

SYNTHESIS OF SOME NEW POLYNUCLEAR COMPOUNDS BY [4 + 2]-CYCLOADDITION REACTION

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ABSTRACT

A large number of 2,3,5-trisubstituted 4-phenylcyclopentadienones have been synthesized by a sequence of reactions involving Friedel-Crafts reaction. Some 2,5-disubstituted derivatives of 3,4-diphenylcyclopentadienones have been prepared by condensation of benzil with 1,3-disubstituted propan-2-ones. Some 1,3-disubstituted derivatives of cyclopent-[a]-acenaphthylen-2(H)-one have been synthesized by condensing acenaphthaquinone with a series of ketones of the type $(RCH_2)_2CO$ with $R = Ph-$, C_2H_5- , $n-C_3H_7-$ and $n-C_5H_{11}-$. A large number of new polynuclear aromatic compounds have been obtained with *m*-terphenyl, naphthalene and fluoranthene nuclei with many alkyl and aryl substituents.

INTRODUCTION

THE role of cyclopentadienone and its derivatives as dienes in Diels-Alder reaction has been observed by many workers¹⁻⁷ and the general observation is that increase in the extent of delocalization of π -electrons by aryl substituents attached to the cyclopentadienone moiety does not reduce the Diels-Alder activity of the latter. In the present communication we report the synthesis of some new polynuclear aromatic compounds with naphthalene, metaterphenyl and fluoranthene nuclei by Diels-Alder reaction involving highly arylated and alkylated cyclopentadienone and the good yields obtained support the same general observation. Several dienophiles, e.g., benzyne, 3,4-dimethylbenzyne, bicycloheptadiene and two newly synthesized biaryl alkynes have been used. The compounds synthesized are potential electron donors in organic charge-transfer complexes.

EXPERIMENTAL PROCEDURE

Synthesis of dienones

Ketones of the type $(RCH_2)_2CO$ with $R = Ph-$, CH_3- , C_2H_5- , $n-C_3H_7-$ and $n-C_5H_{11}-$ were prepared by heating the corresponding acids with iron powder and then dry distilling the ferrous salts.

Each of these ketones (0.075 mol) was mixed with acenaphthaquinone (0.15 mol) in abs. ethanol (60–70 ml) and refluxed for about 2 h on a water bath with dropwise addition of 5% methanolic

KOH solution (15–20 ml) when the colour of the mixture became deep pink. The product was crystallized out and then dehydrated by refluxing with a few drops of conc. H_2SO_4 in acetic anhydride medium when deep pink crystals of 1,3-disubstituted cyclopent-[a]-acenaphthylen-2(H)-ones (A) separated out.

Two of the above ketones ($R = CH_3-$ and $Ph-$) (1 mol) were similarly condensed with benzil in the presence of Triton B as catalyst instead of methanolic KOH to avoid benzylic acid rearrangement⁸. 2,5-Di-substituted-3,4-diphenylcyclopentadienones (B) were thus obtained.

Diketones of the type $R'COCOPh$ (with $R'H = o$ -methoxy and *p*-methoxy toluene, *t*-tralin, indane, naphthalene, 1-methoxynaphthalene and biphenyl ether) were prepared by Friedel-Crafts reaction of $R'H$ (0.3 mol) with phenylacetyl chloride and oxidation of the product by heating with selenium dioxide in oil bath for about 3.5 h at 140° to 150°C. The solvent for the first two cases was CS_2 and for the others, nitrobenzene. These diketones were condensed as above with 1,3-dimethyl and 1,3-diphenylpropan-2-ones in presence of Triton B, to get 2,3,5-trisubstituted 4-phenylcyclopentadienones (C).

Synthesis of dienophiles

Two acetylenic dienophiles of the types $R''-C\equiv C-Ph$ (D) (with $R''H =$ benzene and naphthalene) were prepared by condensing $R''H$ with phenylacetyl chloride in the presence of anhyd. $AlCl_3$ at 0–5°C by the usual Friedel-Crafts method,

oxidising the resulting benzyl ketone by selenium dioxide at 140–150°C, treating the corresponding diketone with hydrazine and refluxing the dihydrazone derivative (0.05 mol) with yellow mercuric oxide (0.125 mol) in 250–300 ml of benzene as solvent.

Benzyne and 4,5-dimethylbenzyne were also used as dienophiles in the present work but they were formed *in situ* from anthranilic and 4,5-dimethyl anthranilic acids by aprotic diazotization^{9–15} during the Diels-Alder reactions.

Diels-Alder reaction

The compounds (I) and (II) were prepared by Diels-Alder addition of the appropriate dienones of type (C) with benzyne followed by elimination of CO. A mixture of the dienone (0.01 mol) and isoamyl nitrite (0.01 mol) dissolved in chloroform (150 ml) was refluxed for about 3 h and to this refluxing mixture a solution of anthranilic acid

(0.01 mol) in acetone (15 ml) was added slowly and dropwise; benzyne was formed *in situ*⁴ by aprotic diazotization and added to the dienone. During the reaction the deep colour of the solution gradually faded away. After removal of solvent a brown liquid remained which was chromatographed on neutral Brockman's alumina (E. Merck) column with benzene as eluent. Finally, (I) was recrystallized from benzene-pet.ether mixture and (II) from benzene-alcohol mixture. Compounds (III) and (IV) were similarly prepared by taking 4,5-dimethyl anthranilic acid instead of anthranilic acid. Since benzyne is highly reactive, care was taken to add the anthranilic acid solution slowly and drop wise so that the very small amount of benzyne, formed in each instalment, immediately added to the nearby dienone molecules. This aprotic diazotization could have been done at low temperatures (say, –10°C) but that would give a low yield of the adduct (vide footnote (2) of ref. 9).

