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ACYLATION/CYCLIALKYLATION OF ALLYLBENZENE: A NOVEL SYNTHESIS OF 4-BENZYL-2-TETRALONE#

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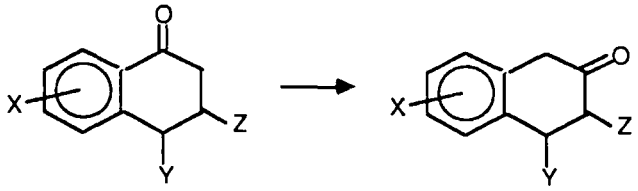
ABSTRACT: A novel synthesis of 4-benzyl-2-tetralone from allylbenzene and phenylacetyl chloride is described.

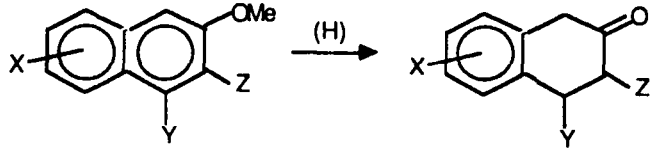
A systematic study[1] of Friedel-Crafts cyclialkylation reactions designed to elucidate their mechanisms, including electronic, steric and ring-strain effects, has been the subject of our interest. In continuation of our investigations on this topic, we required several appropriately substituted benzyltetralols. These benzyltetralols could be obtained from the corresponding tetralones. In this series, one of the tetralones, 4-benzyl-2-tetralone, has not been described in the literature to date.

The problems of the synthesis of 2-tetralone and its substituted derivatives and also the use of 2-tetralone in synthesis have been systematically reviewed.[2,3] Three major routes have been followed for the synthesis of 2-tetralone and its substituted analogs: One route

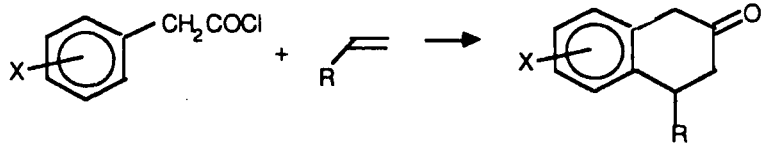
involves a multistep synthesis of the corresponding 1-tetralone and then transposition of the carbonyl group to the 2-position.



Another route involves the reduction of substituted 2-methoxy-naphthalene derivatives with sodium in alcohol; catalytic, electrolytic, and sodium-liquid ammonia reductions were also used.

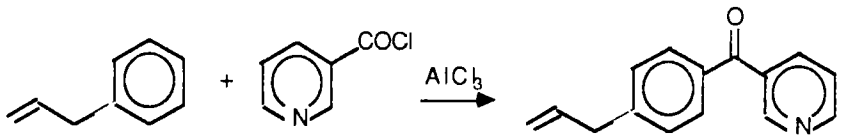


Yet another route involves direct acylation/cyclization using phenylacetyl chloride and an alkene.



The last mentioned method appears to be the method of choice for preparing substituted tetralones, as other routes involve a multistep sequence. 2-Tetralones containing alkyl substituents in the saturated ring have been prepared by this approach, using an alkyl ethylene and phenylacetyl chloride.[4] Similarly, styrene with phenylacetyl chloride gives 4-phenyl-2-tetralone.[5]

In one of the patent reports,[6] allylbenzene has been acylated using nicotinoyl chloride in the presence of $AlCl_3$ to give the ring acylated product.

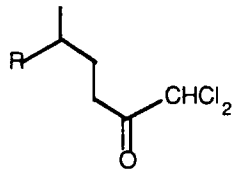


In another report it was observed that 1-alkene reacts with chloral in the presence of catalytic amounts of $AlCl_3$ to give two products, one being the normal ene adduct and the other being an "abnormal product".[7]

ene adduct

R = Alkyl, Ph

+

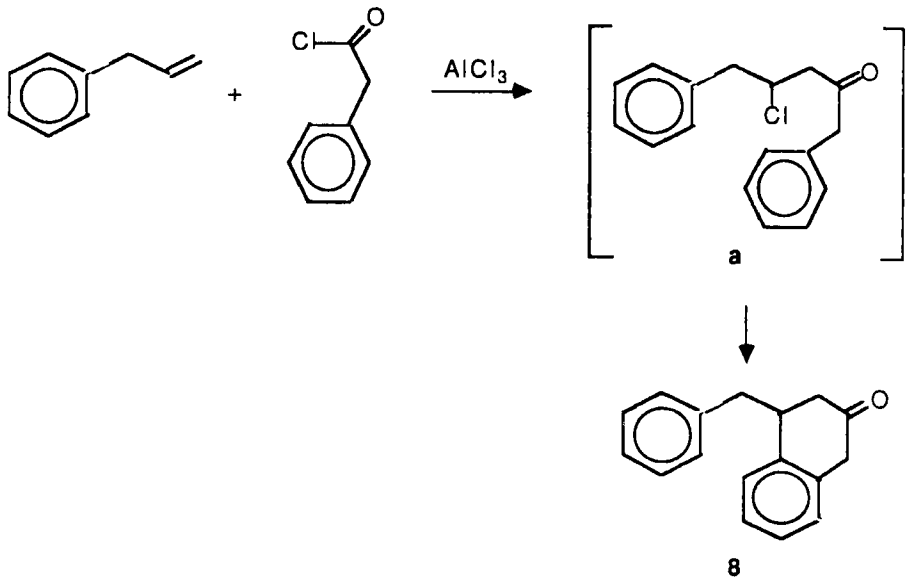


abnormal product

Under these reaction conditions, the authors observed that dichloroacetyl chloride does not react with 1-hexene to give the "abnormal product". Thus, there has been no report in which the acylation of allylbenzene took place on the ethylenic group rather than on the ring.

We now wish to report the synthesis of 4-benzyl-2-tetralone from allylbenzene and phenylacetyl chloride. In the acylation of alkenes with phenylacetyl chloride, it has been shown that the use of dichloromethane improves the yield of 2-tetralone.[8] Treatment of phenylacetyl chloride with allylbenzene in the presence of $AlCl_3$ in dichloromethane at 0° C gave a mixture of products from which 4-benzyl-2-tetralone (**8**) was isolated by column chromatography. This reaction may proceed via the chloroketone **a**, formed by addition of the acyl chloride to the C-C double bond of allylbenzene. The chloroketone

may then undergo internal cyclialkylatlion under the reaction conditions to give 4-benzyl-2-tetralone (**8**); see Scheme 1.

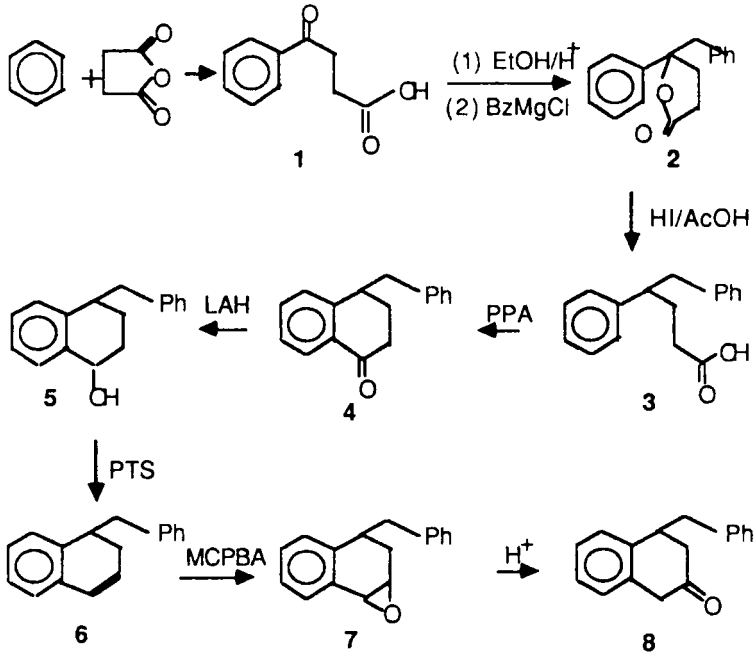


Scheme 1

Carrying out the reaction at lower temperatures, higher temperatures, or increasing the reaction time did not improve the yield of the desired product.

The structure of the product was confirmed by its NMR spectrum and by synthesizing it by another route. On Friedel-Crafts acylation with succinic anhydride, benzene gave 4-oxo-4-phenylbutanoic acid (**1**, Scheme 2). This acid was esterified and treated with benzylmagnesium chloride to yield γ-benzyl-γ-phenyl-γ-butyrolactone (**2**). Lactone **2**, on reduction with HI/AcOH, gave 4,5-diphenylpentanoic acid (**3**), which underwent cyclization in the presence of polyphosphoric acid to yield 4-benzyl-l-tetralone (**4**). This tetralone, on reduction with $LiAlH_4$,

gave the corresponding tetralol, **5**, which could be dehydrated in the presence of catalytic amounts of *p*-toluenesulfonic acid in benzene to yield l-benzyl-l,2-dihydronaphthalene (**6**). This compound was converted to the corresponding epoxide, (**7**), in the presence of *m*-chloroperoxy-benzoic acid and then treated with sulfuric acid to obtain 4-benzyl-2-tetralone (**8**).

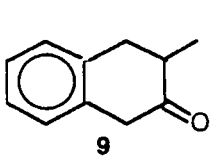


Scheme 2

The product obtained from this route was identical in its spectral and gas chromatographic characteristics with the one obtained from the simpler acylation route.

The NMR spectrum of 4-benzyl-2-tetralone was interesting as it showed a clear AB pattern for the keto-benzylic methylene group. A literature[2] search for related compounds (**9-13**) showed that this keto

methylene appeared as a singlet in the region of δ 3.50 to 3.64 (solvent $CDCl_3$).



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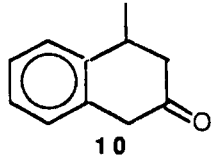
δ 3.50 (s)



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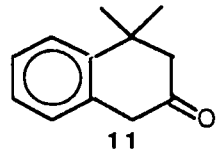
δ 3.50 (s)



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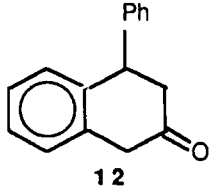
δ 3.62 (s)



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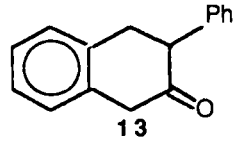
δ 3.60 (s)



13

δ 3.64 (s)

In the case of 4-benzyl-2-tetralone, two overlapping lines were observed for the keto-methylene protons in $CDCl_3$ solvent, and this signal collapsed to a singlet when the solvent was changed to CCl_4. However, when the spectrum was taken on a 300-MHz or 500-MHz instrument, a clear AB pattern (doublet of doublets) could be observed. This was confirmed by carrying out the 2D-COSY NMR experiments.

Thus, 4-benzyl-2-tetralone, a new compound, has been synthesized by the novel acylation/cyclialkylation of allylbenzene with phenylacetyl chloride in the presence of $AlCl_3$ catalyst. The structural assignments are consistent with results of 2D-COSY experiments.

Experimental Section

All temperatures are uncorrected. The IR spectra were recorded on a Beckman Acculab-8 instrument. The NMR spectra were recorded on Varian EM-390, QE 300 and GN 500 instruments. Mass spectra were recorded on a Dupont 21-491 instrument and high resolution mass spectra were recorded on a VG ZAB 2E instrument. GLC was performed with a Hewlett-Packard gas chromatograph, model 5890 equipped with

a flame ionization detector, using helium as a carrier gas and a BP-1 capillary column (25 m).

4-Benzyl-2-tetralone (8) [by Scheme 1]: To a stirred and cooled (0° C) suspension of $AlCl_3$ (8.5 g, 0.06 mol) in dichloromethane (250 mL), phenylacetyl chloride (6.08 g, 0.04 mol) was added under a nitrogen atmosphere. Allylbenzene (4.64 g, 0.04 mol) in dichloromethane (150 mL) was then slowly added to the above red solution during 30 min, keeping the temperature around 0° C. After the addition was complete, stirring and cooling (0° C) was continued for an additional 30 min. Then water (50 mL) was added and the mixture was stirred at RT for 30 min. From this mixture the organic layer was separated and washed with water, saturated sodium bicarbonate solution, and water. The organic solution was dried over anhydrous Na_2SO_4 and the solvent was distilled under reduced presssure. The residue was distilled under vacuum (0.75 mm) and the fraction boiling at 170-175° C was collected. It was further purified by passing through a silica gel column to obtain 4-benzyl-2-tetralone (**8**, 2.5g, 26%): IR (neat) 1720 cm^{-1}; ^{1}HMR ($CDCl_3$, 500 MHz) δ 2.4-3.1 (m, 4H, benzylic CH_2 and keto CH_2), 3.38 (m, 1H, benzylic CH), 3.45-3.61 (dd, 2H, J=20 Hz, keto-benzylic CH_2), 7.0-7.33 (m, 9H, ArH); ^{13}CMR ($CDCl_3$, 300 MHz) δ 210, 139.2, 138.8, 132.9, 129.3, 128.6, 128.4, 127.6, 127, 126.7, 126.6, 126.5, 43.83, 43.78, 43.02, 41.7, 29.7 ppm; MS [m/e (relative intensity)]: 236 (m^+, 23); 147 (77), 145 (61), 144 (32), 117 (100), 116 (19), 115 (38), 91 (67); HRMS: Calcd for $C_{17}H_{16}O$: 236.1201; found: 236.1202.

4-Benzyl-2-tetralone (8) [by Scheme 2]:

1-Benzyl-1,2-dihydronaphthalene (6): 4-Benzyl-1-tetralol[1] (6.5 g, 0.03 mol), *p*-toluenesulfonic acid (300 mg) and benzene (150 mL)

were placed in a 250-ml RB flask equipped with a magnetic stirrer, a reflux condenser and a Dean-Stark water separator. The reaction mixture was stirred and refluxed until no more water separated. It was then cooled, washed with water, saturated sodium bicarbonate solution, and water, and then dried over anhydrous Na_2SO_4. The solvent was distilled to leave crude 1-benzyl-1,2-dihydronaphthalene (**6**, 5.8 g, 96%) which was used as such for the next step. A small sample was distilled under vacuum to give the analytically pure compound, b.p 135-140°C (0.6 mm); ^{1}HMR (360 MHz, $CDCl_3$) δ 2.1-2.6 (m, 2, allylic CH_2), 2.7-3.0 (m, 2, benzylic CH_2), 3.1 (m, I, benzylic CH), 6.0 (m, I, 3-CH), 6.6 (d, I, 4-CH), 7.0-7.8 (m, 9, ArH) ppm; ^{13}CMR: δ 140.5, 138.8, 133.3, 129.2, 128.3, 128.1, 127.6, 127.5, 126.9, 126.6, 126.3, 125.9, 96.1, 40.5, 39.3, 27.2 ppm.; MS [m/e (relative intensity)]: 220 (m^+, 11), 130 (20), 129 (100), 128 (97), 127 (21), 91 (18).

4-Benzyl-2-tetralone (**8**):1-Benzyl-1,2-dihydronaphthalene (5.7 g, 0.26 mol) was dissolved in chloroform (100 mL) and cooled to -10° C with stirring. A solution of *m*-chloro-peroxybenzoic acid (11.5 g, ca. 55%) in chloroform (100 mL) was then added dropwise over a period of 3.5 hrs., the solution was stirred for an additional 2 hrs. at 0° C and then washed with 2 *M* sodium hydroxide solution and water. The organic layer was dried over anhydous Na_2SO_4 and the solvent was distilled under reduced pressure to give 1-benzyl-3,4-epoxy-1,2-dihydronaphthalene (**7**): ^{1}HMR 1.3-3.4 (m, 5H, methylenes and methines), 3.6 - 4.2 (m, 2, -0-CH) 6.7-7.9 (m, 9H, ArH) ppm.

The above crude epoxynaphthalene, (**7**), was refluxed with 30% sulfuric acid solution (100 mL) for 3.5 hr. The reaction mixture was cooled and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water, dried over anhydous Na_2SO_4 and the solvent was distilled under vacuum to

give 4-benzyl-2-tetralone (**8**) which was identical in all spectral characteristics with the compound obtained from the direct acylation route.

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