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# PALLADIUM- OR NICKEL-CATALYZED SEQUENTIAL REACTION OF ORGANIC BROMIDES, BICYCLO[2.2.1]HEPT-2-ENE OR BICYCLO[2.2.1]HEPTA-2,5-DIENE AND ALKYNES

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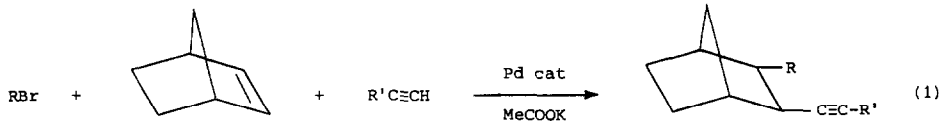
## Summary

The reactions of various types of organic bromides with a mixture of bicycloheptene or bicycloheptadiene and alkynes are reported. The products are bicyclic compounds, containing an organic chain and an alkynyl group in adjacent positions.

In the presence of a $Pd^0$ catalyst, aromatic and vinylic bromides react smoothly in ethereal solvents. Allylic bromides are much less reactive and require protic solvents and arylacetylenes to give satisfactory results. With $Ni^0$ catalysts the situation is reversed: aromatic and vinylic bromides show little or no tendency to undergo the desired reaction and allylic bromides give better results, although the occurrence of secondary reactions between allylic bromides and bicycloheptene derivatives or between allylic bromides and alkynes limits the synthetic value of the reaction. With both Pd and Ni catalysts electron-withdrawing substituents in the arylacetylenes accelerate the reaction. Formation of a Pd complex able to effect reductive coupling of bicycloheptyl and alkynyl groups or of a Ni complex able to abstract hydrogen from the organic chain (resulting from double bicycloheptene and arylacetylene insertion into an allyl–Ni bond) are possibly involved as critical steps, which drive the preceding ones to completion.

## Introduction

We previously described [1] the reaction:




(1)

(R = vinyl, aryl; R' = alkyl, aryl)

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We report here further studies aimed at extending the scope of this reaction, which is particularly useful for the synthesis of prostaglandin analogues [2]. In particular we have found that under special conditions allyl and styryl groups can be brought into reaction in the presence of $Pd^0$ or of $Ni^0$ catalysts. This offers the opportunity for a comparison between the two metals.

## Results

The reaction previously described was carried out in anisole at 80 °C using $Pd(PPh_3)_4$ as catalyst. Bicyclo[2.2.1]hept-2-ene or bicyclo[2.2.1]hepta-2,5-diene were required as the olefinic component. The reaction led to stereoselective *cis,exo*-addition of R and C≡CR′ groups to the double bond. Both alkyl and arylacetylenes were reactive. It is especially noteworthy that 3-substituted 1-alkynes (with hydroxy, amino or other substituents) reacted without difficulty (Table 1). Electron-withdrawing substituents in phenylacetylene increased the reaction rate, as shown by competitive experiments carried out with bromostyrene as the organic bromide (Table 2). These substituents also increased the rate of phenylacetylene oligomerization, however, and yields were lower than those from the parent phenylacetylene (Table 1).

In the case of allyl groups we did not observe any significant reaction unless we used alcohols or other protic solvents, as we shall see later. A nitrogen ligand (tetramethylethylendiamine) was also ineffective. In contrast, complex II, containing the Pd–C bond, formed by bicycloheptene insertion into the allyl–Pd bond, readily reacted with alkynes or with their sodium salts [2]. The phenylbicycloheptyl complex III reacted even at 0 °C. In all cases the reaction with *p*-nitro-substituted phenylacetylene was faster than that with unsubstituted or *p*-methoxy-substituted phenylacetylene.

TABLE 1

REACTION OF ORGANIC BROMIDES RBr WITH BICYCLO[2.2.1]HEPT-2-ENE (BCHE) OR BICYCLO[2.2.1]HEPTA-2,5-DIENE (BCHD), ALKYNES R′C≡CH AND POTASSIUM ACETATE (1/1/1/1 molar ratio) IN ANISOLE AT 80 °C WITH $Pd(PPh_3)_4$ OR $Ni(COD)_2 + 2P(O\text{-}i\text{-}Pr)_3$ AS CATALYST (0.03 and 0.1 mol/mol of bromide, respectively)

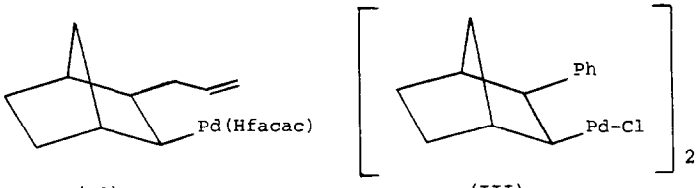
| Metal | R in RBr | BCHE or BCHD | R′ in R′C≡CH | Isolated yield of I (%) |
|---|---|---|---|---|
| Pd | Ph | BCHE | Ph | 42 |
| | PhCH=CH | BCHE | Ph | 77 [a] |
| | PhCH=CH | BCHE | *p*-$C_6H_4OMe$ | 42 [a] |
| | PhCH=CH | BCHE | *p*-$C_6H_4NO_2$ | 60 [a] |
| | PhCH=CH | BCHD | Ph | 59 |
| | PhCH=CH | BCHE | $(CH_2)_5Me$ | 52 |
| | PhCH=CH | BCHE | $C(OH)Me_2$ | 72 |
| | PhCH=CH | BCHE | $C(NH_2)Me_2$ | 86 |
| | $CH_2$=$CHCH_2$ | BCHE | Ph | – |
| Ni | Ph | BCHE | Ph | VII, traces |
| | $CH_2$=$CHCH_2$ | BCHE | Ph | 6 [a] |

[a] Yield determined by GLC.

TABLE 2

COMPETITIVE REACTIONS OF PhCH=CHBr (1 mol) WITH TWO DIFFERENT *p*-SUBSTITUTED PHENYLACETYLENES (1 mol each) AT CA. 25% CONVERSION (conditions as in Table 1)

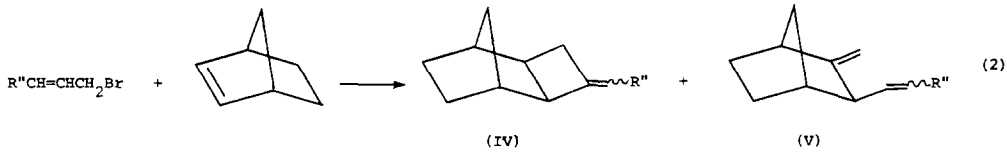
| *para*-Substituents | I (R′ = OMe) / I (R′ = H) | I (R′ = $NO_2$) / I (R′ = H) |
|---|---|---|
| OMe, H | 0.26 | |
| $NO_2$, H | | 8.20 |




(II) (III)

Use of nickel, as $Ni[P(O\text{-}i\text{-}Pr)_3]_4$ or, more effectively, $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) + $2P(O\text{-}i\text{-}Pr)_3$ ($Ni(PPh_3)_4$ gave poor results) led to formation of I (R = allyl) with low selectivity, other competing reactions being preferred. *β*-Bromostyrene mainly decomposed to styryl coupling products (diphenylbutadienes [3]), and bromobenzene did not react appreciably. Alkylacetylenes did not react.

Change of solvent led to significant improvements in the selectivity of the reactions with allylic bromides. Protic solvents were found to be moderately effective with palladium, but results were still, unsatisfactory with nickel owing to the occurrence of other reactions, particularly that of allylic bromides with bicycloheptene or bicycloheptadiene [4] (eq. 2) to give IV and V as the main isomers, and that of allylic bromides with arylacetylenes (eq. 3, R = allyl), to give VI [5]. The former of these reactions was favored by aprotic solvents, whereas the latter was more important in protic and polar solvents:




(IV) (V) (2)

$$RBr + HC{\equiv}CAr \rightarrow \underset{(VI)}{RC{\equiv}CAr} \qquad (3)$$

Use of a solvent of intermediate polarity, such as acetone, gave better results.

The various aspects of the palladium- or nickel-catalyzed reactions will be considered separately.

*Palladium-catalyzed reactions in butanol (Table 3)*

Of the allyl bromides, the simplest representative, allyl bromide, did not react with bicycloheptene or bicycloheptadiene and arylacetylenes in butanol. *E*-2-Butenyl bromide showed a higher reactivity, but yields were moderate; most of the butenyl bromide was recovered as mixture of allylic isomers, however, both as such or as

acetate, and thus selectivity on the butenyl group was generally high. Phenylacetylene and its *p*-nitro derivative gave cyclotrimers (triarylbenzenes [6]) and other oligomers at a faster rate so that little was left for the reaction with allylic bromide. With *p*-methoxyphenylacetylene, however, most alkyne could be recovered and so the low conversion must be ascribed to some sort of catalyst deactivation. The *p*-nitro derivative, which gave I ($R = CH_2CH{=}CHMe$, $R' = p\text{-}C_6H_4NO_2$) in 28% yield, was the most reactive. With other protic solvents such as formamide and its mixture with quinoline a 29% yield ($R' = Ph$) was obtained. Products from the reaction of butenyl bromide with bicycloheptene were also formed in some cases.

Styryl bromide and bromobenzene were also examined in butanol under similar conditions. The former gave the best results (although worse than in anisole), and was rapidly consumed by secondary reactions such as coupling of the styryl group. In this case *p*-nitrophenylacetylene did not give the best results, probably because of the fast disappearance of the acetylenic compound as oligomer. A 57% yield of I was observed with PhC≡CH.

The situation was again different with bromobenzene in butanol. Bromobenzene reacted rather slowly with bicycloheptene, reacting preferentially with arylacetylenes [7] (20% yield of I and 45% of VI with PhC≡CH). The latter, however, gave substantial amounts of cyclotrimers and oligomers, and so the expected increase in yield with $p\text{-}NO_2$ was not observed, and only a 4% yield of I was obtained. Most of

TABLE 3

REACTION OF ORGANIC BROMIDES WITH BICYCLO[2.2.1]HEPT-2-ENE, ALKYNES AND POTASSIUM ACETATE (1/1/1/1 molar ratio) IN BUTANOL (unless otherwise indicated) AT 80 °C WITH $Pd(PPh_3)_4$ OR $Ni(COD)_2 + 2P(O\text{-}i\text{-}Pr)_3$ AS CATALYST (0.05 and 0.1 mol/mol of bromide, respectively)

| Metal | R in RBr | R′ in R′C≡CH | Yield (%) (GLC) | | |
|---|---|---|---|---|---|
| | | | I | IV + V | VI |
| Pd | $CH_2{=}CHCH_2$ | Ph | – [a] | – | – |
| | $MeCH{=}CHCH_2$ | Ph | 19 [b] | 7 | – |
| | $MeCH{=}CHCH_2$ | $p\text{-}C_6H_4OMe$ | 12 [b] | 10 | – |
| | $MeCH{=}CHCH_2$ | $p\text{-}C_6H_4NO_2$ | 28 [b] | – | – |
| | $MeCH{=}CHCH_2$ | Ph | 28 [b,c] | – | – |
| | $MeCH{=}CHCH_2$ | Ph | 29 [b,d] | – | – |
| | $Me(CH_2)_3CH{=}CHCH_2$ | Ph | 19 [b] | 7 | – |
| | PhCH=CH | Ph | 57 [e] | – | – |
| | PhCH=CH | $p\text{-}C_6H_4OMe$ | 39 [e] | – | – |
| | PhCH=CH | $p\text{-}C_6H_4NO_2$ | 44 [e] | – | – |
| | Ph | Ph | 20 [f] | – | 45 |
| | Ph | $p\text{-}C_6H_4OMe$ | 9 [f] | – | 29 |
| | Ph | $p\text{-}C_6H_4NO_2$ | 4 [f] | – | 17 |
| Ni | $CH_2{=}CHCH_2$ | Ph | 6 | 15 | 21 |
| | PhCH=CH | Ph | – | – | – |
| | Ph | Ph | – | – | – |

[a] A dash denotes that only a trace or none of the product was detected. [b] Most unreacted allylic bromides were recovered as such or as acetates (mixtures of allylic isomers); with $R' = Ph$ or $p\text{-}C_6H_4NO_2$ the alkyne mainly disappeared as oligomer. [c] Butanol + quinoline (1/1 vol.) as solvent. [d] Formamide + quinoline (1/1 vol.) as solvent. [e] The remaining bromostyrene gave coupling products and the alkyne was converted into oligomers. [f] The remaining PhBr was recovered. The alkyne was converted into oligomers.

the bromobenzene not converted into I or VI was recovered unchanged.

A comparison with the reactivity of allyl bromide with bicycloheptene and phenylacetylene in presence of $Ni(COD)_2 + 2P(O\text{-}i\text{-}Pr)_3$ is shown in the same Table 3. The low yield of I (6%) and lack of selectivity of the reaction, which gives substantial amounts of IV, V and VI (R = allyl, R′ = Ph), are clearly shown.

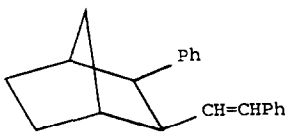
*Nickel-catalyzed reactions in acetone (Table 4)*

Allyl groups tend to insert bicycloheptene and undergo ring closure at the double bond of the allyl group itself [4]. To prevent or limit this reaction, the solvent must be able to compete with the allyl group for coordination. Too polar solvents can interfere with bicycloheptene and alkyne coordination, however, and other reactions such as (3) can take place, and so a solvent of intermediate polarity (acetone) was chosen for the nickel-catalyzed reactions. However, the amount of VI was still high, even with *p*-nitrophenylacetylene, which gave the best result (27% yield of I and 55% yield of VI).

Contrary to the observations with palladium, the steric effect of 3-methyl-substituted allyl group was so high that the reaction leading to I occurred only to a very low extent. A mixture of I (R = $MeCHCH{=}CH_2$) and I (R = $MeCH{=}CHCH_2$) was obtained.

Alkylacetylenes such as 1-octyne were practically unreactive.

Of the other types of bromides, styryl bromide did not give satisfactory results because other reactions, such as coupling of styryl groups, predominated, and bromobenzene gave a small amount (10% yield) of a compound which was identified as VII (dihydro derivative of I (R, R′ = Ph)):




(VII)

TABLE 4

REACTION OF ORGANIC BROMIDES WITH BICYCLO[2.2.1]HEPT-2-ENE, ALKYNES AND POTASSIUM ACETATE (1/1/1/1 molar ratio) IN ACETONE WITH $Ni(COD)_2 + 2P(O\text{-}i\text{-}Pr)_3$ AS CATALYST (0.1 mol/mol of bromide) under reflux

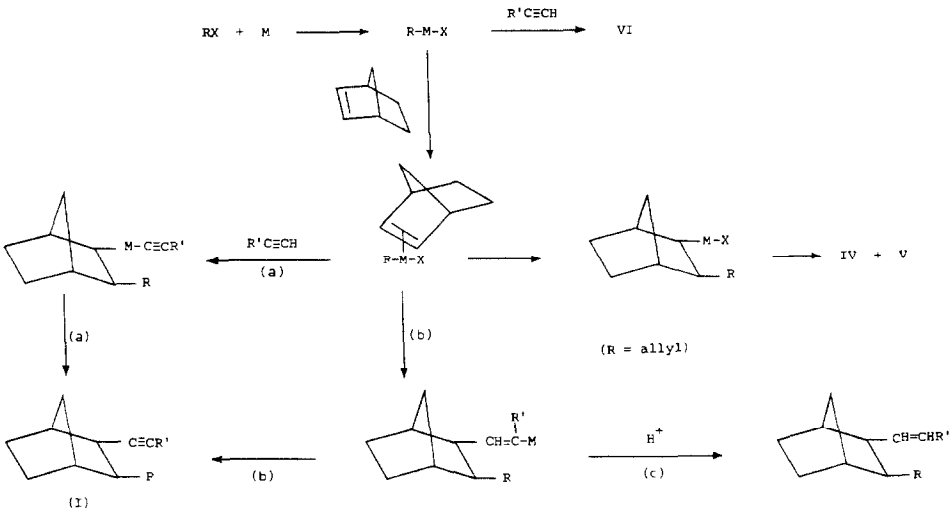
| R in RBr | R′ in R′C≡CH | Yield (%) (GLC) | | |
|---|---|---|---|---|
| | | I | IV + V | VI |
| $CH_2{=}CHCH_2$ | Ph | 22 | 4 | 26 |
| $CH_2{=}CHCH_2$ | *p*-$C_6H_4OMe$ | 11 | 12 | 24 |
| $CH_2{=}CHCH_2$ | *p*-$C_6H_4NO_2$ | 27 | traces | 55 |
| $MeCH{=}CHCH_2$ | Ph | 4 [a] | 5 | 37, 30 [b] |
| Ph | Ph | 10 [c] | – | – |

[a] Three isomers. [b] VI (R = $MeCHCH{=}CH_2$) and VI (R = $MeCH{=}CHCH_2$). [c] Stoichiometric reaction leading to VII (dihydro derivative of I). Other products resulted from the reaction of 1 mol of bicycloheptene with one of phenylacetylene. Most PhBr was recovered.

## Discussion

On the basis of the existing knowledge the course of the reaction can be depicted by the following Scheme (inert ligands are omitted, X = Br, MeCOO; M = Pd, Ni):

SCHEME 1




The first step is an oxidative addition, which is favored by ligands such as triphenylphosphine, both with palladium and nickel. This ligand is also satisfactory for the final reductive elimination step in the case of palladium, but a more electron-withdrawing ligand such as triisopropyl phosphite is more suitable in the case of nickel. The isopropyl group also favors ligand dissociation [8]. The subsequent steps consist of carboxylato group-promoted bicycloheptene insertion [9,10], followed either by alkyne insertion and H-elimination or by coupling with an alkynyl group.

The overall process can be regarded as the result of two different trends: on one hand the electronegativity of the organic group increases on passing from allyl-Pd–X to aryl- or vinyl-Pd–X and from Pd to Ni, and reaches the proper value for bicycloheptene insertion when R in R–Pd–X is aryl or vinyl and when R in R–Ni–X is allyl; on the other hand the reductive elimination step becomes more difficult on passing from Pd to Ni. Accordingly, allyl–Pd–X is rather stable and reaction only occurs under special conditions, namely in presence of protic solvents and of alkyl substituents on the allyl group. The protic solvents possibly cause the allyl group to disproportionate into an allyl cation and an allyl anion, while the alkyl substituent on the allyl group would increase the nucleophilicity of the allyl group in the anion, thus favoring bicycloheptene insertion. Amines such as tetramethylethylendiamine, which have been observed to bring about disproportionation [11], do not induce reaction. This cannot be taken as an evidence against disproportionation, however, because of the possibility of other unfavorable interactions of the amine with the catalytic cycle.

As already mentioned, the reaction in butanol stops at low conversions, and so formation of a stable allylic complex, which no longer acts catalytically, must be postulated.

The reaction proceeds in the best way with more electron-withdrawing palladium-bonded organic groups, as aryl or vinyl groups.

With allyl–Ni–X the problem does not lie in the reactivity but in the selectivity, other reactions also being favored. The styryl–Ni bond readily undergoes vinyl coupling and other reactions, which apparently are faster than the desired one which depends strongly on the feasibility of the final reductive elimination step. This step becomes so difficult with the phenylbicycloheptyl–Ni bond that a stoichiometric reaction occurs, leading to oxidative elimination by proton uptake (the latter originating from traces of water either initially present in the medium or formed by acetone condensation) according to route (b) → (c) in Scheme 1.

The critical step thus appears to be reductive elimination. This may occur in the two different routes shown in Scheme 1. The fact that with nickel we obtain a small amount of the dihydro derivative VII and not compound I itself means that an insertion reaction of PhC≡CH has taken place, as in the first stage of route b, but, H-elimination being difficult for steric and electronic reasons (difficult approach by H-acceptors to C–H *trans* to C–M), route c (H-uptake from the medium) prevails. The generality of this behaviour is difficult to assess. With R = allyl the product is I (R′ = phenyl) and not the dihydro derivative. This may be taken as an indication that route a is operative, chelation by the allyl group preventing alkyne insertion and leaving only route a available; on the other hand the allyl group could offer less steric hindrance to the H-abstraction process than the aromatic ring, and in this case route b should be followed. So far no clear evidence in distinguishing between routes a or b has be obtained. Possible support for route b comes from the absence of the coupling compound I, which means that the alkyne or the complex acetylide undergoes other reactions, such as cyclotrimerization, much faster than coupling with the bicycloheptyl group.

In contrast, the reaction with Pd must follow route a, at least in part, because complexes II and III readily react with arylacetylenes and with their sodium salts to form I, and the latter reaction corresponds to route a. The $NO_2$ group increases the reaction rate probably because displacement of X to form the complex which undergoes coupling is favored. Since the same trend is observed for the overall reaction it can be concluded that this is the key-step, which drives all the preceding ones to completion.

Summing up, the reaction of organic bromides with bicycloheptene or bicycloheptadiene and alkynes appears to be subject to many limitations, depending on the nature of the catalyst and of the organometallic bonds involved.

Allyl groups are less reactive with palladium than with nickel. Phenyl and styryl groups react much better when bonded to palladium, but do not give the expected reaction when complexed with nickel. Allyl groups are reactive with nickel but not selective.

The low back-donation ability of palladium towards allyl groups makes them poorly reactive, whereas nickel has the opposite effect. More electron-withdrawing groups such as phenyl and styryl favor the reaction with palladium.

The superior ability of palladium to undergo reductive elimination favors the entire process by pushing unfavorable equilibria to the right, whereas nickel cannot

prevent other secondary reactions originating from the organometallic indermediates formed in each step of the process. Thus the nickel-bonded styryl group undergoes other coupling-reactions and is not available for the desired process. The nickel-bonded phenyl group undergoes bicycloheptene and alkyne insertion, but the final Ni–C bond is cleaved by oxidative rather than reductive elimination.

The last step with palladium is probably a coupling reaction, whereas with nickel it may consist of H-elimination from an insertion intermediate, but conclusive evidence has still to be obtained.

## Experimental

Most starting materials were pure commercial products (C. Erba, Fluka, and Merck). Complexes $Pd(PPh_3)_4$ and $Ni(COD)_2$ were Strem products. Allylic bromides were prepared by bromination of the corresponding 1-olefin with bromosuccinimide and separation of the isomers. *p*-Methoxyphenylacetylene, *p*-nitrophenylacetylene, and complexes II and III were prepared by literature methods [12–15]. Products were separated by GLC and TLC and characterized by their MS (CH5 Varian and Finnigan 1020 instruments, 70 eV), IR spectra (Perkin–Elmer 298), $^1H$ and $^{13}C$ NMR spectra (Varian EM 360 and XL 100 at 60 and 25.2 MHz, respectively in $CDCl_3$, TMS as internal standard).

*General procedure for the reaction of organic bromides, bicycloheptene and alkynes in presence of $Pd(PPh_3)_4$*

The procedure is illustrated for the case of *E*-1-bromo-2-butene, bicycloheptene and phenylacetylene. In a 3-necked flask, equipped with condenser and magnetic stirrer are placed $Pd(PPh_3)_4$ (200 mg, 0.17 mmol) and MeCOOK (333 mg, 3.4 mmol) under nitrogen. A degassed butanol solution (13 ml) containing bicycloheptene (320 mg, 3.4 mmol), phenylacetylene (347 mg, 3.4 mmol), and 1-bromo-2-butene (459 mg, 3.4 mmol) is then added. The stirred mixture is kept at 80 °C for 48 h then 10% $H_2SO_4$ is added and the organic part is extracted with diethyl ether, dried, and analyzed or separated by conventional methods. The same results are obtained using an 85/15 mixture of 1-bromo-2-butene and 3-bromo-1-butene.

*General procedure for the reaction of organic bromides, bicycloheptene and alkynes in presence of $Ni(COD)_2 + 2P(O\text{-}i\text{-}Pr)_3$*

The procedure is illustrated for allyl bromide, bicycloheptene and phenylacetylene. In the flask mentioned above, $Ni(COD)_2$ (100 mg, 0.36 mmol) and MeCOOK (356 mg, 3.64 mmol) are introduced together with degassed acetone (2 ml) under nitrogen. $P(O\text{-}i\text{-}Pr)_3$ (151 mg, 0.73 mmol) is added and the solution is stirred for some minutes, then a solution of bicycloheptene (342 mg, 3.64 mmol), phenylacetylene (371 mg, 3.64 mmol) and allyl bromide (440 mg, 3.64 mmol) in 4 ml of acetone is added. The mixture is stirred under reflux for 6–8 h, then 10% $H_2SO_4$ is added and the solution is extracted with diethyl ether. Work-up is carried out by conventional procedures.

*Characterization of the products*

Some of the compounds have been described in previous papers I [1], IV + V [4], VI [5,7]. Compound VII was fully hydrogenated on Pd/C and identified by comparison with the hydrogenation product of I (R, R′ = phenyl). Compounds

IV + V, containing a Me or Bu group in the allylic chain, were found to be identical with those obtained in the nickel-catalyzed reaction; these particular compounds were not characterized, although they had not been described in our previous work. The only difference may be the presence of an isomer of the cyclobutane derivative IV, derived from the allylic isomer of the starting bromide.

*I* ($R = CH_2{=}CHCH_2$, $R' = Ph$). Mass spectrum: $M^+$ 236, *m/e* 169, 167, 165, 153, 152, 142, 141, 128, 117, 115, 103, 102, 93, 91, 89, 79, 77, 67, 65, 63, 53, 51, 41; $^1$H NMR: $\delta$ 7.6–7.0 (m, 5H), 6.3–5.4 (m, 1H), 5.2–4.7 (m, 2H), 2.7 (d, *J* 8 Hz, 1H), 2.5–1.9 (m, 4H), 1.9–0.9 (m, 7H) ppm; $^{13}$C NMR: $\delta$ 138.7, 131,3, 127.9, 127.1, 124.1, 114.9 (aromatic and vinylic carbons), 91.7, 82.6 (acetylenic carbons), 45.5, 44.7 (d, C(2), C(3)), 40.3, 39.5 (d, C(1), C(4)), 37.3, 34.0 (t, $CH_2CH{=}$, C(7)), 29.9, 28.4 (t, C(5), C(6)) ppm.

*I* ($R = MeCH{=}CHCH_2$, $R' = Ph$). Mass spectrum: $M^+$ 250, *m/e* 235, 183, 167, 156, 155, 141, 129, 128, 117, 115, 105, 93, 91, 79, 77, 67, 65, 55, 41; $^1$H NMR: $\delta$ 7.4–6.9 (m, 5H), 5.5–5.2 (m, 2H), 2.6 (d, *J* 8 Hz, 1H), 2.4–1.8 (m, 4H), 1.8–0.8 (m, 10H) ppm; $^{13}$C NMR: $\delta$ 131.3, 127.9, 127.1, 125.2, 124.6 (aromatic and vinylic carbons), 92.0, 82.7 (acetylenic carbons), 46.3, 45.0 (d, C(2), C(3)), 40.6, 39.8 (d, C(1), C(4)), 36.1, 34.0 (t, $CH_2C{=}$, C(7)), 30.1, 28.6 (t, C(5), C(6)), 17.8 (q, $CH_3$) ppm.

*I* ($R = MeCH{=}CHCH_2$, $R' = p\text{-}C_6H_4OCH_3$). Mass spectrum: $M^+$ 280, *m/e* 265, 251, 213, 211, 197, 186, 185, 171, 147, 145, 128, 121, 115, 105, 93, 91, 79, 77, 67, 55, 43, 41; $^1$H NMR: $\delta$ 7.4–6.5 (AA'BB' system, 4H), 5.5–5.2 (m, 2H), 3.7 (s, 3H), 2.6 (d, *J* 8 Hz, 1H), 2.5–0.7 (m, 14 H) ppm; $^{13}$C NMR: $\delta$ 158.7, 132.5, 131.3, 125.2, 116.5, 113.6 (aromatic and vinylic carbons), 90.2, 82.1 (acetylenic carbons), 55.1 (q, $OCH_3$), 45.9, 44.8 (d, C(2), C(3)), 40.2, 39.5 (d, C(1), C(4)), 36.1, 33.9 (t, $CH_2C{=}$, C(7)), 29.9, 28.5 (t, C(5), C(6)), 18.0 (q, $CH_3$) ppm.

*I* ($R = MeCH{=}CHCH_2$, $R' = p\text{-}C_6H_4NO_2$). Mass spectrum: $M^+$ 295, *m/e* 228, 180, 178, 166, 165, 153, 152, 139, 128, 117, 116, 115, 106, 105, 102, 93, 92, 91, 89, 81, 80, 79, 78, 77, 68, 67, 66, 65, 63, 55, 54, 53, 44, 41, 40; $^1$H NMR: $\delta$ 8.2–7.2 (AA'BB' system, 4H), 5.4–5.1 (m, 2H), 2.6 (d, *J* 8 Hz, 1H), 2.5–0.9 (m, 14H) ppm; $^{13}$C NMR: $\delta$ 145.1, 130.9, 130.3, 129.7, 124.8, 122.4 (aromatic and vinylic carbons), 97.8, 80.6 (acetylenic carbons), 45.5, 44.3 (d, C(2), C(3)), 39.9, 39.4 (d, C(1), C(4)), 35.8, 33.9 (t, $CH_2C{=}$, C(7)), 29.7, 28.4 (t, C(5), C(6)), 17.9 (q, $CH_3$) ppm.

*I* ($R = Me(CH_2)_3CH{=}CHCH_2$, $R' = Ph$). Mass spectrum: $M^+$ 292, *m/e* 249, 235, 181, 179, 178, 169, 167, 166, 165, 155, 153, 152, 141, 129, 128, 117, 115, 105, 93, 91, 79, 77, 67, 65, 55, 43, 41; $^1$H NMR: $\delta$ 7.5–6.9 (m, 5H), 5.5–5.2 (m, 2H), 2.7 (d, *J* 8 Hz, 1H), 2.5–0.7 (m, 20H) ppm; $^{13}$C NMR: $\delta$ 131.4, 131.1, 130.0, 127.9, 127.1 (aromatic and vinylic carbons), 91.8, 82.7 (acetylenic carbons), 46.3, 45.0 (d, C(2), C(3)), 40.6, 39.8 (d, C(1), C(4)), 36.1, 34.0 (t, C(1-heptenyl), C(7)), 32.3, 31.9 (t, C(4-heptenyl), C(5-heptenyl)), 30.1, 28.6 (t, C(5), C(6)), 22.2 (t, C(6-heptenyl)), 13.8 (q, $CH_3$) ppm.

*I* ($R = PhCH{=}CH$, $R' = p\text{-}C_6H_4OMe$). Mass spectrum: $M^+$ 328, *m/e* 300, 299, 222, 221, 215, 209, 202, 192, 191, 179, 178, 171, 165, 153, 152, 145, 141, 129, 128, 127, 121, 117, 115, 102, 91, 79, 77, 67, 65, 63, 51; $^1$H NMR: $\delta$ 7.4–6.4 (m, 9H), 6.4–6.2 (m, 2H), 3.7 (s, 3H), 2.8 (d, *J* 8 Hz, 1H), 2.6–2.2 (m, 2H), 2.1 (br s, 1H), 2.0–1.0 (m, 6H) ppm; $^{13}$C NMR: $\delta$ 137.9, 133.1, 132.5, 128.7, 128.2, 126.5, 125.9, 116.4, 113.6 (aromatic and vinylic carbons), 89.8, 83.6 (acetylenic carbons), 55.0 (q, $OCH_3$), 49.6 (d, C(3)), 44.3 (d, C(2)), 42.8, 40.7 (d, C(1), C(4)), 34.8 (t, C(7)), 29.3, 28.5 (t, C(5), C(6)) ppm.

*I* ($R = PhCH{=}CH$, $R' = p\text{-}C_6H_4NO_2$) *m.p. 86 °C.* Mass spectrum: $M^+$ 343, *m/e* 315, 249, 203, 202, 191, 189, 179, 178, 165, 152, 141, 139, 129, 128, 117, 115, 105, 102, 101, 91, 79, 77, 67, 65, 63, 51; $^1$H NMR: $\delta$ 8.1–6.9 (m, 9H), 6.4-6.1 (m, 2H), 2.8 (d, *J* 8 Hz, 1H), 2.6–2.3 (m, 2H), 2.2 (br s, 1H), 2.0–1.0 (m, 6H) ppm; $^{13}$C NMR: $\delta$ 143.2, 137.6, 132.3, 131.9, 129.2, 128.3, 126.9, 125.9, 123.1 (aromatic and vinylic carbons), 97.9, 82.4 (acetylenic carbons), 49.6 (d, C(3)), 44.1 (d, C(2)), 42.6, 40.9 (d, C(1), C(4)), 35.0 (t, C(7)), 29.2, 28.6 (t, C(5), C(6)) ppm.

*I* ($R = Ph$, $R' = p\text{-}C_6H_4OCH_3$). Mass spectrum: $M^+$ 302, *m/e* 272, 261, 236, 235, 234, 222, 220, 219, 203, 202, 191, 190, 189, 165, 152, 121, 102, 67.

*I* ($R = Ph$, $R' = p\text{-}C_6H_4NO_2$). Mass spectrum: $M^+$ 317, *m/e* 289, 226, 202, 179, 178, 165, 152, 139, 129, 128, 117, 115, 102, 91, 77, 67, 65, 63, 51.

*VII.* Mass spectrum: $M^+$ 274, *m/e* 183, 170, 155, 143, 142, 141, 129, 128, 117, 115, 91, 79, 77, 67, 65, 51. Hydrogenation on Pd/C gave quantitatively a compound identical with the hydrogenation product of I (R, R' = Ph), 2-phenyl-3-(2-phenylethyl)-bicyclo[2.2.1]heptane. Mass spectrum: $M^+$ 276, *m/e* 185, 157, 143, 130, 129, 128, 117, 116, 115, 105, 104, 103, 92, 91, 81, 79, 78, 77, 67, 65, 53, 51.

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