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CATALYTIC SYNTHESIS OF 3,3-DISUBSTITUTED TRICYCLO[3.2.1.$0^{2,4}$]OCTANES

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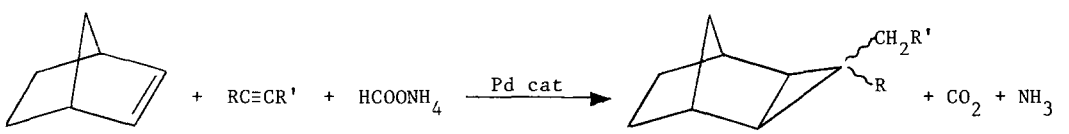
Summary A new cyclopropanation reaction leading to the title compounds is described, based on the use of alkynes as cyclopropanating agents.

We recently reported the catalytic formation of norbornanes containing different carbon chains in position 2 and 3[1,2]. These products were obtained by norbornene insertion into a Pd-C bond, followed by insertion of either carbon monoxide or alkynes and reductive elimination.

We now report a facile reaction leading to 2,3-disubstituted norbornanes with the two carbon chains joined to form a condensed cyclopropane ring.

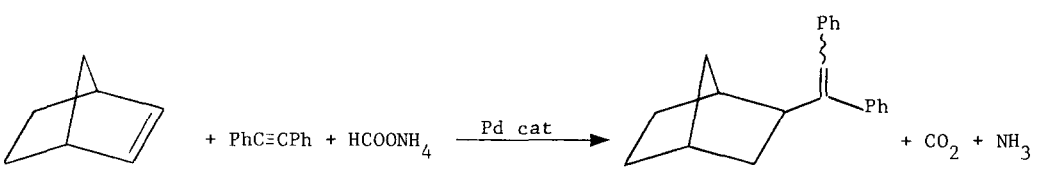
This result can be achieved in a very simple way starting from norbornene, alkynes RC≡CR' (R = alkyl, phenyl, R'=H, alkyl) and ammonium formate according to the overall reaction:



(I)

Alkynes are thus used as cyclopropanating agents to prepare a new class of 3,3-disubstituted tricycloctanes, not easily accessible by other ways, only the corresponding 3,3-disubstituted dihalides (from dihalocarbenes[3]) being known. The most recent methods based on the use of $Pd(OOCMe)_2$ lead to 3-monosubstituted derivatives and require diazocompounds as carbene source[4].

Both monosubstituted and disubstituted alkynes behave satisfactorily, except the diarylsubstituted ones, for which ring closure appears to be difficult and formation of an open chained product is preferred, for example:



(II)

Other bulky substituents as well as the carboxy group (and some other compounds like, for example, propargyl alcohol) also hinder the cyclopropanation reaction. Under the same conditions acetylene at atmospheric pressure gave unsatisfactory results.

The reaction is highly stereoselective, the cyclopropane ring being exclusively exo. When terminal alkynes are used, the methyl group in 3 is also placed stereoselectively. In the case of phenylacetylene the methyl group is likely to be syn to the norbornane bridge, as suggested by the complexity of the aromatic signal and by the absence of the upfield shift of the syn C-8 proton expected for a syn aromatic ring[5]. With dialkynes the two substituents in 3 also are probably placed in preferred positions, depending on their size but no work has been done to define their stereochemistry.

The following Table summarizes the results obtained by reacting norbornene (1 mol), alkyl or arylacetylene (1 mol) and $HCOONH_4$ (2 mol) in anisole at 80°C for 5 hours under nitrogen in presence of $Pd(PPh_3)_4$ (0.03 mol) as catalyst.

R-C≡C-R'		I	I
R	R'	Yield (%)[a,b]	Selectivity (%)[c]
Ph	H	35	77
p-$CH_3OC_6H_4$	H	37	80
	H	36	83
$PhCH(OH)CH_2$	H	39	79
$PhCH_2CH_2$	H	42	84
C_6H_{13}	H	29	73
C_2H_5	C_2H_5	33[d]	75

a) on norbornene put in reaction; only small amounts of the alkyne are recovered, dimers and oligomers being the main by-products; b) isolated yield; products were separated by preparative t.l.c.; c) yield on converted norbornene; d) another isomer (ca. 7%) probably not containing a cyclopropane ring was also present.

The products were characterized by spectroscopic methods. Significant ^1H (60,100 MHz) and ^{13}C (25.2 MHz) NMR data ($CDCl_3$, TMS) are reported below:

I(R=Ph, R'=H), ^1H NMR (100 MHz): δ 7.5-6.9 (m, 5H, aromatic protons), 2.50 (br s, 2H, HC(1), HC(5)), 1.6-1.3 (m, 6H, HC(2), HC(4), $H_2C(6)$, $H_2C(7)$), 1.22 (br d, J 11Hz, 1H, HC(8 syn)), 1.04 (s, 3H, CH_3), 0.74 (br d, J 11Hz, 1H, HC(8 anti)); ^{13}C NMR: δ 152.0, 128.0, 127.9, 125.2 (aromatic carbons), 36.2 (d, C(1), C(5)), 31.2 (t, C(8)), 30.3 (t, C(6), C(7)), 29.5 (d, C(2), C(4)), 26.8 (s, C(3)), 20.3 (q, CH_3).

I(R=p-$CH_3OC_6H_4$, R'=H), ^{1}H NMR (100 MHz): δ 7.3-7.0, 6.9-6.6 (AA'BB' system, 4H), 3.74 (s, 3H), 2.50 (br s, 2H), 1.6-1.3 (m, 6H), 1.22 (br d, J 11Hz, 1H), 1.00 (br s, 3H), 0.75 (br d, J 11Hz, 1H); ^{13}C NMR: δ 157.4, 144.6, 128.8, 113.7, 55.2, 36.3, 31.2, 30.4, 29.9, 26.2, 20.5.

I(R=2-thienyl, R'=H), ^{1}H NMR (100 MHz): δ 7.0-6.6 (m, 3H), 2.48 (br s, 2H), 1.7-1.4 (m, 6H), 1.38 (br d, J 11Hz, 1H), 1.14 (s, 3H), 0.74 (br d, J 11Hz, 1H); ^{13}C NMR: δ 157.0, 125.9, 121.4, 36.5, 33.8, 31.2, 30.1, 22.0, 19.8.

I(R=PhCH(OH)CH_2, R'=H), ^{1}H NMR (60 MHz): δ 7.25 (br s, 5H), 4.80 (dd, J 6Hz, 1H), 2.30 (br s, 1H), 2.22 (br s, 2H), 1.6-1.0 (m, 11H), 0.7, 0.6(2s, 2H); ^{13}C NMR: δ 145.3, 128.1, 127.1, 125.7, 72.9, 53.9, 36.0, 31.2, 30.4, 29.3, 18.1, 16.6.

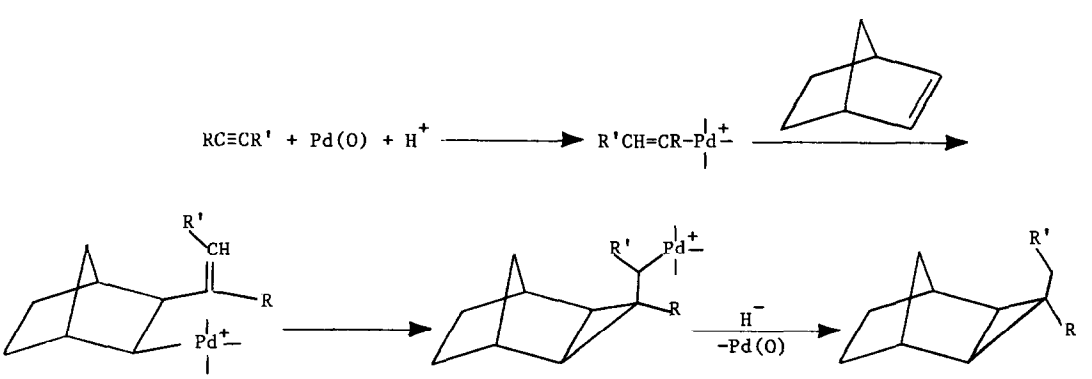
I(R=PhCH_2CH_2, R'=H), ^{1}H NMR (60 MHz): δ 7.4-6.8 (m, 5H), 2.8-2.4 (m, 2H), 2.3 (br s, 2H), 1.5-1.0 (m, 11H), 0.42 (s, 2H); ^{13}C NMR: δ 142.7, 128.0, 127.9, 125.2, 47.1, 35.9, 32.9, 30.9, 30.3, 30.2, 20.1, 16.5.

I(R=C_6H_{13}, R'=H), ^{1}H NMR (100 MHz): δ 2.30 (br s, 2H), 1.5-1.1 (m, 16H), 1.14 (s, 3H), 0.90 (m, 3H), 0.42 (s, 2H); ^{13}C NMR: δ 44.8, 35.9, 31.9, 31.0, 30.4, 30.1, 29.6, 26.2, 22.6, 20.2, 16.4, 14.0.

I(R=R'=C_2H_5), ^{1}H NMR (60 MHz): δ 2.32 (br s, 2H), 1.7-1.0 (m, 12H), 0.9 (m, 6H), 0.4 (s, 2H); ^{13}C NMR: δ 36.7, 35.9, 31.4, 30.9, 30.7, 30.3, 27.0, 21.0, 14.6, 10.9.

Diphenylacetylene gives II: ^{1}H NMR (60 MHz): δ 7.7-6.8 (m, 11H), 2.6-2.1 (m, 3H), 1.7-1.0 (m, 8H); ^{13}C NMR: δ 147.1, 142.0, 137.6, 131.4, 128.9, 128.1, 128.0, 127.5, 126.4, 125.7, 123.7, (aromatic and vinyl carbons), 50.6 (d, C(2)), 40.4 (d, C(1)), 37.0 (t, C(3)), 36.7 (d, C(4)), 36.0 (t, C(7)), 30.5, 28.9 (t, C(6), C(5)).

The course of the reaction can be viewed as involving first protonation of the coordinated alkyne, possibly via Pd-H, addition of the resulting Pd-C bond to norbornene, cyclopropane ring closure on the same Pd-C bond and termination by H^- transfer.



The scope of the reaction here described is being investigated. So far simple olefins failed to undergo cyclopropanation under the same conditions.

Acknowledgement

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