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Polymerization. X. Metalation of Alkylaryl Hydrocarbons and their Use in the Polymerization of Butadiene[1]

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Alkylaryl compounds are metalated either in the ring or on the alpha carbon of the side chain. If the metal enters the ring, the product can function as a catalyst for the polymerization of butadiene in the same way as did phenylsodium.[3] If it enters the side chain it can function as the Alfin catalyst[4] with sodium isopropoxide, provided that a double bond in the benzene ring can serve in place of the double bond in the olefin. Accordingly a large number of these hydrocarbons were metalated in order to see where metalation occurred, and whether any of the products had interest as a catalyst for the polymerization of dienes.

TABLE I

METALATION OF HYDROCARBONS BY AMYLSODIUM

	Total yield based on		Percentage distribution of carboxyl groups					
			In monometalated products					
Hydrocarbon[a]	$C_5H_{11}Cl$[b]	$C_5H_{11}Na$[c]	α Carbon	Ortho	Meta	Para	In dicarbox. acids	In caproic acid
Et	19	28	100					
Iso	35	53		11.5		88.5		
t-Bu	31	46			17.3	67.1	15.6	
t-Bu[e]	48	60			2.7	28.3	4.5	64.5
p-Cy	35	52	56.7				43.3	
β-Me	43	64	100					
Diben.	48	70					100	
Diph.	61	92	100					
Triph.	62	93	100					
Flu.	66	100	100					
Ace.							17.5[b]	

[a] The abbreviations refer respectively to ethylbenzene, isopropylbenzene, *t*-butylbenzene, *p*-cymene, β-methylnaphthalene, dibenzyl, diphenylmethane, triphenylmethane, fluorene and acenaphthene. The quantity of hydrocarbon added in each case was 0.22 mole except in the second experiment with *t*-butylbenzene in which 0.44 mole was added. [b] In each experiment 0.5 mole of amyl chloride and 1 g. atom of sodium were used in the preparation of amylsodium. In all cases, except the second experiment with *t*-butylbenzene, 0.2 mole of isopropyl alochol was used. Hence the actual amount of amyl chloride is as if only 0.3 mole were used. Yields were calculated on this quantity. [c] The yield of amylsodium is usually around 80% of the amyl chloride used; hence, this amount was assumed to be present. [d] Caproic acid represents unused amylsodium. [e] This experiment was the only one in which no sodium isopropoxide was used. [b] The crude mixture weighed 17.5 g. from which some of the same dicarboxylic observed before and isolated as the dimethyl ether was obtained. Some mono carboxylic acid was possibly present in the crude mixture.

Of the hydrocarbons tested two were metalated in the ring and the remainder in the side alkyl group (see Table I). All except fluorene and acenaphthene had a little catalytic activity (see Table II) but only benzylsodium could be said to be moderately good with respect to percentage conversion and intrinsic viscosity of product. The metalation of toluene to give benzylsodium has previously[5] been shown to yield some disubstitution products as the quantity of toluene is made less. Accordingly the benzylsodium catalyst was prepared with three proportions of toluene (see Table III). The best activity with respect to conversion and the intrinsic viscosity and gel of the product was found with the catalyst that should contain the smallest amount of phenylene disodium.

Acenaphthene and fluorene formed no catalyst. The failure of these compounds to yield a catalyst was confirmed by adding each to an allylsodium–sodium isopropoxide (PP) catalyst and observing the destruction of catalytic activity. Acenaphthene gradually reduced the conversion activity to zero over a 100-day interval during which the intrinsic viscosity of the polymer formed also fell from 15 to 0. Fluorene caused the same changes within one day. In each case carbonation of the destroyed catalyst showed only the expected products from fluorene and acenaphthene. By contract the addition of toluene to the same catalyst caused a drop in intrinsic viscosity to 13 in a period of fifty-one days, and the percentage conversion remained at 100.

Incidental matters of interest with respect to the metalation of the hydrocarbon are (a) the high percentage of para substitution in the metalation of isopropylbenzene and *t*-butylbenzene; (b) the metalation of the methyl group of *p*-cymene in preference to the isopropyl group; (c) the formation of *meso*-α,β-diphenylsuccinic acid from metalation and carbonation of dibenzyl,

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[4] Morton, Magat and Letsinger, *ibid.*, **69**, 950 (1947).

[5] Morton, Little and Strong, THIS JOURNAL, **65**, 1339 (1943).

TABLE II

CATALYTIC ACTIVITY OF METALATED HYDROCARBONS

Hydrocarbons[a]	Catalyst age, days	Conver., %	Gel, %	Intrin. vis.
None[b]	1	3	6	1.2
	1	2	30	1.0
Tol.	6	89	23	4.0
	20	70	29	7.4
Tol.[c]	4	100	13	7.6
	73	48	0	7.5
o-Xy.	1	32	28	0.7
	49	34	51	1.3
m-Xy.	1	18	30	1.3
	48	9	38	2.1
p-Xy.	1	43	24	2.3
	32	33	39	2.5
p-Cy.	1	48	46	1.4
	4	33	28	2.1
Et	1	12	21	0.7
	3	14	10	.6
Iso.	1	4	23	.5
	5	3	23	.8
t-Bu	1	1	59	3.9
t-Bu[d]	1	23	31	0.8
β-Me	1	34	27	.5
	7	31	24	.5
Diben.	3	28	26	.5
	10	47	64	1.0
Diph.	7	20	36	0.6
	47	5	31	.8
Triph.	1	18	52	.2
	3	14	20	.2
Fl. Ace.	No rubber formed			

[a] The abbreviations in this column have the same significance as those in Table I with addition of toluene (Tol.) and the three xylenes (Xy.). The quantity of hydrocarbon used in each preparation was 0.22 mole, except in the second experiment with toluene where 1 mole was used. [b] Amylsodium only was used in this test. [c] In the preparation of this catalyst 1 mole of toluene was added to the standard preparation of amylsodium. [d] This reagent is the only one that contained no sodium isopropoxide.

TABLE III

VARIATION IN CATALYTIC ACTIVITY OF THE BENZ PP CATALYST AS THE PROPORTION OF PHENYLENE DISODIUM COMPOUND IS INCREASED

	Increasing quantity of disodum compounds					
Quantity of toluene used in prepn. of cat. mole	1		0.22		0.145	
Age of catalyst, days	4	73	6	20	1	46
Conversion, %	100	48	89	70	63	82
Intrinsic viscosity	7.6	7.5	4.0	7.4	3.9	5.2
Gel, %	13	0	23	29	38	33

indicating that the two sodium ions had taken positions as far apart as possible, (d) the freedom of tarry products[6] from acenaphthene when the metalation–carbonation process is carried out under the present improved conditions and (e) the general success of metalation–carbonation with many of the hydrocarbons such that the process is a good preparative one for certain carboxylic acids.

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Experiments

Metalation of Hydrocarbons.—The hydrocarbons were Eastman Kodak Co. grade, the physical constants of which either agreed with accepted values or did so after redistillation or recrystallization. Each hydrocarbon (0.22 mole) was added to a standard preparation[13] of amylsodium to which sodium isopropoxide (0.2 mole) had previously been added. Larger amounts were used in the same proportions. The mixture was stirred for four hours after which the contents were transferred to a bottle. Samples were withdrawn when tests of catalytic activity (see Table II) were made, after which the mixture was carbonated by pouring onto solid carbon dioxide. The aqueous layer of the sodium salts was usually extracted once with petroleum ether to remove traces of organic material. Hydrochloric acid was then added. Any solid that precipitated was separated by filtration, the aqueous layer was then extracted with petroleum ether. The remaining aqueous layer was saturated with salt and extracted with ethyl ether. In the following paragraph these three fractions will be referred to as the initial precipitate, the petroleum ether fraction and the ethyl ether fraction. The weights of products are those actually obtained but the percentage yields given in Table I are corrected for the quantity of suspension removed for the polymerization test.

The gray-colored suspension from ethylbenzene yielded 7.3 g. of an oil from the petroleum ether portion. Fractionation gave 6.3 g. of liquid that boiled at 120–125° (4 mm.) and 1 g. of a resinous product. The liquid was identified as α-methylphenylacetic acid by its neutralization equivalent of 150.8 (calcd. 150) and the melting point of its amide, 90.7–91.7 cor. (reported[7] value is 91–92°). A yellow gum (1.5 g.) was obtained from the ethyl ether fraction.

The purple colored suspension from isopropylbenzene yielded 19.5 g. of an oil from the petroleum ether portion. Fractionation separated the oil into 13.8 g. that boiled at 104–114° (3 mm.), 4.9 g. that boiled at 114–117° (3 mm.) and 1 g. of a reddish gum. The first fraction was dissolved in 10 ml. of petroleum ether and placed in a refrigerator. Crude crystals of *p*-cuminic acid separated. When recrystallized from 80–20 alcohol-water solution, 11.2 g. of the pure acid, m. p. 115–116° (reported[8] value 115–116°) was recovered. The neutralization equivalent was 163 (calcd. 164). The amide melted at 152–153° cor. (153° reported[9]). The oil recovered from the mother liquor was dissolved in 10 ml. of ethanol and 2 ml. of water and again cooled. *o*-Cuminic acid (2 g.) separated. The neutralization equivalent was 164 (calcd. 164) and the melting point was 48.5–50° (51° reported[10]). The fraction that distilled at 114–117° crystallized in the receiver and, after crystallization from 50 ml. of ethyl alcohol-water (80-20 mixture), yielded 4.1 g. of pure *p*-cuminic acid. The ethyl ether fraction yielded 2 g. of a reddish gum.

The black colored suspension from *t*-butylbenzene yielded 15.5 g. in the initial precipitate and only traces of material from the other two fractions. Extraction of the precipitate with petroleum ether left a residue which yielded 7.1 g. of crystals from 100 ml. of aqueous 80% alcohol. These crystals proved to be *t*-butylbenzoic acid by the neutralization equivalent of 178, the melting point

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(6) Morton and Gibb, THIS JOURNAL, **64**, 2250 (1942).

(7) Janssen, *Ann.*, **250**, 136 (1888).

(8) Persoz, *ibid.*, **44**, 312 (1842).

(9) Gattermann and Schmidt, *ibid.*, **244**, 52 (1888).

(10) Kothe, *ibid.*, **248**, 62 (1888).

of 161.5–162.5° (160–161° reported)[11] and by the amide derivative that melted at 170.5–171° uncor. (171° reported[11]). The crystals (8.4 g.) from the mother liquor melted at 85–90° and proved to be a mixture of the *p*-acid with a little of the *m*-isomer. The mixture was first subjected to multiple fractional extraction[12] which divided it into 8 portions. The first seven portions melted at 90–95° the last melted at 290° and yielded 0.8 g. of a dicarboxylic acid after crystallization from aqueous alcohol. The first seven fractions were then recombined and subjected to alternate crystallizations from benzene and then from aqueous 80% alcohol until 2.9 g. of pure *m*-*t*-butylbenzoic acid and 3.9 g. of the pure para isomer were obtained. The *m*-acid was identified by its neutralization equivalent of 179, its melting point of 127–127.5° cor. (reported[13] 127°) and the melting point of its amide 128–129° (reported[13] 130°). The dicarboxylic acid separated in the extraction process possibly contained one carboxyl group ortho to the *t*-butyl group since the principle by which the separation process operates would insure that the strongest acid would be in that portion and *o*-*t*-butylbenzoic acid is much stronger[14] than the other two isomers. Furthermore this position would be the focus of all the directing influences present after initial metalation on the methyl group.

The products from the metalation of *t*-butylbenzene in the absence of isopropoxide yielded no initial precipitate, but the petroleum ether fraction contained 8 g. of *p*-*t*-butylbenzoic acid and 18 g. of caproic acid, the latter from unused amylsodium which was recovered by distillation after the crystals had separated. The residue from the distillation was subjected to alternate crystallizations from benzene and the aqueous alcohol solution until 4.1 g. of the *p*-acid and 1.1 g. of the *m*-isomer were recovered. The ethyl ether fraction yielded 1 g. of a brownish solid from which 0.6 g. of a dicarboxylic acid (m. p. 310–315° in a sealed tube) was obtained after decoloration with carbon and recrystallization from aqueous alcohol.

The green colored suspension from *p*-cymene yielded 9 g. of an oil from the petroleum ether portion. Fractionation at 118–123° (3 mm.) gave 6.5 g. that solidified, had a neutralization equivalent of 176.5 (calcd. 178) and a melting point of 50–51°, near to the 51–52° reported[15] for 4-isopropylphenylacetic acid. The amide melted at 169–170° cor. (170° reported[15]). Two grams of a resinous material was left as a residue from the distillation. The ethyl ether portion yielded 3 g. of a red gum which was treated with decolorizing carbon in boiling water. A dicarboxylic acid (2.5 g.) was recovered, m. p. 189–190° cor.

The purple colored suspension from β-methylnaphthalene yielded 17 g. in the initial precipitate. Recrystallization from water gave 16.5 of β-naphthylacetic acid that melted at 141.0–141.5° (reported[16] 141–142°). The neutralization equivalent was 186 (calcd. 186). The amide melted at 200–201° uncor. (reported[17] 200°).

The brown colored suspension from dibenzyl yielded 1 g. of a yellow gum from the petroleum ether extract and 8 g. of meso-α,β-diphenylsuccinic acid from the ethyl ether extract. Recrystallization of the latter from aqueous alcohol yielded 7.3 g. of pure acid that melted at 229–230° uncor. (reported[18] value is 229–230°). The neutralization equivalent was 135.6 (calcd. 135). The dimethyl ester was prepared with diazomethane and melted at 220.5–221.5° (reported[18] 219–220°).

The yellow colored suspension from diphenylmethane yielded 31.5 g. of diphenylacetic acid in the initial precipitate. When recrystallized from water, it melted at 147.5–148.5° (148° recorded[19]). The neutralization equivalent was 214 (calcd. 212). The amide melted at 167–168° cor. (167.5–168.5° reported[20]). The ether extract yielded 0.5 g. of a red gum.

The red colored suspension from triphenylmethane yielded 37.2 g. of triphenylacetic acid in the initial precipitate. It melted at 266.3–267.3 cor. (267° reported[21]). The methyl ester melted at 185–185.5° cor. (186° reported[21]).

The yellow colored suspension from fluorene yielded 38.7 g. of crude 9-fluorenecarboxylic acid which melted at 220–222° (222–225° reported[22]) when recrystallized from glacial acetic acid. The neutralization equivalent was 210 (calcd. 210). The methyl ester melted at 62–63° (63° recorded[22]).

The green colored suspension from acenaphthene yielded as an initial precipitate 17.5 g. of a yellow solid that was a mixture of acids. Treatment with diazomethane yielded the dimethyl ester of the carboxylic acid already reported.[6]

The Carbonation Product from Benzylsodium and Sodium Isopropoxide Mixture.—Phenylacetic acid (0.033 mole) was obtained from the petroleum ether portion. Homoisophthalic acid was obtained from the ethyl ether fraction. No other acids could be found.

Polymerization Tests.—The suspensions of metalated hydrocarbons were tested for catalytic activity in the manner described in the previous publication. Twenty ml. of each catalyst was used with 30 ml. of butadiene for one hour. The results are recorded in Tables II and III.

Effect of Acenaphthene and Fluorene on the PP Catalyst.—Two molar equivalents of hydrocarbon per estimated mole of catalyst were stirred together for four hours at room temperature. The respective green and yellow colored suspensions were then tested for catalytic activity in the usual way.

Attempted Use of Cyclohexene.—Cyclohexene (20 g.) was metalated by a standard quantity of amylsodium to which had been added 7.5 g. of isopropyl alcohol. Before addition of cyclohexene the organosodium reagent (20 ml.) caused the polymerization within one hour of 4% of the butadiene (30 ml.) to a polymer that had an intrinsic viscosity of 0.5 and a gel of 5%. After addition of cyclohexene, the metalated hydrocarbon caused 6% conversion to a polymer that had an intrinsic viscosity of 0.6 and no gel.

Summary

A number of alkylaryl hydrocarbons have been metalated by amylsodium in order to observe the position of metalation and the behavior of the products as catalysts for the polymerization of butadiene.

Isopropylbenzene and *t*-butylbenzene are metalated in the nucleus. Ethylbenzene, *p*-cymene, β-methylnaphthalene, diphenylmethane and triphenylmethane are metalated on the side carbon atom, preferably on a methyl group if there is more than one possibility.

Benzylsodium yields an Alfin catalyst of moderate activity. Other alkylaryl compounds, when metalated, yield poor catalysts. Acenaphthene and fluorene destroy the activity of an Alfin catalyst and show no catalytic action when metalated.

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