Scope and Limitations of a Cyclization Leading to Phenanthrene Derivatives

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The scope and limitations of a modified Bogert–Cook cyclization was investigated. It was found that the sequence is applicable only for the unsubstituted and the meta-substituted series.

La généralité et les limitations d'une réaction de cyclisation de Bogert–Cook modifiée ont été examinées. Il a été trouvé que la séquence est applicable uniquement aux séries de composés non substitués ou substitués en mêta. [Traduit par le journal]

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Recently we reported on a sequence (1) which could be regarded as a modification of the Bogert–Cook (2) reaction (**1** → **2** → **3**). For obvious reasons this reaction would be more useful if it could be extended to compounds in which the aromatic nuclei are carrying potential functional groups. The present paper gives a full account on the unsubstituted example and reports on all compounds carrying one methoxy group in the aromatic ring. It has been found that the sequence is applicable only to the meta-substituted and the unsubstituted series. Starting with the ortho- and para-substituted Nef adducts **7***a* and *b* led to no useful products.

Results and Discussion

The addition of the appropriately substituted sodium phenylacetylide to 2,6-dimethylcyclohexanone in liquid ammonia led to the acetylene alcohols **1***a* and **1***b* and **7***a* and **7***b*. Apparently only one stereoisomer was formed in these Nef reactions corroborated by the fact that **7***a* and *b* were obtained in crystalline form. Although *o*-methoxyphenylacetylene was previously prepared from benzofurane using a sealed tube (3, 4), we developed a more practical preparation starting with *o*-methoxyacetophenone. The so far neglected traditional method gives a 35% yield after purifying the product as the silver salt.

The Rupe rearrangment of acetylenic alcohols **1***a* and *b* gave unsaturated ketones **2***a* and *b*, respectively, in 60% yield. In both reactions a less polar unidentified polymer was also formed whose formation could not be avoided under various conditions.

Cyclization of unsaturated ketone **2***a* to the tricyclic product **3***a* was carried out in polyphosphoric acid in 90% yield. The appearance of a saturated carbonyl group (i.r. 1710 cm^{-1}) and a three-proton singlet at 8.93 τ corresponding to the angular methyl group are evidence for the tricyclic structure in **3***a*.

From **2***b* the cyclization in polyphosphoric acid led to a crystalline mixture of monoketone **3***b* and diketone **4***b*. The latter compound must have been formed as a result of atmospheric oxidation. Due to the experimental features of the reaction it was impossible to exclude oxygen completely. Since the two compounds could not be separated by re-crystallization or chromatography the entire sample was subjected to SeO_2 oxidation leading to the pure diketone **4***b* in 75% yield.

For diketone **4***b* there is an alternative structural possibility **6**; a similar structure is possible for the corresponding monoketone **3***b*. It is well known from the vast information concerning aromatic substitutions that the formation of a 1,2,3-vicinal trisubstituted isomer is disfavored in comparison to the 1,2,4-trisubstituted compound (5). Since only one isomer was formed in the cyclization, structure **4***b* rather than **6** is assigned to the diketone. This is corroborated by the 220 MHz n.m.r. of diketone **4***b*. The extracted coupling constants in the aromatic region, $J_{6,8}$ = 3.0 Hz, $J_{5,8}$ = 0.1 Hz, and $J_{5,6}$ = 8.8 Hz are in agreement with the accepted meta, para, and ortho values, respectively (6). Structure **6** would have been expected

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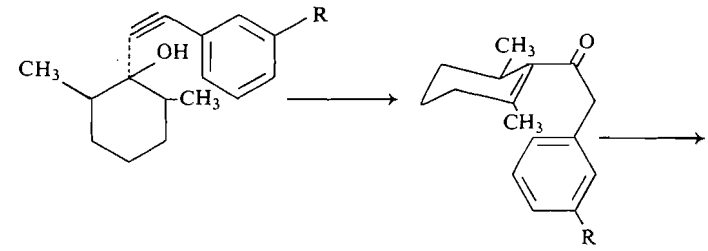
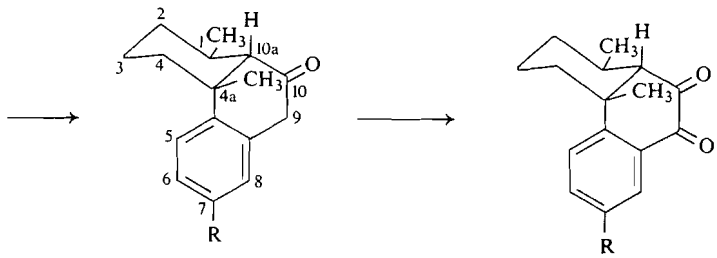
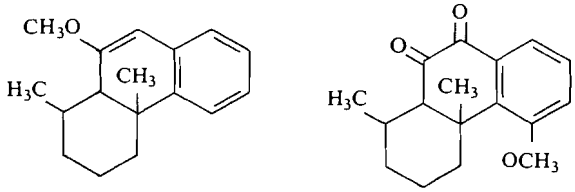


1 2

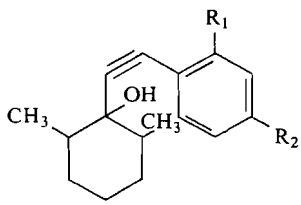


3 4

a R=H
b R=OCH$_3$



5 6



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a R_1=OCH$_3$; R_2=H
b R_1=H; R_2=CH$_3$O

to have two coupling constants of 8 Hz and another of 3 Hz. The central hydrogen should have appeared as a triplet with two ortho couplings, contrary to the actual splitting pattern: τ 2.73 (m), 2.62 (d), and 2.40 (d).

When the *o*-methoxy substituted phenylacetylene alcohol **7***a* was refluxed with formic acid the product formed contained no carbonyl and its n.m.r. showed the absence of the methoxy group. Consequently it was not investigated any further. The para-substituted isomer **7***b* under the same conditions led to the formation of unidentified polymers only.

The stereochemistry of tricyclic ketone **3***a* was erroneously assigned in our previous publication as *trans* (1). This error should now be corrected.

In order to elucidate the stereochemistry of the ring juncture in **3***a* an attempt was made to isomerize it to the thermodynamically more stable product. The alkaline treatment of **3***a* led to complex changes. Refluxing in methyl alcohol containing hydrochloric acid led to the enol ether **5** and diketone **4***a*. In the absence of oxygen under the same conditions only enol ether **5** and monoketone **3***a* were recovered. The fact that enol ether **5** was also formed during the attempted isomerization indicates that enolization indeed took place thus providing suitable conditions for equilibration. This contention could be corroborated by demonstrating that deuterium was incorporated into ketone **3***a* at positions 9 and 10a when the same reaction was carried out in CH_3OD. Therefore, it can be concluded that the thermodynamically more stable isomer was formed during the cyclization, and the necessary conditions were provided for the isomerization.

It is now generally accepted that in angularly methylated hexahydrophenantrene systems the *cis* isomer is more stable than the corresponding *trans*-fused compound (7–9). Therefore, the ring junction in **3***a* is reassigned as *cis*. With SeO_2 the monoketone **3***a* was oxidized to diketone **4***a*. In the n.m.r. of the latter compound a clearly resolved one-proton doublet at $\tau = 7.45$, $J = 10$ Hz indicates a *trans*-diaxial relationship of the two hydrogens at C-1 and C-10*a*. Consequently, the 4-methyl group in **4***a* is assigned equatorial.

The same stereochemistry is assigned to diketone **4***b* since the angular methyl signal and the one-proton doublet assigned to H_{10a} deviated less than 0.04 p.p.m. in the two diketones. While in the Bogert–Cook reaction a *cis–trans* mixture is formed (8,9), in this cyclization only the *cis* isomer is formed. Naturally the possibility cannot be excluded that the *trans*-fused isomer was also formed in this reaction and then it subsequently isomerized to the thermodynamically more stable *cis*-isomer under the conditions of cyclization. The obtained stereochemical outcome can however be explained more coherently on mechanistic grounds. It is recognized that the unexceptional pathway of *trans*-diaxial addition of a proton and an aryl group on the $\Delta^{1,2}$ double bond of unsaturated ketone **2** should produce the stereochemistry of tricyclic ketone **3**.

Due to its predictable stereochemical outcome, the cyclization discussed here is now used in some synthetic studies in the field of diterpenes.

Experimental

All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. The elemental analyses were carried out by Pascher Mikroanalytical Laboratorium, Bonn, West Germany, and Schwarzkopf Mikroanalytical Laboratory, Woodside, N.Y. The i.r. spectra were recorded on a Perkin-Elmer Model 137B infracord spectrophotometer. The u.v. spectrograms were taken on a Coleman-Hitachi Model 124 double-beam grating spectrophotometer. The n.m.r. spectra were recorded on a Varian Associates T60 spectrophotometer. The mass spectra were obtained with a Hitachi Perkin-Elmer Model RMS-4 spectrometer.

1-(Phenylethynyl)-2,6-dimethylcyclohexanol (1a)

To 100 ml of liquid ammonia containing 20 mg of ferric nitrate 240 mg of sodium was added in three portions. The flask was equipped with a magnetic stirrer and a drying tube containing soda lime. After the disappearance of the blue color 1.09 g of phenylacetylene dissolved in 5 ml of dry tetrahydrofuran was added. Stirring was continued for 30 min, then a solution of 1.19 g of 2,6-dimethyl-cyclohexanone in tetrahydrofuran (2 ml) was added in 10 min. The reaction mixture was stirred for 4 h then 2 g of ammonium chloride was added. After the evaporation of ammonia the product was dissolved in water and extracted with ether (4 × 35 ml). The combined ether extracts were washed in succession with saline, diluted sulfuric acid, and sodium bicarbonate solution. After drying ($MgSO_4$) and evaporation 2.0 g (92%) of oily product was obtained. An analytical sample was obtained by microdistillation at 120°/0.5 mm Hg. Mass spectrum (70 eV) *m/e* (relative intensity) 228 (31, parent peak), 210 (13), 171 (80), 129 (38), 102 (100), etc.; i.r. (CCl_4) 3400, 2840, 1600, 1485, 1155 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH) 252 mμ (ε 17 100), 242 (20 000); n.m.r. (CCl_4) τ 8.85 (d, 6, J = 6 Hz, methyls), 8.60 (cyclohexane protons), 2.80 (m, 5, aromatic protons).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.18; H, 8.85.

1-(2,6-Dimethylcyclohexene-1-yl) Benzyl Ketone (2a)

The acetylenic alcohol **1***a* (1.06 g) was refluxed in 50 ml of 80% formic acid for 2 h. The reaction mixture was diluted with water and extracted with ether (4 × 100 ml). The organic layer was washed with sodium bicarbonate solution and then dried ($MgSO_4$). After evaporation 0.90 g of an oil was obtained. The product consisted of two components which were separated by thick layer chromatography on silica gel plates using benzene for development. The more polar compound **6***a* was isolated in 60% yield (0.605 g). An analytical sample was prepared by microdistillation at 95°/0.3 mm Hg. Mass spectrum (70 eV) *m/e* (relative intensity) M^+ ion (228) absent, 138 (25), 137 (65), 109 (100), 91 (63), etc.; i.r. (CCl_4) 2875, 1685, 1450 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH), 244 mμ (3800), 211 (8044); n.m.r. (CCl_4) τ 9.18 (d, 3, J = 8 Hz, CH—CH_3), 8.40 (s, 3, =C—CH_3), 6.40 (s, 2, CO—CH_2—Ph), 2.83 (s, 5, aromatic protons).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.13; H, 8.85.

The less polar compound did not contain a carbonyl (i.r.) and it was not characterized any further.

10(9H)-1,2,3,4,4a,10aα-hexahydro-1α,4aα-dimethylphenanthrone (3a)

(a) Preparation

A sample of 1.046 g of unsaturated ketone **2***a* was heated with polyphosphoric acid (8 g) at 120 °C for 10 min. The cooled reaction mixture was diluted with water and extracted with ether. The organic layer was washed successively with saline and 10% sodium bicarbonate. The ether solution was dried ($MgSO_4$) then evaporated to dryness (1.02 g, 96%). T.l.c. revealed the presence of one component. The solid product was recrystallized from pentane, m.p. 64–65°. Mass spectrum (70 eV) *m/e* (relative intensity) 228 (77, parent), 213 (94), 195 (100), 159 (97); i.r. (CCl_4) 2875, 1710, 1450, 1240 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH) 282 mμ (ε 1384) and 209 (9300); n.m.r. ($CDCl_3$) τ 9.20 (d, 3, J = 7 Hz, 1-methyl), 8.93 (s, 3, angular methyl), 6.50 (s, 2, CO—CH_2—Ph), 2.80 (m, 5, aromatic).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.14; H, 8.80.

(b) Equilibration of Tricyclic Ketone 3a

The alkaline treatment of **3***a* led to a complicated mixture. Next an acidic treatment was tried.

Ketone **3***a* (276 mg) was refluxed for 3 h in 10 ml of methanol containing 2 drops of concentrated hydrochloric acid. After cooling, the reaction mixture was diluted with water and extracted with ether (4 × 40 ml). The combined ether extracts were washed with saline, sodium bicarbonate solution (5%), and saline in succession. The product consisted of three components which were separated by thick layer chromatography on a silica gel plate using 10:90 ether–benzene for development. The most polar product was isolated in crystalline form (66 mg, 24%). This sample was shown to be identical with diketone **4***a* prepared from monoketone **3***a* with SeO_2 oxidation (*vide infra*).

To the least polar oily product (51 mg, 20%) enol ether structure **5** was assigned; i.r. (CCl_4) 2900, 1647, 1486, 1450, 1370, 1282, 1235, 1193, 1152, 1026 cm^{-1}; u.v.$_{max}$ 277 mμ (11 754), 222 (15 557); n.m.r. ($CDCl_3$) τ 9.1 (d, 3, J = 6 Hz, 1-methyl), 8.87 (s, 3, angular methyl), 6.28 (s, 3, O—CH_3), 4.55 (s, 1, proton at C-9), 2.33 (m, 4, aromatic protons) mass spectrum (70 eV) *m/e* (relative intensity) 242 (38, parent peak), 227 (31), 173 (25), 172 (100), 141 (33), 129 (37), 128 (38). A sample was distilled for analysis at 100°/1 mm Hg.

Anal. Calcd. for $C_{17}H_{22}O$: C, 84.25; H, 9.14. Found: C, 84.23; H, 9.16.

From the middle band of the chromatogram monoketone **3***a* (75 mg) was recovered. When the reaction was carried out under nitrogen only the starting material **3***a* and the enol ether **5** were isolated.

The same isomerization experiment was carried out in the presence of CH_3OD. Ketone **3***a* (200 mg) was refluxed in CH_3OD (2 ml) in the presence of CF_3COOD (0.1 ml) + D_2O (0.2 ml) for 3 h in a nitrogen atmosphere. After evaporation to dryness the entire sample was chromatographed on a silica gel plate (20 × 20). From the least polar band ketone **3***a* (75 mg) was recovered. Its n.m.r. showed that the singlet at 6.50 (CO—CH_2—Ph) decreased to about one fourth its original height. Another slight change was noticeable at 7.9 attributable to position 10*a*. In the aromatic region the signals decreased also by 25%. The position and intensity of the signals at 9.1 (d) and 8.87 (s) have not changed.

1,2,3,4,4a,10aα-Hexahydro-1α,4aα-dimethylphenanthrenequinone (4a)

A solution of monoketone **3***a* (150 mg) in 3 ml of dioxane was mixed with sublimed selenium dioxide (100 mg) and a drop of water. The mixture was stirred and refluxed for 6 h. When the oxidation was complete (t.l.c.) the mixture was filtered. The filtrate was diluted with ether and washed with saline. After drying ($MgSO_4$) and evaporation to dryness, 140 mg (88%) of crystalline diketone was obtained. It was recrystallized from pentane, yellow needles, m.p. 115–117°. Mass spectrum (70 eV) *m/e* (relative intensity) 242 (35, parent), 214 (11), 199 (29), 181 (31), 171 (30), 159 (57), 129 (71), 128 (100); i.r. (CCl_4) 2860, 1730, 1695, 1435, 1370, 1307, 1235 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH) 283 mμ (ε 8750), 209 (10 454), n.m.r. τ 9.18 (d, 3, J = 6 Hz, 1-methyl), 8.67 (s, 3, angular methyl), 7.45 (d, 1, J = 10 Hz, proton at C-10a), 2.47 (m, 4, aromatic protons).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.34; H, 7.51.

1-(m-Methoxyphenylethynyl)-2,6-dimethylcyclohexanol (1b)

The acetylene alcohol **1***b* was prepared as described for **1***a* in a 90% yield using *m*-methoxyphenylacetylene (10). T.l.c. examination showed only one major component and a small amount of polymers. It was purified by thick layer chromatography on silica plates using benzene for development. An analytical sample was distilled at 102°/0.3 mm Hg. Mass spectrum (70 eV) *m/e* (relative intensity) 258 (36), 240 (67), 225 (25), 201 (54), 155 (100); i.r. (CCl_4) 3400, 2890, 1587, 1497, 1157 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH) 298 mμ (ε 2921), 290 (2900), 252 (15 357), 243.5 (15 357); n.m.r. ($CDCl_3$) τ 8.83 (d, 6, J = 6 Hz, methyls), 8.55 (cyclohexane protons), 6.20 (s, 3, OCH_3), 3.0 (m, 5, aromatic protons).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.07; H, 8.53.

1-(2,6-Dimethylcyclohexene-1-yl) m-Methoxybenzyl Ketone (2b)

The acetylenic alcohol **1***b* (9.3 g) was refluxed with 80% formic acid for 2 h and worked-up as described for **2***a*. The two-component mixture was separated by column chromatography on silica gel eluting with benzene. The less polar component contained no carbonyl and had a tendency to polymerize.

The more polar component (5.2 g) was isolated as an oil in 55% yield. Mass spectrum (70 eV) *m/e* (relative intensity) 258 (3, parent), 243 (2), 225 (1), 150 (50), 137 (82), 135 (100); i.r. (CCl_4) 2825, 1675, 1587, 1477, 1443, 1250, 1143, 1042 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH) 310 mμ (ε 690), 282 (2670), 275 (2987), 208 (15 960); n.m.r. ($CDCl_3$) τ 9.08 (d, 3, J = 6 Hz, CH—CH_3), 8.38 (s, 3, =C—CH_3), 6.23 (s, 5, OCH_3 and CO—CH_2—Ar), 3.20 (m, 4, aromatic). A sample was distilled at 105°/0.3 mm Hg for analysis.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.05; H, 8.56.

10(9H)-1,2,3,4,4a,10aα-Hexahydro-1α,4aα-dimethyl-7-methoxyphenanthrone (8b) and 1,2,3,4,4a,10aα-Hexahydro-7-methoxy-1α,4aα-dimethylphenanthrenequinone (4b)

A 1.2 g sample of unsaturated ketone **2***b* was heated with polyphosphoric acid (8 g) at 110° for 10 min. The

reaction mixture was worked-up as described for **3***a*. The yield of the crystalline product, m.p. 71–75 °C was nearly quantitative. However, even after several recrystallizations from different solvents the pure ketone **3***b* could not be isolated. The contaminant was the corresponding α-diketone, **4***b*, as recognized from the mass and n.m.r. spectra of the samples.

Consequently the mixture was oxidized to pure **4***b*. A solution of **3***b* and **4***b* (142 mg) in dioxane (3 ml) was mixed with sublimed selenium dioxide (80 mg) and a drop of water and heated under reflux for 6 h. When the oxidation was complete (t.l.c.) the product was filtered, diluted with ether, washed with brine, and dried ($MgSO_4$). After evaporation 103 mg (73%) of crystalline diketone was isolated. It was recrystallized from pentane, m.p. 133–135°. Mass spectrum (70 eV) *m/e* (relative intensity) 272 (93, parent), 257 (12), 244 (25), 229 (100), 201 (50); i.r. ($CHCl_3$) 2850, 1724, 1678, 1602, 1493, 1460, 1319, 1285 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH) 286 mμ (ε 5900), 226 (17 400); n.m.r. at 220 MHz ($CDCl_3$) τ 9.20 (d, 3, J = 6 Hz, CH—CH_3), 8.72 (s, 3, angular methyl), 7.49 (d, 1, J = 10 Hz, proton at C-10a), 6.13 (s, 3, OCH_3), 2.73 (m, 1, $J_{5,6}$ = 8.8 Hz, $J_{6,8}$ = 3.0 Hz, H_6), 2.62 (d, 1, $J_{5,6}$ = 8.8 Hz, $J_{5,8}$ = 0.1 Hz, H_5), 2.40 (d, 1, $J_{6,8}$ = 3.0 Hz, $J_{5,8}$ = 0.1 Hz, H_8).

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.99; H, 7.42.

o-Methoxyphenylacetylene

To a well-cooled solution of *o*-methoxyacetophenone (35 g) in benzene (100 ml) phosphorous pentachloride (50 g) was added in 45 min while stirring. The product was allowed to stand overnight at room temperature. The yellow solution was poured on ice and extracted with ether (3 × 100 ml). The combined ether extracts were washed with water, dried ($MgSO_4$) and evaporated to dryness. The product was mixed with 95% ethanol (42 ml) and potassium hydroxide (34 g) and refluxed for 24 h. Prior to working-up the mixture was tested for the complete disappearance of the dichloride (t.l.c.). The brown reaction mixture was poured on ice-water and extracted with ether (3 × 100 ml), then the ether was removed by atmospheric distillation. The residue was dissolved in ethyl alcohol (100 ml) and to the magnetically stirred solution 5% $AgNO_3$ solution was dripped until no more precipitate formed. The precipitate was filtered by suction, washed with ethyl alcohol then with ether. After suspending the precipitate in water (200 ml), 35 g of NH_4SCN was added and the mixture was stirred in the presence of ether (200 ml). The AgSCN was removed by filtration on a Buchner funnel and the filtrate was extracted with ether (4 × 100 ml). The combined ether extracts were washed with saline, dried ($MgSO_4$), and the product was distilled at 78–84°/7 mm Hg. Yield: 12 g (35%) colorless oil. Mass spectrum (70 eV) *m/e* (relative intensity) 132 (45, parent), 131 (33), 117 (11), 89 (100); u.v.$_{max}$ (95% C_2H_5OH) 301 mμ (ε 3945), 292 (3945), 250 (11 000), 239 (10 620); i.r. (CCl_4) 3448, 1600, 1274, 1242, 1042 cm^{-1}; n.m.r. ($CDCl_3$) τ 6.70 (s, 1, C≡CH), 6.2 (s, 3, OCH_3), 3.1 (s, 4, aromatic protons). The product was previously characterized (3,4).

1-(o-Methoxyphenylethynyl)-2,6-dimethylcyclohexanol (7a)

Preparation

The Nef addition between 2,6-dimethylcyclohexanone and *o*-methoxyphenylacetylene was carried out as described for **1***a*. A crystalline product was obtained (yield 97%). The analytical sample was prepared by recrystallization from ether, m.p. 84–86°. Mass spectrum (70 eV) *m/e* (relative intensity) 258 (36, parent), 240 (3), 227 (19), 201 (61), 159 (20), 131 (34), 69 (100); i.r. ($CHCl_3$) 3550, 2837, 1595, 1486, 1453, 1282, 1250, 1151, 1117, 1045, 954, 939 cm^{-1}; u.v.$_{max}$ (95% C_2H_5OH) 301 mμ (ε 6161), 292 (6140), 154.5 (20 026), 243 (17 713); n.m.r. ($CDCl_3$) 8.77 (d, 6, J = 6 Hz, methyls), 8.53 (cyclohexane protons), 6.47 (s, 3, OCH_3), 2.90 (m, 4, aromatic protons).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.01; H, 8.60.

Formolysis of acetylene alcohol (7a)

A 1.925 g sample of **7***a* was refluxed with 80% formic acid (25 ml) for 3 h. The solution was then diluted with water and extracted with chloroform (3 × 100 ml). The combined chloroform extracts were washed in succession with water, 10% sodium bicarbonate, and water. The dried ($MgSO_4$) solution was evaporated to dryness. A single compound was produced according to t.l.c., which did not contain any carbonyl (i.r.) and lost the methoxy group (n.m.r.). Therefore it was not fully characterized.

1-(p-Methoxyphenylethynyl)-2,6-dimethylcyclohexanol (7b)

Preparation

The Nef addition between 2,6-dimethylcyclohexanone and *p*-methoxyphenylacetylene (11) was carried out as described for **1***a* in 93%. The crystalline product was homogeneous according to t.l.c. It was recrystallized from pentane, m.p. 46–47°. Mass spectrum (70 eV) *m/e* (relative intensity) 258 (24, parent), 244 (21), 243 (100), 225 (31), 201 (33), 135 (98); i.r. (CCl_4) 3500, 2840, 1603, 1500, 1450, 1280, 1260, 1170, 1153, 1035, 960, 940, 833 cm^{-1}; u.v. max (95% C_2H_5OH) 297 mμ (ε 3354), 285.5 (4128), 261 (23 220), 252 (24 940); n.m.r. ($CDCl_3$) τ 8.87 (d, 6, J = 6 Hz, CH—CH_3), 3.0 (g, 4, aromatic).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.05; H, 8.56.

The formolysis of **7***b* led to an unidentified polymer.

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1. C. Schmidt and J. Thazhuthaveetil. Tetrahedron Lett. **31**, 2653 (1970).
2. M. T. Bogert. J. Am. Chem. Soc. **57**, 151 (1935).
3. V. Prey and G. Pich. Monatsh. **80**, 790 (1949).
4. A. D. Allen and C. D. Cook. Can. J. Chem. **41**, 1085 (1963).
5. C. R. Noller and R. Adams. J. Am. Soc. **46**, 1892 (1924).
6. L. M. Jackman and S. Sternhell. Applications of nuclear magnetic resonance spectroscopy in

organic chemistry. 2nd Ed. Pergamon Press, New York. 1969. p. 306 and references cited therein.
7. (*a*) M. JULIA and R. LABIA. Bull. Soc. Chim. 4151 (1972); (*b*) Z. G. HAJOS, K. J. DOEBLH, and M. W. GOLDBERG. J. Org. Chem. **29**, 2527 (1964); (*c*) Z. G. HAJOS, D. R. PARRISH, and M. W. GOLDBERG. J. Org. Chem. **30**, 1213 (1965).
8. J. DELOBELLE and M. FETIZON. Bull. Soc. Chim. Fr. 1630 (1961).
9. J. DELOBELLE and M. FETIZON. Bull. Soc. Chim. Fr. 1894 (1961).
10. W. S. JOHNSON, D. K. BANERJEE, W. S. SCHNEIDER, C. D. GUTSCHE, W. E. SHELBERG, and L. J. CHINN. J. Am. Chem. Soc. **74**, 2843 (1952).
11. E. E. SMISSMAN, R. H. JOHNSEN, A. W. CARLSON, and B. F. AYCOCK. J. Am. Chem. Soc. **78**, 3395 (1956).