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A PALLADIUM-CATALYZED CYCLOCARBONYLATION REACTION LEADING TO SYNTHONS FOR CYCLOPENTANOID CHEMISTRY

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Summary

Tricyclic compounds, containing a cyclopentanone ring and an alkylidene group α to the carbonylic function, have been obtained by reaction of allylic halides with bicyclo[2.2.1]hept-2-ene or bicyclo[2.2.1]hepta-2,5-diene and carbon monoxide in the presence of a triarylphosphine palladium as complex catalyst. Retro Diels–Alder type reactions, which in part occur during the carbonylation, lead to alkylidencyclopentenones.

Introduction

As previously reported [1], carbonylation of aryl or vinyl halides with insertion of bicyclo[2.2.1]hept-2-ene (BCHE) or bicyclo[2.2.1]hepta-2,5-diene (BCHD), in the presence of salts of carboxylic acids in anisole as solvent, gives anhydrides. The following example refers to the use of styryl bromides (eq. 1):

(1)

We also attempted to extend this procedure to bring about ring formation on the double bond but without success. Using allylic halides in protic solvents, however, resulted in a new type of cyclocarbonylation.

Results and discussion

We found that palladium(0) complexes with triarylphosphines in solvents such as alcohols or primary amides are effective catalysts for the reaction of allylic bromides $RCH{=}CHCH_2Br$ with BCHE or BCHD compounds and carbon monoxide accord-

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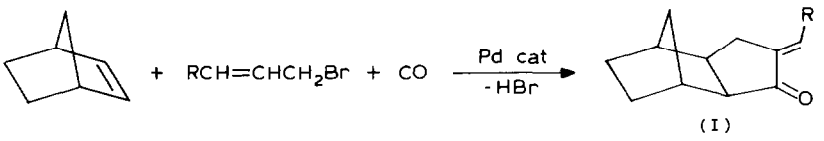
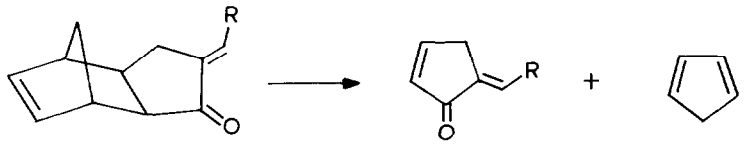
ing to eq. 2 (written for BCHE):



(I) (2)

The reaction takes place in presence of salts of carboxylic acids at temperatures of ca. 80°C and at atmospheric pressure of CO. Both *E* and *Z* allylic bromides and their branched isomers can be used with the same results. Allylic chlorides can also be used.

Among the compounds thus obtained the most interesting ones result from application of the synthesis to BCHD. This leads to a useful class of compounds, II, which by thermolysis give alkylidencyclopentenones (III), according to eq. 3:



(II) (III) (3)

An interesting feature of the process described is that the retro-Diels–Alder type reaction also occurs in part during the carbonylation. Results are reported in Table 1.

With R = H the product has a strong tendency to dimerize. With BCHE it was isolated as a dimer, the structure of which is reported in Fig. 1 [2].

When long times were required to complete the reaction as in the case of higher

TABLE 1

REACTION OF ALLYLIC BROMIDES WITH BCHE OR BCHD AND POTASSIUM ACETATE IN 1/1/1 MOLAR RATIO, CONCENTRATION OF ca. 0.0035 mol OF ALLYLIC BROMIDE FOR 10 ml OF SOLVENT, $Pd(PPh_3)_4$ AS CATALYST (0.02 mol/mol of allylic bromide) AT 80°C UNDER CO AT ATMOSPHERIC PRESSURE

R in $RCH{=}CHCH_2Br$	Bicyclic olefin	Solvent	*t*(h)	Yield [a](%) of I or of II + (III)	Mol of I or II + III / Mol of catalyst
H	BCHD	BuOH	4	25 [b]	12
Me	BCHD	BuOH	8	89(34)	45
Me	BCHD	HCONHMe	8	79(30)	40
Bu	BCHD	BuOH	24	52(20)	26
Ph	BCHD	BuOH	24	30 [b,c]	15
H	BCHE	BuOH	24	40 [d]	20
Me	BCHE	BuOH	24	35	18

[a] On the allylic bromide put in reaction; part of the latter was recovered as allylic acetate and/or ether; heavy oligomeric compounds, containing the carbonyl group, were also formed. [b] Compound III could not be detected, probably owing to its high reactivity. [c] A 20% of hydrocarbon products from the reaction of the allylic bromide with BCHD was present. [d] As dimer.

homologues of butenyl bromide, heavier carbonylation products were formed, which probably originated from oligomerization and cooligomerization with CO and BCHD or BCHE. Different *endo*-cooligomers of BCHD with CO have been reported [3].

The complex $Pd(PPh_3)_4$ was generally used as catalyst. Other triarylphosphines such as *o*-tolyl- or bis(diphenylphosphino)-ethane did not appear to offer advantages over the triphenyl one. Mixed ligand complexes, such as dibenzylidenacetone triphenylphosphine, can also be used.

The reactions leading to the monomer and to the dimer are both characterized by a very high stereoselectivity, the junction of the cyclopentanone ring with the bicyclic olefin being *cis,exo* and the R group being *trans* (opposite side to the carbonyl group). The alkylidencyclopentenone with R = Me has been described previously [4]. The dimer also appears to result from a regioselective Diels–Alder type reaction.

Beside X-ray data, structural assignments are based on MS, IR and NMR spectra, which are in accord with the proposed structure and on the chemical evidence provided by hydrogenation and by the retro-Diels–Alder type reaction (eq. 3). The stereochemistry of the alkylidene group in the products has been assigned on the basis of previously described structural correlations [5].

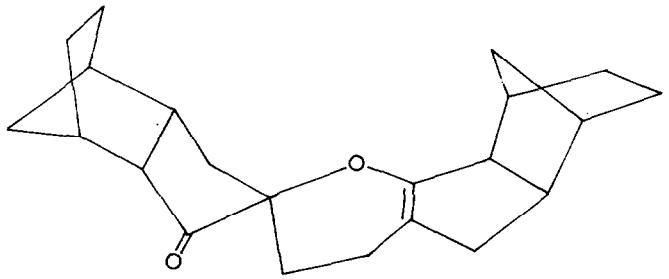
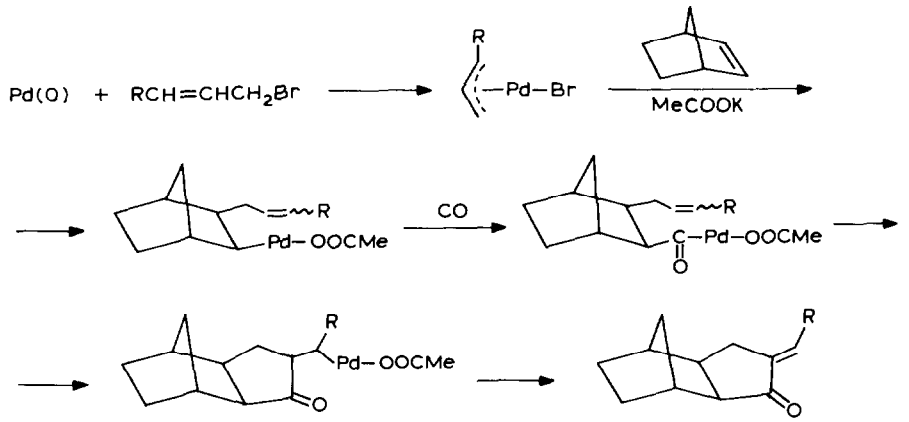


Fig. 1. Perspective view of the dimer of I (R = H) [2].



SCHEME 1

From the mechanistic point of view the reaction can be interpreted as an oxidative addition of the allylic bromide to palladium(0) followed by double bond insertion, carbonylation, cyclization and H-elimination. Scheme 1 refers to BCHE, but it also holds for BCHD.

The retro-Diels–Alder type reaction is worth noting, because it is catalyzed by palladium. Neither $Pd(PPh_3)_4$ nor $Pd(OOCMe)_2$ were effective, however, if added to II in a separate reaction, and so the action of Pd must occur when the organic group is still bonded to Pd.

Experimental

Starting materials were pure commercial products (Carbo Erba and Fluka). Triarylphosphine complexes were prepared by published methods [6]. Mass spectra were taken on CH5 Varian and on Finnigan 1020 instruments (70 eV) and IR spectra on a Perkin–Elmer Model 298 instrument. ^1H and ^{13}C NMR spectra were recorded on Varian EM 360 and XL 100 instruments at 60 and 25.2 MHz respectively, in $CDCl_3$, using TMS as internal standard.

2-Methylen-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-inden-1-one (II, R = H)

In a 100 ml flask equipped with stirrer and reflux condenser were placed $Pd(PPh_3)_4$ (80 mg, 0.069 mmol) and potassium acetate (339 mg, 3.46 mmol). A solution of BCHD (319 mg, 3.46 mmol) and 1-bromo-2-propene (418 mg, 3.46 mmol) in 10 ml of n-butanol was added under nitrogen. The latter was replaced by CO from a graduated burette. The flask was placed in an oil bath and kept at 80°C for 4 h with stirring. When the CO adsorption was close to 0.9 mol per mol of bromopropene, Pd black began to separate. Light products (starting compounds, butenyl acetate and solvent) were recovered by distillation at normal pressure. A 25% yield of II (R = H) was determined by GLC.

Retro-Diels–Alder type products III were not observed by GLC probably because of their instability. Heavy products, probably derived from cooligomerization of BCHD with CO (IR 1700 cm^{-1}) [3] were also formed, but not investigated further. Separation by TLC (SiO_2, n-hexane/THF 9/1 as eluents) gave compound II (R = H).

II (R = H) IR (film): 3025, 1710, 1630 cm^{-1}; MS: *m/e* 160, 95, 94, 66, 65, 40, 39; ^1H NMR: δ 6.3–6.1 (AB system, 2H, HC(5), HC(6)), 6.0–5.8 (m, 1H, =CH), 5.4–5.2 (m, 1H, =CH), 3.1 (br s, 1H, HC(7)), 3.0–2.6 (m, 2H, HC(4), HC(3)), 2.5–2.0 (m, 3H, HC(3), HC(3a), HC(7a)), 1.3 (br s, 2H, H_2C (methano)).

2-Ethyliden-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-inden-1-one (II, R = Me)

(a) The reaction was run as above for 8 h using $Pd(PPh_3)_4$ (80 mg, 0.069 mmol), potassium acetate (339 mg, 3.46 mmol), BCHD (319 mg, 3.46 mmol) and *E*-1-bromo-2-butene (468 mg, 3.46 mmol) in 10 ml of n-butanol. An 89% overall yield was determined by GLC (55% of II (R = Me), and 34% of ethylidencyclopentenone III (derived from retro-Diels–Alder reaction)).

(b) The same reaction was also run using HCONHMe instead of n-butanol as solvent (CO absorption ca. 0.8 mol per mol of bromide) with 79% total yield (49% of II (R = Me) and 30% of III (R = Me) (by GLC)).

(c) Similar results were obtained using *Z*-1-bromo-2-butene, 3-bromo-1-butene and *E*-1-chloro-2-butene.

II (R = Me), IR (film): 3030, 1710, 1640 cm^{-1}; MS: *m/e* 174, 109, 91, 79, 77, 66, 65, 54, 52; ^1H NMR: δ 6.8–6.3 (m, 1H, =HC–CH_3) 6.3–6.1 (AB system, 2H, HC(5), HC(6)), 3.1 (br s, 1H, HC(7)), 2.9–2.5 (m, 2H, HC(4), HC(3)), 2.5–2.0 (m, 3H, HC(3), HC(3a), HC(7a)), 1.8 (br d, *J* 7Hz, 3H, CH_3), 1.3 (br s, 2H, H_2C (methano)) ppm; ^{13}C NMR: δ 194.3 (s), 142.1 (s), 138.3 (d), 137.6 (d), 131.7 (d), 55.3 (d), 49.9 (d), 47.8 (d), 42.9 (t), 38.5 (d), 30.7 (t), 15.0 (q) ppm.

III (R = Me): spectroscopic data were identical with those in the literature [4].

2-Pentyliden-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-inden-1-one (II, R = Bu)

The reaction was run as above for 24 h using 614 mg (3.46 mmol) of *E*-1-bromo-2-heptene instead of *E*-1-bromo-2-butene. GLC analysis gave a 52% total yield (32% of II (R = Bu) and 20% of III (R = Bu), the latter resulting from retro-Diels–Alder reaction). Heavy compounds not detectable by GLC, were also formed. Unreacted 1-bromo-2-heptene (5%) was recovered along with the corresponding acetate (7%) as the main allylic isomers.

II (R = Bu), IR (film): 3030, 1710, 1640 cm^{-1}; MS: *m/e* 216, 151, 95, 77, 66, 55, 41; ^1H NMR: δ 6.8–6.3 (m, 1H), 6.3–6.0 (AB system, 2H), 3.1 (br s, 1H), 2.9–2.6 (m, 2H), 2.5–1.9 (m, 5H), 1.8–1.1 (m, 6H), 1.1–0.8 (m, 3H) ppm; ^{13}C NMR: δ 194.2 (s), 140.9 (s), 138.3 (d), 137.5 (d), 137.0 (d), 55.3 (d), 49.9 (d), 47.8 (d), 42.9 (t), 38.5 (d), 30.8 (t), 30.4 (t), 29.2 (t), 22.5 (t), 13.8 (q) ppm.

III (R = Bu): MS, *m/e*: 150, 121, 95, 82, 79, 77, 66, 55.

2-Benzyliden-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-inden-1-one (II, R = Ph)

The reaction was run as above for 24 h using 683 mg (3.46 mmol) of *E*-1-bromo-3-phenyl-2-propene instead of *E*-1-bromo-2-butene. A 30% yield of II (R = Ph) (240 mg) was obtained after separation by TLC.

Two isomeric hydrocarbons with mass 208, resulting from the reaction of the starting bromide with BCHD without CO insertion (probably analogous to those formed with Ni [7]), were also obtained, but not further characterized (150 mg, 21% yield). Heavy compounds, not detectable by GLC, were also formed. Unreacted bromide was recovered mainly as butyl ether (ca. 8%).

II (R = Ph), IR (film): 3020, 1700, 1610, 1580, 750, 690 cm^{-1}; MS: *m/e* 236, 171, 170, 169, 141, 115, 91, 77, 66, 65, 64, 51; ^1H NMR: δ 7.7–7.0 (m, 6H), 6.3–6.0 (AB system, 2H), 3.2–2.9 (m, 1H), 2.9–2.5 (m, 2H), 2.5–2.2 (m, 3H), 1.4–1.1 (m, 2H) ppm; ^{13}C NMR: δ 207.9 (s), 139.3 (s), 138.4 (d), 137.5 (d), 132.7 (d), 135.3, 130.6, 129.1, 128.5 (aromatic carbons), 54.3 (d), 49.8 (d), 48.0 (d), 42.9 (t), 39.2 (d), 33.8 (t) ppm.

Octahydro-2-ethyliden-4,7-methano-1H-inden-1-one (I, R = Me)

$Pd(PPd_3)_4$ (80 mg, 0.069 mmol), potassium acetate (339 mg, 3.46 mmol) and BCHE (326 mg, 3.46 mmol) were caused to react with 468 mg (3.46 mmol) of *E*-1-bromo-2-butene in 10 ml of n-butanol under CO. The reaction was much slower than with BCHD and required ca. 24 h for absorption of the same amount of CO. I (R = Me), 215 mg (35% yield, was separated by TLC as above). Heavy compounds, not detectable by GLC, were also formed. A little unreacted 1-bromo-2-butene was recovered as acetate.

I (R = Me), IR (film): 1710, 1640 cm^{-1}; MS: *m/e* 176, 161, 148, 133, 119, 109, 108, 105, 93, 91, 82, 81, 80, 79, 77, 67, 66, 65, 54, 53; ^1H NMR: δ 6.7–6.2 (m, 1H),

2.7–1.9 (m, 6H), 1.75 (br d, $J = 7$ Hz, 3H), 1.5–0.8 (m, 6H) ppm: ^{13}C NMR: δ 209.2 (s), 139.7 (s), 130.9 (d), 57.0 (d), 44.4 (d), 42.1 (d), 39.8 (d), 33.6 (t), 31.7 (t), 28.7 (t), 28.4 (t), 15.3 (q) ppm.

Octahydro-2-methylen-4,7-methano-1H-inden-1-one (I, R = H), dimer (Fig. 1)

A mixture of $Pd(PPh_3)_4$ (80 mg, 0.069 mmol), potassium acetate (339 mg, 3.46 mmol), BCHE, (326 mg, 3.46 mmol) and 1-bromo-2-propene (418 mg, 3.46 mmol) in 10 ml of n-butanol was caused to react as above for 24 h. Separation by TLC gave 225 mg (40% yield) of I (R = H) as dimer (Fig. 1) and heavier carbonylation products. Crystallization from ethyl alcohol gave white crystals suitable for X-ray determination (m.p. 89–90°C). IR (KBr): 1740, 1690 cm^{-1}; MS: *m/e* 324, 175, 163, 162, 95, 91, 79, 77, 67, 66, 55, 41, 40.

Hydrogenation of compounds I (R = Me) and II (R = Me). Compound I (R = Me) (100 mg, 0.57 mmol) was dissolved in EtOH 95% (5 ml) and the mixture hydrogenated on Pd/C 10% at room temperature. The same procedure was used for compound II (R = Me). The hydrogenated products proved to be identical by GLC and MS analyses. MS: *m/e* 178, 150, 93, 83, 80, 79, 77, 67, 66, 55, 53, 42, 41.

Thermolysis of compound II (R = Me)

Compound II (R = Me) was passed through a quartz tube kept at 500°C under 0.1 mm/Hg [8] and decomposed quantitatively. The vapour of III (R = Me) was condensed in a liquid nitrogen trap.

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