β-Styrylcinnamic acid was similarly prepared in yield of 40%: mp 146–147° (lit.[12] mp 145–146°).

Saturated Acid. β,β-Diphenylisobutyric Acid.—A mixture of 2.6 g of *t*-butyl β-hydroxy-β,β-diphenylisobutyrate, 25 ml of glacial acetic acid, 1.5 g of red phosphorus, 0.5 g of iodine, and 1 ml of water was heated to boiling for 80 min. The cooled solution was filtered through sintered glass, the red phosphorus was washed with acetone, and the filtrate and washings were combined and concentrated under reduced pressure. The residue was treated with 80 ml of water containing a little sodium bisulfite and extracted with ether. The ethereal solution was washed with water, and the acid was extracted from this solution with 10% sodium carbonate solution. The alkaline extract was acidified with concentrated hydrochloric acid and the isobutyric acid which separated was filtered. The acid obtained weighed 1.0 g (50%) and melted at 160.5–161° (lit.[13] mp 160–161°).

Similar operations were applied to the other *t*-butyl β-hydroxy esters and the results are summarized in Table II.

Acknowledgment.—The author wishes to thank Professors K. Sisido and H. Nozaki of Kyoto University for their encouragement and also the late Miss K. Ogawa for microanalyses.

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Aromatization Reactions of Acetylenic Hydrocarbons in the Presence of the $(Ph_3P)_2NiCl_2$–$NaBH_4$ Catalyst

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Received February 18, 1965

Luttinger[1–3] and Green[4] proposed recently a new type of catalyst in the cyclization reactions of acetylenes. These catalysts consist of a mixture of a salt of a transition metal [*i.e.*, $Co(NO_3)_2$, $(Bu_3P)_2NiCl_2$, etc.) and a hydridic reducing agent, such as $NaBH_4$ or $LiAlH_4$.

According to these authors the new catalytic system offers many advantages over the Ziegler–Natta-type catalysts, being easy to prepare and more stable toward moisture and oxygen.

We examined the activity of the catalytic system, $(Ph_3P)_2NiCl_2$–$NaBH_4$, on the cyclization reactions of acetylene, methylacetylene, phenylacetylene, and isopropenylacetylene in order to compare the activity of this catalytic system with that of the $TiCl_4$–$Al(C_2H_5)_3$ Ziegler–Natta-type catalyst used by us in our previous investigations on the aromatization reactions of acetylenic hydrocarbons.[5–8]

Experimental Section

Polymerization of Acetylene.—Anhydrous tetrahydrofuran (50 ml) was introduced into a three-necked reaction flask equipped with a magnetic stirrer. The solvent was deaerated by a nitrogen stream, and 612 mg of $(Ph_3P)_2NiCl_2$ and 500 mg of $NaBH_4$ were added. The nitrogen stream was interrupted and the reaction flask was connected to an acetylene gas buret. The nitrogen atmosphere was replaced by flushing about 200 cc of acetylene into the reaction vessel. The absorption of acetylene stopped spontaneously after about 5 hr. In a typical polymerization run, 1300 cc of acetylene was absorbed. The reaction temperature was kept constant at about 10° by cooling the reaction flask with an external water bath. During the course of the reaction, a black precipitate separated and the reaction solution became dark brown. At the end of the reaction, the catalyst was decomposed by adding HCl (1:1), until no more gaseous evolution was observed. The black product was filtered (mean yield 8.2% of the absorbed monomer). This black product has a very similar infrared spectrum and behavior on chlorination to the black polymers obtained in the polymerization reactions of acetylene carried out over Ziegler–Natta catalysts.

Gas chromatographic analysis of the reaction solution revealed only traces of benzene.

The yield of benzene was not improved by using $LiAlH_4$ as the reducing agent.

Cyclization Reaction of Methylacetylene.—The cyclic trimerization of methylacetylene can give 1,3,5- and 1,2,4-trimethylbenzene.

In order to get a better yield of aromatic products, we varied some reaction factors: (a) reaction temperature, (b) amount of the catalyst, (c) $NaBH_4$:$(PH_3P)_2NiCl_2$ ratio, (d) reaction solvent, (e) the order in which Ni complex, reducing agent, and monomer were added to the reaction solvent, (f) amount of oxygen and water impurities present in the reaction mixture, (g) amount of triphenylphosphine, and (h) type of reducing agent.

The aromatic products were analyzed by gas chromatography, using *o*-xylene as internal standard.

The results are summarized in the Table I. The best yield of aromatic products (about 15%) was achieved using a reaction procedure very similar to that reported above for acetylene: that is reaction temperature, 20°; $(Ph_3P)_2NiCl_2$:$NaBH_4$, 1:14; and solvent, anhydrous tetrahydrofuran.

We also carried out some polymerization runs adding an excess of triphenylphosphine to the reaction solvent in order to prevent decomposition of the $(Ph_3P)_2NiCl_2$ complex. However, stabilization before addition of the reducing agent did not improve the yield of aromatic products [Table I, (g) 13–15].

Cyclic Cotrimerization of Acetylene and Methylacetylene.—The cyclic cotrimerization of these two hydrocarbons can give benzene, 1,2,4- and 1,3,5-trimethylbenzene, and *o*- *m*-, and *p*-xylene.

The reaction procedure used was similar to the preceding ones. Nitrogen was displaced by flushing with a mixture of 300 cc of methylacetylene and 300 cc of acetylene. Two gas burets, containing acetylene and methylacetylene, were connected to the reaction flask; in a typical reaction run, 1160 cc of acetylene and 720 cc of methylacetylene were absorbed spontaneously. The reaction solution was analyzed gas chromatographically, using the same procedure reported in our previous study.[6] In all polymerization reactions we identified only toluene and *m*-xylene in a ratio of about 4:1. The total yield of these two hydrocarbons was about 14%, based on the monomers absorbed.

Cyclization Reaction of Phenylacetylene.—The aromatization reaction of phenylacetylene can give 1,2,4- and 1,3,5-triphenylbenzene.

The catalyst used in this series of polymerization reactions was 1.22 g of $(Ph_3P)_2NiCl_2$ and 1 g of $NaBH_4$. The monomer (4.64 g dissolved in 50 ml of solvent) was added dropwise to the solvent–catalyst mixture. The best yield in aromatic product (47%) was achieved by refluxing the reaction mixture for 1.5 hr. The yield of aromatic products does not seem, however, to be noticeably lowered by using commercial tetrahydrofuran under an air atmosphere (see Table II).

The synthesized products were extracted with benzene and analyzed gas chromatographically with a Perkin-Elmer Model 800 gas chromatograph with flame-ionization detector; 200 × 0.4 cm o.d. coiled stainless steel column containing 10% SE-30 on Chromosorb (60–80 mesh); column temperature, 250°; carrier

[1] L. B. Luttinger, *Chem. Ind.* (London), 1135 (1960).

[2] L. B. Luttinger, *J. Org. Chem.*, **27**, 1591 (1962).

[3] L. B. Luttinger and E. C. Colthup, *ibid.*, **27**, 3752 (1962).

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[5] A. Furlani, E. Cervone, and M. A. Biancifiori, *Rec. Trav. Chim.*, **81**, 585 (1962).

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[7] G. Stea, E. Cervone, and G. Moretti, *ibid.*, **33**, IIA, 619 (1963).

[8] A. Furlani and A. Guerrieri, *ibid.*, **34**, IIA, 287 (1964).

TABLE I

AROMATIZATION REACTIONS OF METHYLACETYLENE

Run no.	Solvent (ml)	Reaction temp, °C	$(Ph_3P)_2$-$NiCl_2$, mg	$NaBH_4$, mg	Ph_3P, mg	Methylacetylene, cc (STP) absorbed	1,3,5-Trimethylbenzene, mg	1,2,4-Trimethylbenzene, mg	Total yield of aromatics, %
(a) 1	Anhyd THF (50)	8	612	500	...	2670	145.8	114.7	5.2
2	Anhyd THF (50)	8	306	250	...	620	Traces	Traces	
3	Anhyd THF (50)	20	612	500	...	1440	220.5	166.6	15.0
4	Anhyd THF (50)	20	612	500	...	1250	173.4	134.0	13.7
5	Anhyd THF (50)	35	612	500	...	740	18.2	18.0	2.7
(b) 6	Anhyd THF (50)	20	1224	1000	...	1286	153.7	129.2	12.3
(c) 7	Anhyd THF (100)	20	1224	3420	...	1480	183.1	160.1	13.0
(d) 8	Anhyd ethanol (50)	20	612	500	...	810	57.9	41.0	6.8
9	Acetonitrile (50)	20	720	1254	...	1000	...	...	...
(e) 10[a]	Anhyd THF (50)	20	612	500	...	1630	Traces	Traces	
11	Anhyd ethanol (100)	20	1243	3420	...	630	...	...	...
(f) 12[b]	Commercial THF (100)	20	1224	1000	...	1385	161.9	135.3	12.0
(g) 13	Anhyd THF (50)	20	612	500	1500	1000	...	...	...
14	Anhyd THF (50)	20	612	1000	1500	680	Traces	Traces	
15	Anhyd THF (50)	20	612	5000	1500	1930	32.1	39.6	2.1
(h) 16	Anhyd THF (50)	20	612	500 ($LiAlH_4$)		1050	Traces	Traces	

[a] The reducing agent was added to the reaction solvent before the $(Ph_3P)_2NiCl_2$ complex. [b] The reaction was carried out using commercial (nonanhydrous) tetrahydrofuran and in an air atmosphere.

TABLE II

AROMATIZATION REACTIONS OF PHENYLACETYLENE

Run no.	Solvent	Monomer, g	Reaction temp, °C	Time, hr	1,2,4-Triphenylbenzene, mg	1,3,5-Triphenylbenzene, mg	Total yield of aromatics, %
1	Anhyd THF	4.64	30	2	1485	505	42.8
2	Anhyd THF	4.64	Reflux	1.5	1680	517	47.0
3	Anhyd THF	4.64	Reflux	2.5	1608	468	44.7
4	Anhyd THF	4.64	Reflux	3.5	1316	433	37.7
5	Commercial nonanhyd THF	4.64	Reflux	2.5	1252	379	35.0

TABLE III

AROMATIZATION REACTIONS OF ISOPROPENYLACETYLENE

Run no.	Solvent	Monomer, g	Reaction temp, °C	Time, hr	1,2,4-Triisopropenylbenzene, mg	1,3,5-Triisopropenylbenzene, mg	Total yield of aromatics, %
1	Anhyd THF	3.4	30	1.5	615.6	55.3	19.7
2	Anhyd THF	3.4	Reflux	1.5	939.6	118.9	31.0
3	Anhyd THF	3.4	Reflux	2.5	767.0	85.5	25.0
4	Commercial non-Anhyd THF	3.4	Reflux	2.5	842.1	91.3	27.0

gas, nitrogen at 1800 cc/hr; internal standard, 1,3,5-triphenylbenzene.

Cyclization Reaction of Isopropenylacetylene.—The cyclic trimerization of isopropenylacetylene can give 1,2,4- and 1,3,5-triisopropenylbenzene.

The reaction procedure was the same as that reported for phenylacetylene. In each polymerization run 3.4 g of freshly distilled monomer was used. The best yield of aromatic compounds (31%) was achieved using anhydrous air-free solvent and refluxing the reaction mixture for about 1.5 hr. Some polymerization reactions were carried out in commercial nonanhydrous tetrahydrofuran (see Table III).

After decomposition of the catalyst, the aromatic products were extracted with benzene and analyzed gas chromatographically. The chromatograph and column were the same as that used for the 1,3,5- and 1,2,4-triphenylbenzene analysis: column temperature, 140°; carrier gas, nitrogen at 3600 cc/hr; internal standard, 1,3,5-triisopropylbenzene.[9]

Discussion of Results

The $(Ph_3P)_2NiCl_2$–$NaBH_4$ system has been shown to have a catalytic activity lower than that of the Ziegler–Natta $TiCl_4$–$Al(C_2H_5)_3$ catalyst in aromatization reactions of acetylenes, using similar reaction conditions. In fact, the maximum yield of aromatic hydrocarbons, using the $TiCl_4$–$Al(C_2H_5)_3$ catalyst, was 70–80% based on the monomer, when the monomer was isopropenylacetylene or phenylacetylene, and only a little lower with other monomers.[5–8]

In the presence of the $(Ph_3P)_2NiCl_2$–$NaBH_4$ catalytic system, phenylacetylene gives the better yield of aromatic derivatives (about 50%). Lower yields of cyclic trimers are obtained with isopropenylacetylene and methylacetylene.

The phosphinic catalytic system normally gives a greater percentage of asymmetrical trisubstituted isomers, the ratios of 1,2,4-/1,3,5-trisubstituted benzenes are about 3.3 for 1,2,4- and 1,3,5-triphenyl-

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[9] A similar procedure for detection and determination of 1,2,4- and 1,3,5-triisopropenylbenzene was proposed by P. Chini and coworkers[10] in a very recent paper.

[10] P. Chini, G. De Venuto, T. Salvatori, and N. De Maldé, *Chim. Ind.* (Milan), **46**, 1049 (1964).

benzene and about 9 for 1,2,4- and 1,3,5-triisopropenylbenzene. Using the $TiCl_4$–$Al(C_2H_5)_3$ catalyst, larger quantities of the symmetrical isomer have always been obtained, the ratio 1,3,5/1,2,4 being about 1.3 (when the total yield was at maximum).

The most important advantage offered by the $(Ph_3P)_2NiCl_2$–$NaBH_4$ system is the greater stability toward moisture and oxygen. Polymerization reactions carried out in nonanhydrous solvents and in air gave only slightly lower yields of aromatic products. Analogous conclusions were drawn by Luttinger and Colthup[3] from observations on similar catalytic systems.

Studies are continuing in order to find new more active catalysts and to define the mechanisms of the cyclization reactions.

Acknowledgment.—We are indebted to Professor G. Sartori for helpful discussions and to the Shell International Research Mij.N.V. for financial support of this work.

Preparation of 2,5-Bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones

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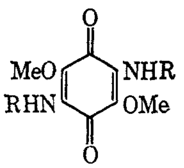
Received September 10, 1965

Reaction of tetramethoxyquinone[1] with primary amines yielded 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones (**1**). Table I lists new quinones prepared in this manner. Nonbasic amines such as *p*-nitroaniline, *o*-chloroaniline, and 2-bromo-4-methylaniline failed to react with tetramethoxyquinone. Sterically hindered amines did not react normally under the reaction conditions. For example, *t*-butylamine reacted with tetramethoxyquinone in aqueous solution to yield 2,5-dihydroxy-3,6-dimethoxy-*p*-benzoquinone as the main product. This behavior suggests that, in this case, hydroxide acts as a better nucleophile than the sterically hindered *t*-butylamine. Reaction under anhydrous conditions, however, yielded 2,5-bis(*t*-butylamino)-3,6-dimethoxy-*p*-benzoquinone.



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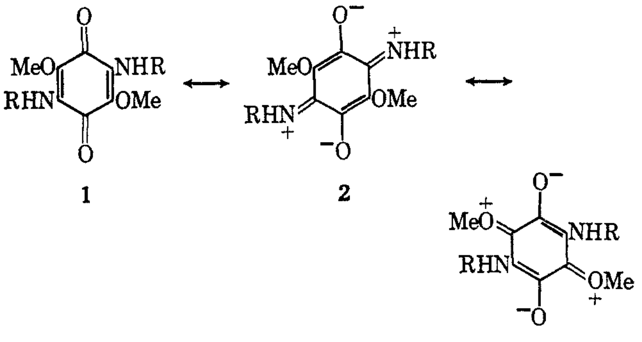
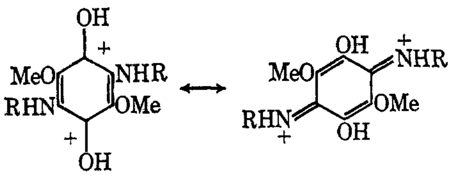
The 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones underwent amine exchange. For example, 2,5-bis(isopropylamino)-3,6-dimethoxy-*p*-benzoquinone (**1**, R = isopropyl) reacted with octylamine to yield 2,5-bis(octylamino)-3,6-dimethoxy-*p*-benzoquinone (**1**, R = octyl). In a similar manner, hexylamine displaced ethylamine from 2,5-bis(ethylamino)-3,6-dimethoxy-*p*-benzoquinone. The preferential displacement of an amino group over a methoxy group in this amine exchange reaction deserves some comment. These quinones contain both vinylogous amide and vinylogous ester groupings. Since esters react with nucleophiles more readily than amides,[2] one might predict that reaction of 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones with amines would yield 2,3,5,6-tetrakis(alkylamino)-*p*-benzoquinones, rather than yield quinones formed by amine exchange. Consideration of the resonance forms of 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinone offers an explanation of this paradox. Canonical form **2** would be expected to contribute more to the structure of 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinone than canonical form **3**, since from electronegativity considerations[3] nitrogen bears a positive charge more readily than oxygen. Because of this, positions 2 and 5 would suffer nucleophilic attack more readily than positions 3 and 6.



1 **2** **3**

A related reaction occurred in acid solution. Reflux of 2,5-bis(isopropylamino)-3,6-dimethoxy-*p*-benzoquinone with 2 *N* hydrochloric acid yielded 2,5-dihydroxy-3,6-dimethoxy-*p*-benzoquinone instead of 2,5-bis(isopropylamino)-3,6-dihydroxy-*p*-benzoquinone. A similar rationale applies here. Acid-catalyzed attack of water probably occurs on resonance hybrid **4** in which positions 2 and 5 are most prone to nucleophilic attack.



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An earlier report states that alkoxide displaces only two chlorines from chloranil.[4] Although treatment of chloranil with sodium methoxide in methanol at reflux did indeed yield 2,5-dichloro-3,6-dimethoxy-*p*-benzoquinone, heating the reactants in an autoclave yielded tetramethoxyquinone. Thus, all four chlorines of chloranil can be displaced by methoxide under forcing conditions. This procedure offers advantages over the literature procedure for the preparation of tetramethoxyquinone, methylation of tetrahydroxyquinone with diazomethane.[1]

A report of conversion of tetramethoxyquinone to 2,5-dihydroxy-3,6-dimethoxy-*p*-benzoquinone by treatment with sodium hydroxide has recently appeared.[1]

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[2] R. C. Fuson, "Reactions of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1962, p 316.

[3] L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewoods Cliffs, N. J., 1963, p 314.

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