TREATMENT OF DIAZOALKANES WITH UNSATURATED COMPOUNDS.

NO. 5. CATALYTIC CYCLOPROPANATION OF UNSATURATED HYDROCARBONS WITH DIAZOETHANE*

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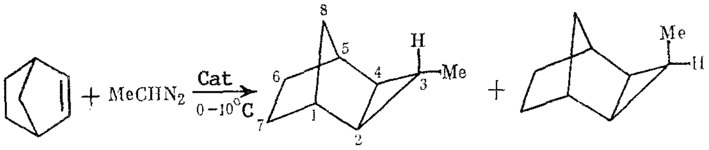
The catalytic reaction of diazomethane with olefins is one of the most versatile methods for the preparation of cyclopropane derivatives [2, 3]. Nevertheless, at the present time there is very little data in the literature concerning the direct cyclopropanation of olefins with other simple diazoalkanes. One of the reasons for this omission is the ease of carbene-olefin isomerization and other intramolecular conversions of the intermediate alkylcarbene products [4, 5]. In this regard, studies of carbene complexes of transition metals have demonstrated that complex formation not only stabilizes the alkylidene ligand, but also is capable of transferring it (the alkylidene fragment) to an olefin to generate the corresponding cyclopropane [6]. For example, the electrophilic complex $(C_5H_5)(CO)(L)Fe^+{=}CHCH_3$ reacts with alkenes to give predominant formation of cis-(syn)-cyclopropanes [7].

In the present paper we have examined the catalytic cyclopropanation of various mono- and diolefins with diazoethane (DAE). The experiments were carried out at 0-10°C by the addition of 0.6-0.65 M solutions of DAE in a CH_2Cl_2–pentane (ca. 3:1) mixture to a solution of unsaturated hydrocarbon and 3-5 mole % CuCl or 0.5-1 mole % $(PhCN)_2PdCl_2$ in the same solvent. For instance, treatment of DAE with an equimolar amount of norbornene (NB) in the presence of CuCl or $(PhCN)_2PdCl_2$ leads to a mixture (ca. 1:1) of syn- and anti-3-methyl-exo-tricyclo[3.2.1.$0^{2,4}$]octanes (I), in 70% total yield.



1 : 1 anti-(I), ~35% syn-(I), ~35%

The structures of (I), which were isolated in pure form by means of preparation GLC (PGLC), were solved based on their high-resolution PMR spectra (300 MHz). The signals due to the protons at C^2 and C^4 appear as broad doublets, with spin-spin coupling constants J = 2.9 or 8.5 Hz, in both isomers; the magnitude of the spin-spin coupling constant forms the basis for the stereochemical assignment of the methine proton attached to C^3 in the cyclopropane fragment, and, consequently, permits the determination of the orientation of the CH_3 group. Furthermore, the small values of the spin-spin coupling constants ($J \leq 1$ Hz), corresponding to long-range spin-spin interactions which broaden these signals, are indicative of the exo-orientation of the cyclopropane fragment; these spin-spin coupling constant values are characteristic of the vicinal interaction between the endo-H protons attached to C^2 and C^4 and the protons at C^1 and C^5 in norbornane derivatives. Thus, just as in the case of the cyclopropanation of NB with diazomethane [2], syn- and anti-(I) are formed exclusively as the exo-isomers. It should be noted that similar results were obtained previously in a study of the cyclopropanation of NB with excess $MeCHI_2$ in the presence of diethylzinc [8], as well as in the thermal or photolytic decomposition of 5-methyl-3,4-diazatricyclo-[5.2.1.$0^{2,6}$]decanes [9].

The polycyclic analog of NB, exo-endo-tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodec-4-ene (II), undergoes cyclopropanation with diazoethane in a similar fashion as NB. Treatment of equi-

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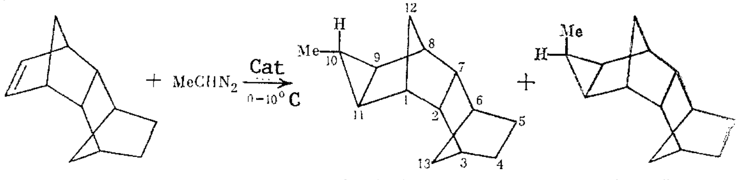
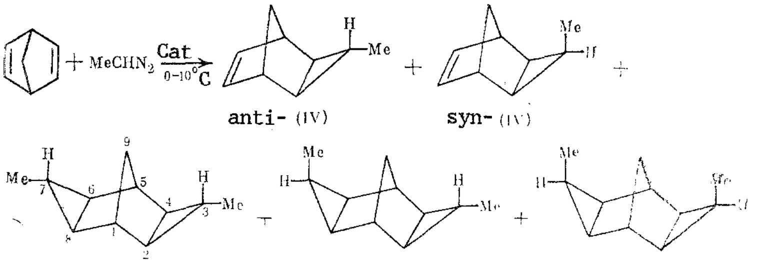
molar amounts of DAE and (II) at 0-10°C in the presence of CuCl or $(PhCN)_2PdCl_2$ results in the formation of a mixture of the corresponding 10-methylpentacyclo[$6.3.1.1^{3,6}.0^{2,7}.0^{9,11}$] tridecanes (III) in 65-70% total yield. The main components of the product mixture, namely, syn- and anti, exo,endo-(III), which are formed in approximately equal amounts, were identified and isolated by means of PGLC.



(II) 1 : 1 anti- (III), ~35% syn- (III), ~33%

The reaction of DAE with norbornadiene (NBD) in the presence of CuCl or $(PhCN)_2PdCl_2$ leads to the formation of both mono- and diadducts. The monoadducts, syn- and anti-3-methyl-exo-tricyclo[$3.2.1.0^{2,4}$]oct-6-enes (IV) (55-60% yield, isomer ratio = 1:1.15), were formed predominantly upon reaction of equimolar amounts of DAE and NBD, whereas the doubly cyclopropanated products, 3,7-dimethyl-exo-exo-tetracyclo[$3.3.1.0^{2,4}.0^{6,8}$]nonanes (V) (60-65% yield, (Va):(Vb):(Vc) isomer ratio = 1.8:2.9:1), were formed predominatly when using a threefold excess of DAE.



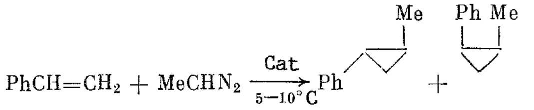
anti- (IV) syn- (IV)

(Va) (Vb) (Vc)

The cyclopropanation products were isolated by PGLC and identified based on their PMR spectral data; the criteria used in the analysis of (I) were used to determine the isomer composition in these products as well. As might be expected, the cyclopropane fragment occupies the exo-orientation in all of the isolated adducts.

One interesting note concerns the unconventional character of the multiplicity of the methine protons at the methyl substituent. For the anti-isomers the multiplicity of these signals is close to the expected triplet of quartets pattern, whereas for the syn-isomers the signal due to these protons is close to a doublet of quintets, with spin-spin coupling constant values of ca. 8.5 and 6.5 Hz, which is also found for example in syn-(I) or (Vb). This effect can be explained in terms of a distortion of the symmetry of the molecule in the case of syn-isomers, due to steric interaction of the CH_3 group with the bridge hydrogen atom attached to C^8 or C^9. It should also be noted that in all cases the protons of the CH_3 group are characteristically at lower field in the syn-isomers (δ 1.15-1.25 ppm) than in the anti-isomers (δ 0.85-0.91 ppm).

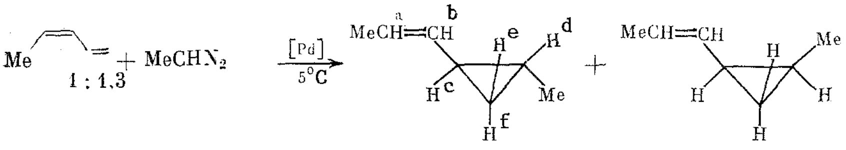
Treatment of DAE with styrene in the presence of either CuCl or $(PhCN)_2PdCl_2$ leads to the formation of trans- and cis-2-methyl-1-phenylcyclopropanes (VI) in 65-70% total yield; the trans-isomer predominates to a small extent.



1 : 1 trans-(VI), ~38% cis-(VI), ~30%

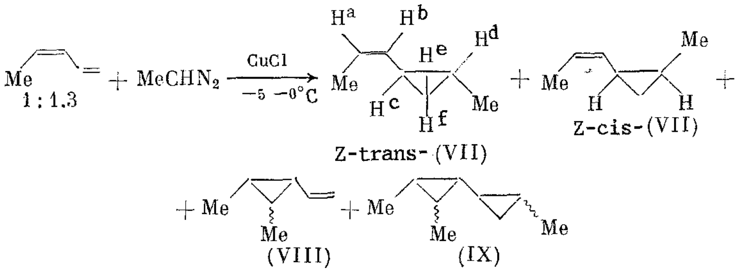
In contrast, reaction of styrene with the electrophilic complex $(C_5H_5)(CO)(L)Fe^+{=}CHMe$ ($L = PPh_3$ or CO) leads to the predominant formation of cis(VI) [7, 10]; the isomer ratio is 4.7:1 in that case.

In order to determine the regioselectivity of the catalytic cyclopropanation of olefins with DAE, we have examined its reaction with cis-1,3-pentadiene. In the presence of $(PhCN)_2PdCl_2$ the reaction occurs mainly at the terminal vinyl group to give trans- and cis-1-propenyl-2-methylcyclopropanes (VII) in 65-70% total yield. The PMR spectra of trans- and cis-(VII), which were isolated by PGLC, contain a characteristic set of signals corresponding to a Z-propenyl fragment. However, the PMR spectra contain, in addition to the signals for the Z-isomers of (VII), with spin-spin coupling constants $J_{cis\text{-}HC=CH}$ = 10-11 Hz corresponding to the configuration of the starting diene, another set of signals which point conclusively to the presence of up to 20% of the E-isomer in each of the components; the spin-spin coupling constant values $J_{trans\text{-}CH=CH}$ are equal to 15 Hz for the E-isomers. The formation of E-isomers probably takes place via partial cis-trans-isomerization of the double bond upon reaction with the palladium complex catalyst at the intermediate metal complex formation stage.



trans-(VII), ~35%   cis-(VII), ~35%

Treatment of cis-1,3-pentadiene with DAE in the presence of CuCl results in the nonselective formation of cyclopropanation products at both double bonds, just as was observed in the case of cyclopropanation with diazomethane and the same catalyst; doubly cyclopropanated products were also formed in the product mixture (based on chromato-mass spectroscopic data). At a molar diene:DAE ratio of 1:1.3, the total yield of monocyclopropanation products (VII) and (VIII) is 50-55%, and all four of the possible isomeric vinylcyclopropanes are formed in approximately equal amounts; at the same time, the yield of the doubly cyclopropanated products, the isomeric 1-(2-methylcyclopropyl)-2,3-dimethylcyclopropanes (IX), is 15-18%.



Z-trans-(VII)   Z-cis-(VII)   (VIII)   (IX)

The formation of isomers of (VIII) is indicated by the presence of three characteristic signals in the olefinic region of their PMR spectra, which correspond to the terminal vinyl group protons. It should also be noted that the use of CuCl as catalyst results in complete retention of the Z-configuration of the starting diene in the reaction products (in contrast to the case with the Pd catalyst).

We have shown that, in most respects, the nature of the reactions of DAE with unsaturated hydrocarbons in the presence of Cu and Pd catalysts is identical to that of the corresponding reactions of diazomethane [2, 3]. Several peculiarities do emerge however. For one thing, in the presence of $(PhCN)_2PdCl_2$ the yields of cyclopropanation products are significantly lower than those obtained with diazomethane; as DAE is added to the system, a loss of catalytic activity of the system is noted, and it is necessary to add fresh portions of catalyst. Apparently, in the case of DAE, some reactions occur which do not involve the loss of nitrogen, and these lead to compounds which can complex effectively with the catalyst. In contrast, in the presence of CuCl active decompostion of DAE takes place, although in this case separation of metallic copper does not occur, as it does with diazomethane [2]; formation of 2-butenes is a side reaction in this case. Furthermore, in the case of CuCl as catalyst, 10-15% of the DAE present decomposes via reaction with EtOH, whose formation and conversion into Et_2O we have demonstrated by PMR study of the generation of DAE by basic hydrolysis of nitrosoethylurea in CD_2Cl_2.

EXPERIMENTAL

Reaction mixtures were analyzed by GLC on an LKhM-8MD chromatograph equipped with a flame ionization detector and an I-02 integrator (using 200 × 0.3 cm columns filled with ether 5% SE-30 or carbowax 20 M on N-AW-DMCS chromatone, or a 300 × 0.3 cm column filled with 5% SP-2100 on N-super chromatone, with a helium carrier gas flow rate of 30 ml/min). Preparative separations were carried out on an LKhP-7I chromatograph (using a 200 × 1.2

cm column filled with 5% SE-30 on N-AW-DMCS chromatone, 0.25-0.36 mm, with a nitrogen carrier gas flow rate of 240 ml/min). PMR spectra were recorded on a Bruker WM-250 (250 MHz) or Bruker AM-300 (300 MHz) spectrometer using 5-7% solutions in $CDCl_3$ and TMS as internal standard. Chromato-mass spectra of multicomponent mixtures were obtained on a Varian MAT-111 spectrometer.

All of the hydrocarbon starting materials were distilled under argon prior to use. Solutions of DAE were prepared by addition of N-nitrosoethylurea to 40% KOH solution, according to [12]; the solvent mixture consisted of CH_2Cl_2–pentane in a 3:1 ratio. PMR spectrum (CD_2Cl_2, δ, ppm): 3.38 q (1H, CHN_2, J = 6 Hz), 1.73 d (3H, CH_3, J = 6 Hz); the spectrum also contains signals due to EtOH at δ 3.65 q, 1.9 br s, and 1.18 t (15-20 mole %). Based on titrimetric data, the concentration of DAE in solution is 0.60-0.65 mole/liter.

3-Methyl-exo-tricyclo[$3.2.1.0^{2,4}$]octane (I). a) A mixture of 0.95 g norbornene (NB), 0.04 g CuCl, and 3 ml CH_2Cl_2 at 0-10°C was treated dropwise with 16 ml of a 0.64 M solution of DAE. Vigorous gas evolution was observed; the solution remained colorless over the length of the experiment. The main solvent portion was removed on a column, and the remainder was distilled almost completely in vacuo within the range 50-75°C (70 mm Hg). Based on GLC data the mixture contains ca. 30% of NB starting material and ca. 70% of the isomers of (I) in approximately equal ratios; these were further separated by means of PGLC (125°C).

anti-(I). PMR spectrum (δ, ppm): 2.22 m (2H, $H^{1,5}$), 1.40 m (2H, exo-$H^{6,7}$), 1.20 m (2H, endo-$H^{6,7}$), 0.93 d of q (1H, anti-H^8, J_{gem} = 10.4, J = 2.1 Hz), 0.84 d (3H, CH_3, J = 6.0 Hz), 0.66 m (1H, H^3), 0.58 d of q (1H, syn-H^8, J_{gem} = 10.4, J = 1.3 Hz), 0.37 br d (2H, $H^{2,4}$, $J_{2,3}$ = 2.9 Hz).

syn-(I). PMR spectrum (δ, ppm): 2.35 m (2H, $H^{1,5}$), 1.43 m (2H, exo-$H^{6,7}$), 1.23 m (2H, endo-$H^{6,7}$), 1.14 d and 1.13 m (4H, CH_3 and H^8, J = 6.5 Hz), 0.65 m (2H, $H^{2,4}$), 0.62 d of q (1H, syn-H^8, J_{gem} = 10, J = 1.4 Hz), 0.49 d of q (1H, anti-H^3, J = 8.4 and 6.5 Hz).

b) A mixture of 0.95 g NB, 0.02 g $(PhCN)_2PdCl_2$, and 3 ml CH_2Cl_2 at 0-10°C under an argon atmosphere was treated dropwise with 16 ml of a 0.65M solution of DAE. With time during the course of DAE addition the amount of N_2 gas evolution was retarded, and fresh catalyst was added throughout the reaction (2 × 0.02 g). After 1 h 10 ml of pentane was added to the reaction mixture and it was filtered through a small layer of silica gel; the filtrate was worked up as described above. The yield of anti- and syn-(I) was ca. 65%. The residue remaining after distillation of the hydrocarbon fraction (ca. 0.4 g) was a very intense red in color.

10-Methyl-exo,endo,exo-pentacyclo[$6.3.1.1^{3,6}.0^{2,7}.0^{9,11}$]tridecane (III). In analogy with the above experiment, 1.6 g tetracyclo[$6.2.1.1^{3,6}.0^{2,7}$]dodec-4-ene (II) and 16 ml of 0.65 M DAE solution in the presence of 3 × 0.02 g $(PhCN)_2PdCl_2$ gave, after distillation, 0.35 g of a fraction with bp 82-90°C (7 mm), which contained 85-87% of the starting material and a second 1.1 g fraction with bp 100-105°C (7 mm), which contained ca. 90% of cyclopropanation products, in ca. 67% yield. The two main components were isolated by means of PGLC (183°C); they are found in approximately equal amounts, and the anti-isomer elutes first.

anti-(III). PMR spectrum (δ, ppm): 2.36 m (2H, $H^{1,8}$), 2.29 d of q (1H, H^{13}, J_{gem} = 10.0, J = 2.2 Hz), 2.20 m (2H, $H^{3,6}$), 1.59 d of t (2H, $H^{2,7}$, $J_{1,2} = J_{7,8}$ = 2.6, J = CH_3, syn-H^{10} and 1 H^{12}), 0.56 d of q (1H, H^{12}, J_{gem} = 10.3, J = 1.4 Hz), 0.48 br d (2H, $H^{9,11}$ $J_{9,10} = J_{10,11}$ = 2.3 Hz).

syn-(III). PMR spectrum (δ, ppm): 2.41 m (2H, $H^{1,8}$), 2.19 m (2H, $H^{3,6}$), 2.02 d of q (1H, H^{13}, J_{gem} = 10.1, J = 2.3 Hz), 1.65 m (2H, $H^{2,7}$), 1.44 m (2H, exo-$H^{4,5}$), 1.16 d syn-CH_3, J = 6.4 Hz) and 1.14 d of q (H^{12}, J_{gem} = 10.5, J = 1.8 Hz) for a total of 4H, 0.97 m (2H, endo-$H^{4,5}$), 0.84 d of q (1H, H^{13}, J_{gem} = 10.1 J = 1.3 Hz), 0.73 m (2H, $H^{9,11}$), 0.65 d of q (anti-H^{10}, J = 8.8 and 6.5 Hz) and 0.63 d of q (H^{12}, J_{gem} = 10.5, J = 1.5 Hz), for a total of 2H.

Cyclopropanation of Norbornadiene with Diazoethane. In an manner analogous to method a), 0.93 g norbornadiene (NBD) and 16 ml 0.63 M DAE solution in the presence of 0.04 g CuCl, or 3 × 0.02 g $(PhCN)_2PdCl_2$ (method b), gave a mixture containing 30-35% of NBD starting material, 55-60% 3-methyl-exo-tricyclo[$3.2.1.0^{2,4}$]oct-6-ene (IV), bp 85-90°C (140 mm), and 7-9% of doubly cyclopropanated products.

In an analogous manner, 0.93 g NBD and 50 ml 0.63 M DAE solution gave a mixture containing ca. 5% NBD, 23-27% (IV), and 60-65% 3,7-dimethyltetracyclo-[3.3.1.0^{2,4}.0^{6,8}]nonanes (V), bp 80-85°C (50 mm). The mixture was separated by PGLC (125-140°C); the isomeric composition is presented below in order of increasing retention time.

anti-3-Methyl-exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (anti-IV). PMR spectrum (δ, ppm): 6.28 t (2H, $H^{6,7}$, J = 1.8 Hz), 2.72 m (2H, $H^{1,5}$), 1.78 t of q (1H, syn-H^3, $J_{2,3} = J_{3,4}$ = 2.8 Hz, J = 6.0 Hz), 0.91 d (3H, anti-CH_3, J = 6.0 Hz), 1.1 br d and 0.75 br d (2H on C^8, J_{gem} = 9.7 Hz), 0.64 br d (2H, $H^{2,4}$, J = 2.8 Hz).

syn-(IV). PMR spectrum (δ, ppm): 6.50 t (2H, $H^{6,7}$, J = 1.7 Hz), 2.83 m (2H, $H^{1,5}$), 1.64 m (1H, anti-H^3), 1.36 d (3H, syn-CH_3, J = 6.6 Hz), 1.33 br d and 0.91 br d (2H on C^8, J_{gem} = 9.5 Hz), 0.95 br d (2H, $H^{2,4}$, J ∿ 7.5 Hz).

anti-anti-3,7-Dimethyl-exo,exo-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (Va). PMR spectrum (δ, ppm): 2.30 br t (2H, $H^{1,5}$, J ∿ 1.8 Hz), 1.02 m (2H, $H^{3,7}$), 0.85 d (6H, anti-CH_3, J = 6.0 Hz), 0.64 br d (4H, $H^{2,4,6,8}$, J = 2.8 Hz), 0.41 br t (2H on C^9, J = 1.8 Hz).

anti-syn-Isomer (Vb). PMR spectrum (δ, ppm): 2.38 m (2H, $H^{1,5}$), 1.21 d (3H, syn-CH_3, J = 6.5 Hz), 1.12 m (1H, syn-H^3), 0.91 m ($H^{6,8}$), 0.88 d (anti-CH_3, J = 6.0 Hz) and 0.83 m (anti-H^7) for a total of 6H, 0.71 br d ($H^{2,4}$, $J_{2,3} = J_{3,4}$ = 2.7 Hz), 0.69 d of q and 0.47 d of q (2H on C^9, J_{gem} = 12.0 and J ∿ 1.6 Hz).

syn,syn-Isomer (Vc). PMR spectrum (δ, ppm): 2.48 br t (2H, $H^{1,5}$, J ∿ 1.6 Hz), 1.26 d (6H, syn-CH_3, J = 6.6 Hz), 0.88-1.0 m (6H, $H^{2,3,4,6,7,8}$), 0.73 br t (2H on C^9, J ∿ 1.6 Hz).

trans- and cis-2-Methyl-1-phenylcyclopropane (VI). In an analogous manner, 1.05 g styrene and 16 ml 0.64 M solution of DAE in the presence of 0.05 g CuCl or 4 × 0.02 g $(PhCN)_2PdCl_2$ gave, after solvent removal and distillation, 0.9-0.95 g of a fraction containing 93-95% (VI) and 5-7% styrene, bp 77-80°C (30 mm); yield of (VI) equal to 65-70%, trans:cis isomer ratio = 1.3:1. The PMR spectrum is consistent with the literature [13].

trans- and cis-1-Propenyl-2-methylcyclopropane (VII). A mixture of 1.03 g 1,3-pentadiene containing ≥95% of the cis-isomer, 0.02 g $(PhCN)_2PdCl_2$, and 3 ml CH_2Cl_2 at 5°C was treated dropwise with 30 ml of 0.65 M DAE solution; fresh catalyst was added throughout the reaction (3 × 0.15 g). After conventional workup and distillation, 1.1 g of a fraction with bp 49-56°C (200 mm) was obtained; it consisted mainly of isomers of (VII) in 65-70% yield (GLC, two peaks in approximately equal ratios). The pot residue (ca. 0.35 g) was an intensely red liquid. Trans- and cis-(VII) were separated by PGLC at 85°C.

trans-1-Z-Propenyl-2-methylcyclopropane. PMR spectrum (δ, ppm): 5.34 d of d of q (H^a, J_{ab} = 10.6, J_{a,CH_3} = 6.8, J_{ac} = 1.1 Hz), 4.80 d of d of q (H^b, J_{ab} = 10.6, J_{bc} = 9.4, J_{b,CH_3} = 1.8 Hz), 1.72 d of d (C=C—CH_3, J_{a,CH_3} = 6.8, J_{b,CH_3} = 1.8 Hz), 1.26 m (H^c), 1.10 d (CH_3, J_{d,CH_3} = 6.0 Hz), 0.70 m (H^d, J_{de} = 7.9, J_{df} ∿ J_{d,CH_3} = 6.0, J_{cd} = 3.6 Hz), 0.5 m ($H^{e,f}$). In addition to these signals, the spectrum also contains signals due to trans-1-E-propenyl-2-methylcyclopropane (Z:E ca. 4:1): 5.45 br d of q (H^a, J_{ab} = 15, J_{a,CH_3} = 6.6 Hz), 5.01 d of d of q (H^b, J_{ab} = 15, J_{bc} = 8.4, J_{b,CH_3} = 1.7 Hz), 1.64 d of d (C=C—CH_3, J_{a,CH_3} = 6.6, J_{b,CH^3} = 1.7 Hz), 1.05 d (CH_3, J_{d,CH_3} = 6.0 Hz); the signals due to the cyclopropane ring protons are overlapped by the signals due to the Z-isomer.

cis-1-Z-Propenyl-2-methylcyclopropane. PMR spectrum (δ, ppm): 5.50 d of d of q (H^a, J_{ab} = 10.5, J_{a,CH_3} = 6.8, J_{ac} = 1.2 Hz), 5.07 d of of q (H^b, J_{ab} = 10.5, J_{bc} = 9.2, J_{b,CH_3} = 1.8 Hz), 1.72 d of d (C=C—CH_3, J_{a,CH_3} = 6.8, J_{b,CH_3} = 1.8 Hz), 1.57 m (H^c, J_{bc} = 9.2, J_{cd} ∿ J_{cf} ∿ 8.5 Hz, J_{ce} ∿ 5.4, J_{ac} = 1.2 Hz), 1.05 m (CH_3 and H^d), 0.93 m (H^f), 0.08 m (H^e). In addition to these signals, the spectrum also contains signals due to cis-1-E-propenyl-2-methylcyclopropane (Z:E ca. 4:1): 5.54 br d of q (H^a, J_{ab} = 15, J_{a,CH_3} = 6.3 Hz), 5.20 d of d of q (H^b, J_{ab} = 15, J_{bc} = 8.3, J_{b,CH_3} = 1.7 Hz), 1.70 d of d (C=C—CH_3, J_{a,CH_3} = 6.3, J_{b,CH_3} = 1.7 Hz), 1.40 br d of q (H^c, J_{bc} ∿ J_{cd} ∿ J_{cf} = 8-8.5, J_{ce} = 5.2 Hz), 0.81 d of t (H^f, J_{cf} ∿ J_{df} ∿ 8.2, J_{ef} ∿ 4.6 Hz); the other signals overlap those of the Z-isomer.

Cyclopropanation of 1,3-Pentadiene in the Presence of CuCl. A mixture of 1.03 g cis-1,3-pentadiene and 0.05 g CuCl at —5°C was treated dropwise with ca. 30 ml of 0.61 M DAE solution. The reaction was colorless throughout the remainder of the experiment. Based on GLC (versus n-octane as internal standard) and chromato-mass spectroscopic data, the reaction mixture consists of 50-55% of monocyclopropanation products (four peaks, two of which are identical to trans-Z- and cis-Z-(VII), all with M^+/z 96) and 15-18% of isomeric 1-(2-methylcyclopropyl)-2,3-dimethylcyclopropanes (IX), which are the doubly cyclopropanated products (four peaks, all with M^+/z 124). By means of PGLC a fraction containing cis-Z-(VII), without contamination by its E-isomer, and 1-vinyl-2,3-dimethylcyclopropane (VIII) was isolated; the latter was identified spectrally based on the presence of a characteristic set of signals in the olefin region, corresponding to a terminal vinyl group: 5.59 d of d of d (J_{trans} = 1.5, J_{cis} = 9.8, J = 13.5 Hz), 5.18 d of d (J_{trans} = 16.5, J_{gem} = 2.5 Hz), 5.06 d of d (J_{cis} = 9.8, J_{gem} = 2.5 Hz).

CONCLUSIONS

The preparative catalytic cyclopropanation of unsaturated hydrocarbons with diazoethane has been achieved for the first time. Addition of the ethylidene fragment to the C=C double bond occurs in a nonstereoselective manner and leads to the formation of the corresponding methylcyclopropanes in 55-70% total yields. In the presence of CuCl, all double bonds of unsaturated hydrocarbons are cyclopropanated with equal facility, whereas in the presence of $(PhCN)_2PdCl_2$ preferential regioselective cyclopropanation of strained endocyclic and terminal double bonds is observed, just as was true in the case of reactions with diazomethane.

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