

TRANSBUTYLATION OF AROMATIC HYDROCARBONS  
BY 3,6-DI-*tert*-BUTYL PYROCATECHOL IN PRESENCE  
OF SULFURIC ACID

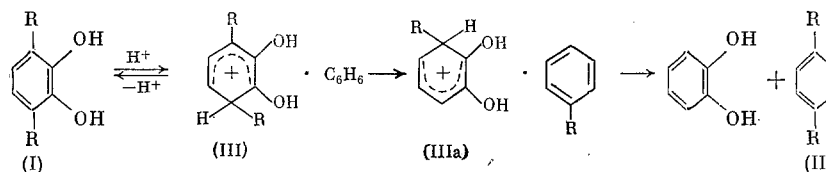
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UDC 542.91:547.536:547.565.2:546.226-325

Alkylphenols in the presence of  $H_2SO_4$ , especially at high temperatures, undergo isomerization, transalkylation, and dealkylation [1]. We found that transalkylation occurs when conc.  $H_2SO_4$  is added to a benzene solution of 3,6-di-*tert*-butylpyrocatechol (I) at  $\sim 20^\circ C$  to give *p*-di-*tert*-butylbenzene (II) in 92% yield. The close process for the transbutylation of aromatic compounds by *tert*-butylphenols to give mono-*tert*-butyl derivatives is also realized when catalyzed by metal salts ( $AlCl_3$ ,  $SnCl_4$ , etc.) and can be explained by the reversibility of Friedel-Crafts alkylation [2]. Usually the dealkylation of *tert*-butylphenols, catalyzed by  $H_2SO_4$ , proceeds at elevated temperatures [1]. Moreover, one of the methods for obtaining the indicated phenols is the alkylation of phenol and its homologs with isobutylene in benzene medium in the presence of  $H_2SO_4$  [3], in which connection the formation of alkylbenzenes was not observed here.

Stratification occurs when  $H_2SO_4$  is added to a benzene solution of (I). Chromatographic analysis of the upper colorless layer 7 h after mixing the reactants reveals that the starting (I) and other alkylpyrocatechols are absent, and only hydrocarbon (II) was isolated as the sole product. Pyrocatechol was detected in the lower light brown layer after dilution with water and neutralization.

It is natural to assume that the observed transbutylation is realized via the arenonium ion (III), which is formed by the protonation of (I). Ion (III) is apparently solvated by benzene.



Here and subsequently  $R = C(CH_3)_3$ .

In contrast to the data given in [2], the formation of mono-*tert*-butylbenzene was not observed. Ion (III) is probably most firmly bonded in the complex with one benzene molecule, and after transfer of the first *tert*-butyl group the reorganization of the complex via exchange of the ligand with the solvate shell does not occur. It is also essential that the steric situation when forming the transition state for transfer of the alkyl groups apparently shows little change when compared with the starting complex. The role of steric factors in transalkylation reactions is also indicated by the data that were obtained when the transbutylation is run in the binary benzene-toluene mixture (20:1), whose total basicity when compared with that of pure benzene is only slightly greater and does not affect the conversion rate of (I) (the reaction is completed in the same time as in benzene). Despite the greater basicity of toluene, the sole product in the hydrocarbon fraction also proved to be (II).

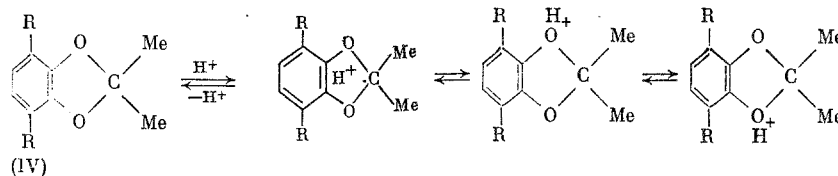
In order to establish the effect of the basicity of the aromatic acceptor of the *tert*-butyl group we made a study of the transbutylation process in toluene, xylene, and halobenzenes. Reaction in toluene leads to the formation of 1-methyl-4-*tert*-butylbenzene, but the rate of this process is slower than in benzene. The complete conversion of (I) with the same ratios of the reactants is realized in 2 days (and not in several hours as when benzene is used). On going to *m*-xylene the transbutylation process is slowed up even more. In this system dimethyl-*tert*-butylbenzene is formed in 15% yield in 10 days.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, pp. 2128-2130, September, 1981. Original article submitted December 2, 1980.

A retardation of the transbutylation process in the order: benzene > toluene > xylene, which corresponds to an increase in the basicity, can be explained by an increase in the ability of the solvent to protonate in this order, which naturally leads to a decrease in the equilibrium concentration of the (III) ion. The effect of the steric factors is apparently less important, since transbutylation in the system (I) - H<sub>2</sub>SO<sub>4</sub> - C<sub>6</sub>H<sub>5</sub>Hal (Hal = Cl, Br) is practically as fast as in benzene; the corresponding p-halo-tert-butylbenzenes are formed in ~ 100% yields. The addition to the (I) - H<sub>2</sub>SO<sub>4</sub> - benzene system of additives that increase its basicity, for example phenol, inhibit or even completely suppress the transbutylation process.

In view of these data it becomes understandable why alkylbenzenes are not formed when sterically hindered phenols are synthesized by the alkylation of phenol with isobutylene in benzene in the presence of H<sub>2</sub>SO<sub>4</sub>. The role of bases, which inhibit transalkylation in this system, are apparently played by phenol and isobutylene.

Finally, it should be mentioned that hydroxyaromatic compounds are ambident bases, which are capable of protonation both at the aromatic ring and at the oxygen center. Transbutylation involving (I) is accomplished via the C-protonated form. A shift toward O-protonation should inhibit (or even suppress) transfer of the tert-butyl groups to the aromatic hydrocarbon. This case is realized when cyclic ethers of pyrocatechol, for example 2,2-dimethyl-4,7-di-tert-butyl-1,3-benz-dioxolane (IV), are used.



Actually, in the system: (IV) - H<sub>2</sub>SO<sub>4</sub> - benzene (under analogous temperature conditions) the degree of transbutylation is slight for several days. It is interesting to mention that a maximum at λ 230 nm (which is absent in the spectrum of (IV) in hexane) appears in the UV spectrum of (IV) in H<sub>2</sub>SO<sub>4</sub>, which is characteristic for the O-protonated forms of hydroxyaromatic compounds [4].

Analogous results were obtained when 3,5-di-tert-butylpyrocatechol (V) and the mono-tert-butylpyrocatechols were used as the donors of the tert-butyl group. The isomerization of (I) to (V) is also usually observed when (I) is used.

Naturally, the possibility of realizing transbutylation should also depend on the basicity of the employed tert-butyl-substituted pyrocatechol, which is determined by the nature of the substituents in its molecule. For example, 5,6-dibromo-3-tert-butylpyrocatechol does not enter into the transbutylation reaction in benzene in the presence of H<sub>2</sub>SO<sub>4</sub>.

## EXPERIMENTAL

All of the experiments were run with a constant ratio of the reactants: To a 0.005 M solution of the substituted pyrocatechol in 50 ml of the ArH was added 1 ml of H<sub>2</sub>SO<sub>4</sub>. The completeness of debutylation was checked by TLC on Silufol UV-254 in the system: 6:1 hexane-ether. The hydrocarbon fraction was repeatedly washed with water and dried: the solvent was evaporated. The PMR spectra were recorded on a Varian MAT CH-6 spectrometer (60 MHz) in CCl<sub>4</sub> solution.

1,4-Di-tert-butylbenzene (II) (solvent = benzene or a 20:1 benzene-toluene mixture), mp 77-78° (hexane). PMR spectrum (δ, ppm): 1.3 s (9H), 5.8 s (2H).

1-Methyl-4-tert-butylbenzene (solvent = toluene), 87% yield (purified by chromatography; reaction time 2 days). PMR spectrum (δ, ppm): 1.27 s (9H), 2.27 s (3H), 7.0 m (4H).

1,3-Dimethyl-5-tert-butylbenzene (solvent = m-xylene), 15% yield (after 10 days). PMR spectrum (δ, ppm): 1.52 s (3H), 2.54 s (2H), 7.17 m (1H). Pyrocatechol (V), identified by comparing with an authentic specimen, was isolated in 80% yield.

4-Chloro-1-tert-butylbenzene (solvent = chlorobenzene), 90% yield, bp 216°C.

4-Bromo-1-tert-butylbenzene (solvent = bromobenzene), 90% yield, bp 232°C.

## CONCLUSIONS

1. The transbutylation of the aromatic substrate takes place in the system 3,6-di-tert-butylpyrocatechol-H<sub>2</sub>SO<sub>4</sub>-aromatic hydrocarbon.

2. The efficiency of transbutylation depends on the basicity of the aromatic hydrocarbon and on the presence in the system of bases that are capable of acting as competitive proton binders.

## LITERATURE CITED

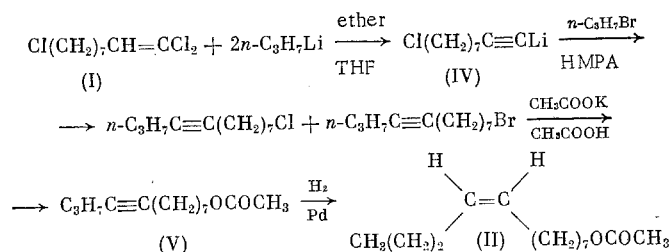
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## SYNTHESIS OF 8Z-1-DODECENYL ACETATE AND 9Z-1-TETRADECENAL FROM 1,1,9- TRICHLORO-1-NONENE

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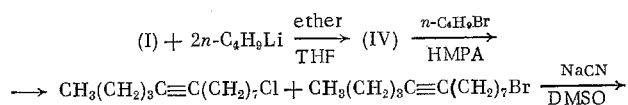
UDC 542.91:547.381

1,1,9-Trichloro-1-nonene (I) is easily obtained by the catalytic dehydrochlorination of 1,1,1,9-tetrachlorononane, the telomerization product of ethylene with CCl<sub>4</sub> [1]. We found that (I) can serve as a convenient starting compound in the synthesis of 8Z-1-dodecanyl acetate (II) (sex pheromone of *Grapholita molesta*) and 9Z-1-tetradecenal (III) (sex pheromone of *Heliothis virescens*). It proved that the conversion of α,α-dichloroalkenes RCH=CCl<sub>2</sub> by treatment with R'Li in RC≡CLi [2] is applicable to (I) and leads in high yield to Cl(CH<sub>2</sub>)<sub>7</sub>C≡CLi (IV) without involving the single chlorine atom. Employing this reaction, we synthesized (II) from (I) by the following scheme:



The treatment of (I) with two moles of n-C<sub>3</sub>H<sub>7</sub>Li in an ether-THF mixture gives acetylide (IV), which, without isolation, when treated with excess n-propyl bromide in HMPA leads in good yield to a mixture of the 1-chloro- and 8-bromo-dodecynes. This mixture when treated with potassium acetate quantitatively gives 1-acetoxy-8-dodecyne (V), which when hydrogenated over Lindlar catalyst gives the pure 8Z-1-dodecanyl acetate (II)

9Z-1-Tetradecenal was synthesized from (I) by the following scheme:




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