Cyclopropanation of Terminal Olefins Using Diazomethane/Palladium(II) Acetate

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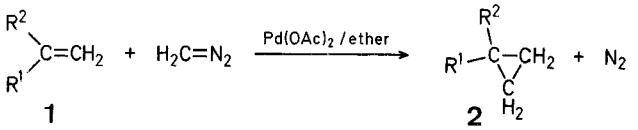
Diazomethane/palladium(II) acetate is a useful reagent for the cyclopropanation of activated alkenes such as styrene[1] and α,β-unsaturated carbonyl compounds[2]. Simple olefins such as cyclohexene have been reported not to react with the above reagent, although strained alkenes (norbornadiene etc.) readily react at room temperature[3].

In this communication, we report our findings that non-activated terminal olefins (1-alkenes, **1**) do react smoothly with diazomethane in the presence of palladium(II) acetate in ether at ~5°C. The products **2** were isolated by distillation and identified on the basis of their ^{1}H-N.M.R. spectra and by element analysis (only for new compounds). 2-Mono- and 2,2-disubstituted 1-alkenes **(1)** are cleanly cyclopropanated. Highly selective cyclopropanation of 1-alkenes is observed in the reaction with 4-vinylcyclohexene from which only 4-cyclopropylcyclohexene was isolated in 77% yield. This marked selectivity is in sharp contrast to the known cyclopropanation methods using diiodomethane/zinc[4] and metal carbenoids[5] which in all cases produced a mixture of mono-cyclopropanated products.



1 2

Cyclopropylmethyl Phenyl Ether; Typical Procedure:
A solution of allyl phenyl ether (400 mg, 2.98 mmol) and diazomethane (prepared from 2 g of *N*-methyl-*N*-nitrosourea) in ether (20 ml) is cooled in an ice-water bath, and palladium(II) acetate (10 mg) is added. Vigorous gas evolution is observed. After 10 min stirring, the ether is removed in vacuo and the residual product is distilled in vacuo; yield: 430 mg (97%); b.p. 92–95°C/13 torr. The product contains ~1% of impurity (by G.L.C. analysis, SE 30, 110°C).

$C_{10}H_{12}O$	calc.	C 81.04	H 8.16
(148.2)	found	81.28	8.12

^{1}H-N.M.R. ($CDCl_3$/TMS): δ=0.3 (m, 2H); 0.5–0.7 (m, 2H); 1.2 (m, 1H); 3.76 (d, 2H, J=6 Hz); 6.8–7.0 (m, 3H); 7.2–7.4 ppm (m, 2H).

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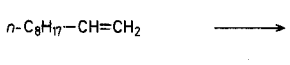
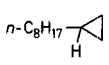
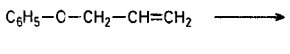
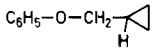
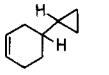
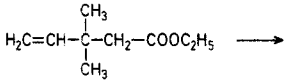
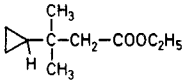
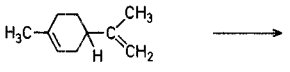
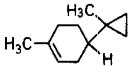
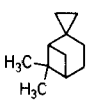
Table. Cyclopropanation of 1-Alkenes using Diazomethane/Palladium(II) Acetate

1	2	Yield [%]	b.p. [°C]/torr	Molecular formula or b.p. [°C]/torr reported
		89	72–75°/12	65–66°/5[6]
		97	92–95°/13	$C_{10}H_{12}O$ (148.2)
		77	35°/13	28–34°/10[4]
		90	72–75°/13	$C_{10}H_{18}O_5$[a] (170.2)
		82	80°/13	73°/8.5[4]
		63	57–61°/13	36.5°/7[4]

[a] calc. C 70.55 H 10.66
found 70.65 10.59

^{1}H-N.M.R. ($CDCl_3$/TMS): δ=0.2–0.4 (m, 4H); 0.6–0.9 (m, 1H); 0.90 (s, 6H); 1.27 (t, 3H); 2.23 (s, 2H); 4.10 ppm (q, 2H).

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