solution of 0.85 g (0.01 mole) of (Ia) in 6 ml of dichloromethane with 0.1 g of CuCl was passed slowly at 0°C diazomethane, generated from 3.1 g of nitrosomethylurea and diluted with nitrogen (1:10) at such a rate that the mixture remained almost colorless. It was then filtered through a layer of silica gel and separated by preparative GLC (80-95°C). The products are given below in order of increasing retention times.

1-Methoxy-2-vinylcyclopropane (V). Trans-cis ~78:19, yield ~10%. PMR spectrum (δ, ppm): trans-(V): 5.50 d.d.d (H^3, $J_{2,3}$ = 8.4, $J_{3,4}$ = 10.6, $J_{3,5}$ = 17.5 Hz), 4.99 d.d (H^5, $J_{3,5}$ = 17.5, $J_{4,5}$ = 2.0 Hz), 4.89 d.d (H^4, $J_{3,4}$ = 10.6, $J_{4,5}$ = 2.0 Hz), 3.37 s (OCH_3), 3.11 d.d.d (H^1, $J_{1,2}$ = 2.6, J_{trans} = 3.8, J_{cis} = 6.5 Hz), 1.56 m (H^2), 1.0 and 0.7 m (CH_2); cis-(V): 5.61 d.d.d (H^3, $J_{2,3}$ = 9.4, $J_{3,4}$ = 10.5, $J_{3,5}$ = 17.5 Hz), 5.18 d.d (H^5, $J_{3,5}$ = 17.5, $J_{4,5}$ = 1.9 Hz), 5.01 d.d (H^4, $J_{3,4}$ = 10.5, $J_{4,5}$ = 1.9 Hz), 3.36 s (OCH_3), 3.32 d.t (H^1, J_{cis} = 6.7, J_{trans} = 3.8 Hz), 1.50 m (H^2), 1.0 and 0.7 m (CH_2). Mass spectrum (m/z): 98 M^+, 97 $[M-H]^+$, 83 $[M-CH_3]$.

1-Methoxy-2-cyclopropylethylene (IVa). E:Z ~ 88:10, yield ~35%, PMR spectrum given in Table 1.

1-Methoxy-2-cyclopropylcyclopropane (VI). Trans:cis ~ 82:13, yield ~40%. PMR spectrum (δ, ppm): 3.42 s (OCH_3 in cis-isomer), 3.29 s (OCH_3 in trans-isomer), 3.20 d.t (H^1 in cis-isomer, J_{cis} = 6.5, J_{trans} = 3.5 Hz), 2.92 d.t (H^1 in trans-isomer, J_{cis} = 6.6 and J_{trans} = 3.0 Hz), 1.0 m, 0.76 m, 0.60 m, 0.52 m, 0.30 m, and 0.03 m (8H, cyclopropane rings in trans- and cis-isomers). Mass spectrum (m/z): 112 M^+, 111 $[M-H]^+$, 97 $[M-CH_3]^+$, 81 $[M-OCH_3]^+$, 80 $[C_6H_5]^+$, 79 $[C_6H_5]^+$, 71 $[M-C_3H_5]^+$.

Ethoxycyclopropane (IX). To a solution of 15 mmoles of diazomethane in 25 ml of dichloromethane were added at 0°C 0.36 g of vinyl ethyl ether and 12 mg of $(PhCN)_2PdCl_2$ in 1 ml of dichloromethane. According to GLC, the yield of (IX) was 12-15%.

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