[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY]

Controlled Hydrogenation of Polyalkylphenols

BY A. C. WHITAKER

It has been observed in this Laboratory that certain polyalkylphenols appear to be strongly hindered and undergo sluggishly, if at all, the usual phenol reactions.[1] The purpose of the work herein described was to discover whether the attenuated activity would be manifested in catalytic hydrogenation.

Thymol had been hydrogenated in aqueous alkaline solution, at a conversion of 65%, to a product consisting of 80% ketonic and 20% alcoholic material.[2] The ketone yield was less at higher conversions, indicating that the rate of addition of the third mol of hydrogen was too great to permit the preparation of the cyclohexanone with high yield and conversion. If this rate were sufficiently small compared to the rate of addition of the first two mols of hydrogen, it would seem that the reaction would be subject to a high degree of control. It had been previously demonstrated that the behavior of a ketone under reducing conditions is strongly influenced by steric hindrance[3]; *e. g.*, 3,5,5-trimethyl-3-*t*-butyl-2-hexanone is not reduced by sodium in alcohol, sodium in moist benzene, aluminum isopropylate, or hydrogen in the presence of Raney nickel or platinum oxide. Similarly, it has now been found that the molecular structure of a polyalkylphenol determines what products are obtainable from it by hydrogenation. On this basis, the phenols studied may be classified according to three generalizations which will be stated and discussed below.

Experimental

The apparatus and procedure employed were essentially those recommended by Adkins.[4] The reactor charge was 60–100 g. of material to be hydrogenated, with about 10% by weight of Raney nickel; a rocking autoclave of 1500-ml. capacity was used. For complete saturation, 140–240° and 1500–2500 p. s. i. of hydrogen gave very satisfactory results; when it was desired to add less than three mols of hydrogen, the conditions selected were the mildest under which reaction proceeded at an appreciable rate. In the latter case, the reaction was stopped, by turning off heat and rocking motor, when the observed pressure drop was about 0.9 of the theoretical value, which was calculated as follows

$$\Delta P = \frac{\text{wt. of charge} \times 82.06 \times T\ (^\circ\text{K}) \times 14.7 \times n}{\text{mol. wt. of charge}\ x\ (V - v)}$$

where 82.06 is the gas constant in cc.-atm./mole-degree for ideal gases, 14.7 is p. s. i. per atmosphere, n is the number of mols of hydrogen to be added, V is the volume of the autoclave and v is the volume of the charge. When the reaction was complete, the autoclave was allowed to cool and the contents were withdrawn and filtered to remove catalyst. The liquid products were purified by distillation; the solid products were distilled, sublimed, or recrystallized.

Estimation of the alcoholic and ketonic constituents of the products was attempted by acetate[5] and oxime[6] formation, respectively, but it was found that where steric hindrance was a factor, these reactions were useless as quantitative determinations. For example, the relatively unhindered 6-*t*-butyl-3-methylcyclohexanone, prepared by oxidation of 6-*t*-butyl-3-methylcyclohexanol and purified by precision distillation, gave a hydroxylamine number of 313, compared with the theoretical value of 333; 6-*t*-butyl-2-methylcyclohexanone gave a hydroxylamine number of 9.2. Acetylation was somewhat more effective but inconclusive in most cases. Measurement of the amount of hydrogen absorbed, boiling point differences, ultimate analyses, and, in some cases, examination by infrared and ultraviolet absorption, served to establish the character of the products.

The procedure was essentially the same for all preparations. In order to avoid repetition, the conditions are included in Table I, which presents a list of compounds prepared and their physical properties. For complete saturation, three temperatures and three pressures, corresponding to initiation of reaction, point of most rapid pressure drop, and conclusion of reaction, are given. For partial hydrogenation, two temperatures and two pressures, corresponding to start of reaction and point of desired pressure drop, are given.

6-*t*-Butyl-3-methylcyclohexanol.—One hundred grams of 6-*t*-butyl-3-methylphenol, 9 g. of Raney nickel and 1590 p. s. i. of hydrogen were charged to a 1500 ml. rocking autoclave and heated. Reaction began at 150° and 2150 p. s. i., was most rapid at 200° and 1800 p. s. i., and was complete at 195° and 1680 p. s. i. The product was filtered and distilled through a four-foot McMillan-type column[7]; nearly all of it boiled at 108–109° at 20 mm.

Discussion of Results

Since the addition of hydrogen to polyalkylphenols results in the formation of compounds containing asymmetric carbon atoms, it was expected that mixtures of inseparable diastereoisomers would be obtained. This was invariably the case following complete saturation, but partial hydrogenation, in two instances, yielded crystalline derivatives having sharp melting points, indicating preferential, or possibly exclusive, formation of a single pair of enantiomorphs in each case. Aside from these, no attempt was made to separate mixtures of *dl* pairs. Only a reasonable homogeneity with respect to molecular formula was sought.

It became apparent early in the investigation that the hindered phenols exhibited differences in behavior in their reactions with hydrogen. For example, 4,6-di-*t*-butyl-3-methylphenol could not be converted to the ketone directly; the products consisted of approximately two-thirds cyclohexanol derivative and one-third unchanged phenol. On the other hand, 2,6-di-*t*-butyl-4-methylphenol accepted only two moles of hydrogen under severe conditions to form the cyclo-

---

[1] Stillson, Sawyer and Hunt, THIS JOURNAL, **67**, 303 (1945).

[2] Barney and Hass, *Ind. Eng. Chem.*, **36**, 85 (1944).

[3] Whitmore and George, THIS JOURNAL, **64**, 1239 (1942).

[4] Homer Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937.

[5] Bryant and Smith, THIS JOURNAL, **57**, 57 (1935).

[6] Smith and Bryant, *ibid.*, **57**, 61 (1935).

[7] McMillan, *J. Inst. Petroleum Tech.*, **22**, 616 (1936).

TABLE I

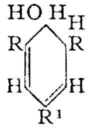
Compound	B. p. at 20 mm., °C.	Reaction temp., °C.			Pressure p. s. i.			Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sp. gr. 60/60	$n^{20}D$
Cyclohexanol													
6-*t*-Butyl-3-methyl-[a]	108–109	150	200	195	2150	1800	1680	77.58	77.55	13.02	13.01	0.9083	1.4651
4,6-Di-*t*-butyl-2-methyl-[a]	142–144	185	200	220	2250	2200	2100	79.64	79.37	13.27	13.22	....	....
4,6-Di-*t*-butyl-3-methyl-[a]	149–153	170	195	220	2200	2150	2000	79.64	79.70	13.27	13.22	....	....
6-*t*-Butyl-2-methyl-[a]	103.5–107	140	180	240	1800	1600	1500	77.58	77.68	13.02	13.30	.9106	1.4673
Cyclohexanone													
6-*t*-Butyl-2-methyl-	98.5–100	135	150	...	1750	1500	..	78.57	78.52	11.90	12.03	.9030	1.4565
6-*t*-Butyl-3-methyl-[b]	102–103	...	...	...	..	..	..	78.57	78.57	11.90	11.94	.9030	1.4562
4,6-Di-*t*-butyl-2-methyl-[a]	139–140.5	160	183	...	2150	2020	..	80.36	79.95	12.50	12.66	.8961	1.4640
2,4,6-Tri-*t*-butyl-[a]	136[c]	195	234	...	2100	2100	..	81.20	80.97	12.78	12.91	....	....
2,6-Di-*t*-butyl-4-methyl-[a]	132–134	190	240	...	2350	2470	..	80.36	80.39	12.50	12.50	.8883	1.4598
2,6-Di-*t*-butyl-4-methyl-2-cyclohexen-1-one[a]	40[d]	200	215	...	2000	1900	..	81.08	80.73	11.71	11.78	....	....

[a] New substances. [b] Prepared by chromic acid oxidation of 6-*t*-butyl-3-methylcyclohexanol. [c] Melting point, purified by sublimation. [d] Melting point, purified by recrystallization from methanol.

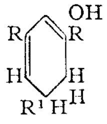
hexanone as an end-product. The complete data pertaining to all polyalkylphenols investigated allowed the formulation of the following three general rules.

1. If one ortho position of a phenol is unsubstituted, partial hydrogenation is not possible (in the absence of an additional agent, such as sodium hydroxide), even though the other ortho position is occupied by a strongly hindering group, such as *t*-butyl. Examples are 6-*t*-butyl-3-methylphenol and 4,6-di-*t*-butyl-3-methylphenol, from which only the corresponding cyclohexanols are directly obtainable by non-destructive hydrogenation.
2. If one ortho position is occupied by a *t*-butyl group and the other by a methyl group, it is possible to add two, or three, mols of hydrogen, depending on severity of conditions. Examples are 6-*t*-butyl-2-methylphenol and 4,6-di-*t*-butyl-2-methylphenol, from which it is possible to prepare either the cyclohexanols or, with proper control, the cyclohexanones.
3. If both ortho positions are occupied by *t*-butyl groups, it is possible to add one, or two, mols of hydrogen, but not three, under the conditions employed in this investigation. An example is 2,6-di-*t*-butyl-4-methylphenol, which adds two mols of hydrogen to yield 2,6-di-*t*-butyl-4-methylcyclohexanone, a liquid. By terminating the reaction after the absorption of one mol of hydrogen, it was possible to isolate from the product a crystalline material melting at 40°.

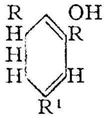
The primary hydroxylic product, prior to ketonization, resulting from the addition of one mol of hydrogen to 2,6-di-*t*-butyl-4-methylphenol, has two double bonds. There are three possible structures for this dienol. The compound was examined by infrared and ultraviolet absorption and found to be an equilibrium mixture comprising about equal proportions of ketone and enol. Structure A is ruled out because no possibility of ketonization exists. Of the other two, structure B is favored for two reasons. First, in such a strongly hindered structure, it would seem reasonable for the one mol of hydrogen to enter at the point of least resistance; and second, it may be seen that both the keto and enol forms of this structure are characterized by conjugated unsaturation. Therefore, the compound is called 2,6-di-*t*-butyl-4-methyl-2-cyclohexen-1-one.



A



B



C

Two other products of partial hydrogenation were also examined by infrared and ultraviolet absorption. Both 2,6-di-*t*-butyl-4-methylcyclohexanone and 2,4,6-tri-*t*-butylcyclohexanone were found to be completely or nearly completely of ketonic form.

Acknowledgment.—The services of Dr. G. H. Stillson, Mr. Arthur R. Rescorla, and Dr. N. D. Coggeshall were of inestimable value in determining the character of the hydrogenation products.

Summary

It has been found that the molecular structure of a polyalkylphenol determines, through steric hindrance, what products are directly obtainable from it by non-destructive hydrogenation; these range from cyclohexanols, on complete saturation, to an unsaturated cyclohexanone, when only one mol of hydrogen is added. Polyalkyphenols have been classified into three groups, according to structure. In the first group are those which are hindered only slightly, if at all, and, as a result, their reactions with hydrogen cannot be stopped at a stage of partial reduction, in the absence of an additional agent; the second group consists of those phenols which are somewhat more hindered and will add two, or three, mols of hydrogen, depending on conditions; the third group is characterized by extreme hindrance and its members will add one, or two, mols of hydrogen, but not three.

PITTSBURGH, PENN. RECEIVED APRIL 14, 1947