into 50 ml of water and extracted with four 50-ml portions of pentane. The combined pentane extracts were dried and the pentane removed by flask evaporation to give 0.23 g of crude product. Glpc analysis showed 42% 21, 8% of an unidentified compound and 35% of 1-methylene-2-isopropylidene-3,3,4,4-tetramethylcyclobutane (29): ir 3.21 (C=CH), 6.0 (C=C), 6.12 (C=C), and 11.6 μ (C=CH$_2$, strong); 100 MHz nmr τ 8.98 (s, 6), 8.87 (s, 6), 8.29 (s, 3), 8.25 (s, 3), 5.36 (m, 1), and 5.19 (m, 1); uv max (hexane) 248 mμ (ϵ 14,300).

Anal. Calcd for C$_{12}$H$_{20}$: C, 87.73; H, 12.27. Found: C, 87.40; H, 12.11.

B.—To a solution of 3.5 g of 31 in 30 ml of pyridine was added dropwise a solution of 4.0 g of phosphorous oxychloride in 20 ml of pyridine. After stirring for 4 hr, the reaction mixture was poured into 100 ml of water and extracted with four 100-ml portions of pentane. The combine pentane extracts were washed with two 100-ml portions of 5% hydrochloric acid solution, 100 ml of saturated sodium bicarbonate solution and 100 ml of saturated sodium chloride solution and dried. Removal of the pentane by flash evaporation gave 1.7 g of crude product. Glpc analysis showed 52% 29 and 48% of 1-isopropenyl-2,3,3,4,4-pentamethylcyclobut-1-ene (32): ir 3.20 (=CH), 6.06 (C=C), 6.22 (C=C) and 11.4 μ (C=CH$_2$, strong); 100 MHz nmr τ 9.02 (s, 6), 8.87 (s, 6), 8.30 (s, 3), 8.13 (s, 3), 5.31 (m, 1), and 5.26 (m, 1); uv max (hexane) 243 mμ (ϵ 19,000); mass spectrum with a molecular ion at m/e 164.1562 (Calcd for C$_{12}$H$_{20}$: 164.1565).

Pyrolysis of 32.—A 1.0-g sample of 32 was pyrolyzed on the vacuum pyrolysis system at 360° and 0.25 mm to give 0.91 g of

crude product. Glpc analysis and preparative collection showed sample to be 96% 21 and 4% 32.

Pyrolysis of 29.—A 168-mg sample of 29 was pyrolyzed on the vacuum pyrolysis system at 460° and 0.25 mm to give 160 mg of crude product. Glpc analysis showed 72% 21, 4% 29, and five other minor unidentified components.

Pyrolysis of 21.—A 66-mg sample of 21 was pyrolyzed on the vacuum pyrolysis system at 580° and 0.25 mm to give 55 mg of crude product. Glpc analysis showed 17% 21, 50% *p*-xylene, 33% *o*-xylene, and four other unidentified minor products.

An apparatus consisting of a vacuum pyrolysis system followed by a Dry Ice trap and liquid nitrogen trap connected together in series was used to analyze the low-molecular-weight gaseous products. A 71-mg sample of 21 was pyrolyzed at 620° and 0.15 mm using the above system. Glpc analysis of the product in the Dry Ice trap showed 21, *p*-xylene, and *o*-xylene in the ratio of 1:6:4 along with a number of minor products. Analysis of the products in the liquid nitrogen trap by infrared and mass spectral analysis showed propylene as the major product along with a substantial amount of ethylene.

Registry No.—6, 13831-98-6; 7, 13303-33-8; 8, 13303-32-7; 15, 24730-83-4; 16, 25914-01-6; 17, 25914-02-7; 20, 24730-82-3; 21, 24730-81-2; 22, 25914-05-0; 24, 25914-06-1; 25, 25914-07-2; 29, 24730-80-1; 31, 25914-09-4; 32, 25914-10-7; 45, 25914-11-8; 46, 25914-12-9; 47, 25914-13-0.

Quinone Methide Chemistry.   The Benzylic Oxidative Methoxylation of 2,6-Di-*tert*-butyl-*p*-cresol

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Oxidation of 2,6-di-*tert*-butyl-*p*-cresol (1) with excess *active* manganese dioxide and lead dioxide in methanol followed by hydrolysis affords 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (5, 72%) and methyl 3,5-di-*tert*-butyl-4-hydroxybenzoate (7, 47%), respectively. Evidence for the intermediacy of quinone methides in these reactions has been obtained by the isolation and characterization of the methanol addition products 3, 4, and 6. A mechanism for metal oxide oxidations of 1 in methanol is presented.

A major subject of investigation of the chemistry of 2,6-di-*tert*-butyl-*p*-cresol (1) has been the mechanism of oxidation.[1,2] A substantial understanding of the oxidation of 1 in aprotic solvents has been achieved.[1b,c] However, the oxidations of 1 in protic media have not been as intensively studied. We have now undertaken a product study of the oxidations of 1 in methanol with two commonly used inorganic phenol oxidants, lead dioxide and *active* manganese dioxide.[1b]

Results

A.   Manganese Dioxide.[3]—The reaction of 1 with manganese dioxide in a 1:10 weight ratio[4] in methanol

at 25° for 72 hr gave, after hydrolysis, a 72% yield of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (5). A minor product of this reaction, detected to be present to about 5% by vpc, was methyl 3,5-di-*tert*-butyl-4-hydroxybenzoate (7). The oxidation of 1 (see Table I) with an equal weight of oxidant was found to give a moderate yield of 2,6-di-*tert*-butyl-α-methoxy-*p*-cresol (3). Subsequent reaction of 3 with an equal weight of the oxidant in methanol led to 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde dimethyl acetal 4 in 37% yield. The acetal displayed moderate stability and could be purified by recrystallization from hexane. However, upon standing at room temperature for extended periods, the acetal slowly hydrolyzed to the corresponding aldehyde 5. Further complete oxidation of 4 in methanol with this oxidant in a 1:5 weight ratio finally gave trimethyl 3,5-di-*tert*-butyl-4-hydroxyorthobenzoate (6) in 13% yield. An independent synthesis of 6 by the classical method of Pinner[6] employing 3,5-di-*tert*-butyl-4-hydroxybenzonitrile was not successful since the intermediate methyl 3,5-di-*tert*-butyl-4-hydroxybenzimidate was stable to further methanolysis.

B.   Lead Dioxide.—Whereas the oxidation of 1 with

(1) (a) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957), and references cited therein. (b) H. Musso, *Angew. Chem. Int. Ed. Engl.*, **2**, 723 (1963), and references cited therein. (c) E. R. Altwicker, *Chem. Rev.*, **67**, 475 (1967), and references cited therein. (d) L. V. Gorbunova, N. S. Valileiskaya, M. L. Khidekel, and B. A. Razuvaev, *J. Org. Chem. USSR*, **2**, 1227 (1966). (e) J. Sugita, *Nippon Kagaku Zasshi*, **87**, 1082 (1966); *Chem. Abstr.*, **66**, 9477w (1967). (f) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 5619 (1967). (g) C. M. Orlando, Jr., *J. Org. Chem.*, **33**, 2516 (1968). (h) H.-D. Becker, *ibid.*, **34**, 1203 (1969).

(2) H.-D. Becker, *ibid.*, **30**, 982 (1965).

(3) Hereafter, manganese dioxide will be used in the text to represent *active* manganese dioxide.

(4) In manganese dioxide oxidations, the quantity of oxidant employed is generally in considerable excess of the substrate since only part of the oxygen in this metal oxide is available for oxidation.[5]

(5) H. B. Henbest and A. Thomas, *J. Chem. Soc.*, 3032 (1957).

(6) Examples of the application of the Pinner method in synthesis of orthobenzoates have been described: H. Kwart and M. B. Price, *J. Amer. Chem. Soc.*, **82**, 5123 (1960).

TABLE I

LEAD DIOXIDE (A) AND MANGANESE DIOXIDE (B) OXIDATIONS IN METHANOL AT 25°

Entry No.	Reactant (mol)	Oxidant	Ratio^a	Methanol, ml	Time, hr	Product	% yield	Mp, °C	Ir (CCl4), cm^-1	Nmr (CCl4), τ
1	1 (0.022)	A	1:3	100	20	7^b	47	157–159^c	2610, 2950, 1710, 1590, 1420, 1295, 1225, 1148, 1125, 993, 690	8.58 (18), 6.21 (3), 4.46 (1), 2.24 (2)
2	1 (0.01)	A	1:1	50	17	3	47	98–99^d	3625, 2950, 1425, 1370, 1310, 1228, 1150, 1093, 870	8.60 (18), 6.76 (3), 5.79 (2), 5.0 (1), 3.0 (2)
3	1 (0.022)	A	1:3	100	5	6^e	22	135–136	3630, 2950, 2830, 1430, 1295, 1230, 1155, 1118, 1090, 1040, 895	8.54 (18), 6.95 (9), 4.88 (1), 2.74 (2)
						4^f	13	82–84	3630, 2950, 2830, 1430, 1355, 1230, 1205, 1190, 1155, 1110, 1050, 990, 880, 700	8.58 (18), 6.8 (6), 4.89 (1), 4.74 (1), 2.85 (1)
4	3 (0.015)	A	1:1	50	7	4	52	82–84	g	g
5	3 (0.02)	A	1:2	60	7	6	23	134–136	g	g
6	4 (0.0075)	A	1:1	50	7	6	27	133–135	g	g
7	1 (0.01)	B	1:10	100	72	5^b	72	185–187^h	3605, 2945, 1680, 1580, 1420, 1233, 1188, 1150, 885, 680	8.55 (18),^i 4.17 (1), 2.3 (2), 0.14 (1)
						7^b,i	5	157–159	k	k
8	1 (0.01)	B	1:1.2	60	72	3	27	100–101	l	l
9	1 (0.01)	B	1:10	100	72	4	17	82–84	g	g
10	3 (0.02)	B	1:1	35	48	4	34	82–84	g	g
11	4 (0.0035)	B	1:5	25	13.5	6	13	133–135	g	g

^a Ratio = reactant:oxidant (oxidant A, mole ratio; oxidant B, weight ratio). ^b The reaction mixture was filtered and the filtrate stirred with 50 ml of 1% aqueous HCl for 3 hr before product isolation. ^c Mp 159–161°: E. Muller, A. Rieker, R. Mayer, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **645**, 36 (1961). ^d Mp 99.5°: M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957). ^e *Anal.* Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.60; H, 9.52. ^f *Anal.* Calcd for $C_{17}H_{28}O_3$: C, 72.80; H, 10.00. Found: C, 72.50; H, 10.17. ^g Same as entry 3. ^h Mp 189°: G. M. Coppinger and T. W. Campbell, *J. Amer. Chem. Soc.*, **75**, 734 (1953). ^i Identified by vpc using a 4-ft 10% UCW98 column; T = 100–300° and 11°/min. ^j Spectrum taken in CDCl3. ^k Same as entry 1. ^l Same as entry 2.

excess manganese dioxide in methanol gave the aldehyde **5** as a major product after hydrolysis, the reaction of **1** with excess lead dioxide resulted in the formation of methyl 3,5-di-tert-butyl-4-hydroxybenzoate (**7**) in 47% yield. With only 3 mol equiv of oxidant, the oxidation in methanol, when interrupted after 5 hr, gave a mixture of 13% of the dimethyl acetal **4** and 22% of the trimethyl orthobenzoate **6** (see Table I). The main product of the oxidation of **1** with 1 equiv of oxidant was the α-methoxy-p-cresol **3**. Further oxidation of **3** with 1 equiv of oxidant gave the dimethyl acetal **4** which could be further oxidized with another equivalent of oxidant to the trimethyl orthobenzoate **6**.

Finally, when a concentrated solution of **1** in methanol was oxidized with only 0.5 equiv of lead dioxide under nitrogen, 4-(2,6-di-tert-butyl-4-methylphenoxy)-2,6-di-tert-butyl-4-methyl-2-cyclohexadien-1-one (**2**) was obtained in 19% yield. This product was identical in all respects with a sample prepared by the oxidation of **1** with dichlorodicyano-p-benzoquinone (DDQ) in methanol.[2] The attempted isolation of **2** from the corresponding oxidation of **1** with manganese dioxide in methanol was unsuccessful.
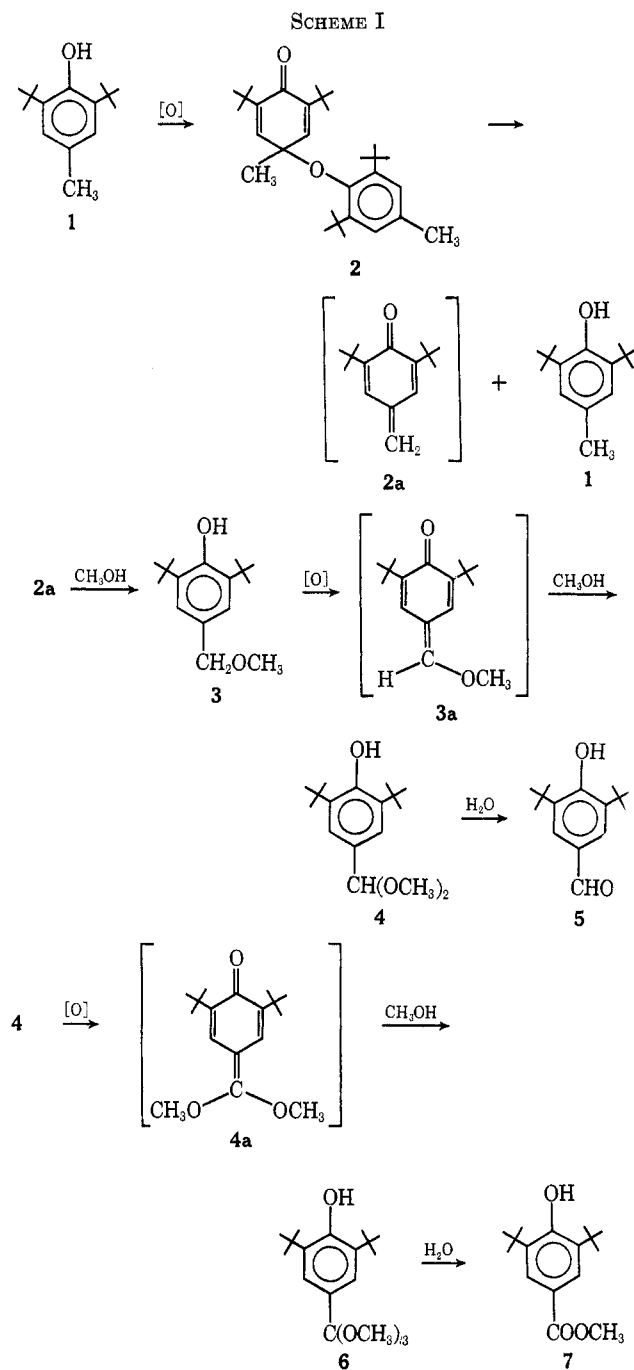
Discussion

Addition reactions of methanol to quinone methides are well known.[7] The oxidations of **1** with DDQ[2] and 2,6-di-tert-butyl-4-cyanophenoxy radical[8] in methanol give 2,6-di-tert-butyl-α-methoxy-p-cresol (**3**) through the intermediacy of the quinone methide **2a**. Recently, it has been established that **2a** results from an irreversible disproportionation of the quinol ether **2**, a dimer of the 2,6-di-tert-butyl-4-methylphenoxy radical.[2] Both the α-methoxyquinone methide **3a** and the dimethyl acetal **4** have been postulated as intermediates in the oxidation of α-methoxy-p-cresol **3** to 3,5-di-tert-butyl-4-hydroxybenzaldehyde (**5**)[2,8] (Scheme I).

The manganese dioxide and lead dioxide oxidations of **1** in methanol have now been demonstrated to proceed by stepwise benzylic methoxylation to α-methoxy-p-cresol **3**, dimethyl acetal **4**, and the trimethyl

(7) (a) E. Adler and B. Stenemur, *Ber.*, **89**, 291 (1956); (b) C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **78**, 3797 (1956); (c) K. Freudenberg and H.-K. Werner, *Ber.*, **97**, 579 (1964); (d) L. Filar and S. Winstein, *Tetrahedron Lett.*, **25**, 9 (1960).

(8) E. Muller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, *Ber.*, **92**, 2278 (1959).

SCHEME I

1

2

2a + 1

2a $\xrightarrow{\text{CH}_3\text{OH}}$ 3 $\xrightarrow{\text{[O]}}$ 3a $\xrightarrow{\text{CH}_3\text{OH}}$

4 $\xrightarrow{\text{H}_2\text{O}}$ 5

4 $\xrightarrow{\text{[O]}}$ 4a $\xrightarrow{\text{CH}_3\text{OH}}$

6 $\xrightarrow{\text{H}_2\text{O}}$ 7

orthobenzoate **7**. The formation of the aldehyde **5** and the methyl benzoate **7** in these oxidations under certain conditions (see Table I) involves respective methoxylation to acetal **4** and ortho ester **6** followed by hydrolysis. The intermediacy of the α-methoxyquinone methide **3a** in the oxidation of **3** to the acetal **4** is clearly indicated by the fact that a methanolic solution of the α-methoxyquinone methide, prepared by an alternative method, gave a quantitative yield of the acetal. The conversion of the acetal **4** to the ortho ester **6** presumably involves the intermediacy of the dimethoxyquinone methide **4a**.

In a preliminary examination of the metal oxide oxidations of 4,6-di-*tert*-butyl-*o*-cresol in methanol, a mixture of the 4,6-di-*tert*-butyl-α-methoxy-*o*-cresol and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde dimethyl acetal was obtained with manganese dioxide. How-

ever, the lead dioxide oxidation of the *o*-cresol gave only the acetal. Attempts to prepare trimethyl 3,5-di-*tert*-butyl-2-hydroxyorthobenzoate using either oxidant was not successful. The formation of methoxy-4,-6-di-*tert*-butyl-*o*-cresol derivatives in these oxidations presumably involves *o*-quinone methide intermediates in analogy with the chemistry of the para isomer described above. An alternate method of trapping *o*-quinone methides using dienophiles has been described by Bolon.[9]

Experimental Section

Melting points were determined using a Thomas–Hoover apparatus and are corrected. Infrared and nmr spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer and a Varian A-60 spectrometer, respectively. Elemental analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reagents.—4,6-Di-*tert*-butyl-*o*-cresol and 2,6-di-*tert*-butyl-*p*-cresol were purchased from City Chemical Corporation, New York, N. Y., and Eastman Kodak Company, Rochester, N. Y., respectively, and were recrystallized before use. "Active" manganese dioxide was prepared by Dr. J. R. Ladd according to the literature description.[10] The lead dioxide (96.3%) was certified ACS grade material purchased from Fisher Scientific Company, Fairlawn, N. J. Anhydrous reagent grade methanol was used as solvent.

General Oxidation Procedure for the Isolation of Methanol Addition Products.—A suspension of manganese dioxide (1–10 times the weight of cresol derivative) or lead dioxide (1, 2, or 3 mol equiv) in a solution of 1 mol equiv of the cresol (1), α-methoxy cresol (3), or dimethyl acetal (4) in absolute methanol was stirred at 25°. The period of reaction varied over a range of 5.0–72 hr depending upon the oxidant and the cresol derivative. The reaction mixture was filtered and the filtrate was evaporated to a residue which was further purified by recrystallization. The results of these experiments are listed in Table I.

Oxidation of 1 with 0.5 Mol Equiv of Lead Dioxide.—Lead dioxide (0.66 g, 0.0027 mol) was rapidly added to a solution of 1.0 g (0.0045 mol) of 1 in 20 ml of methanol and the mixture was agitated with a stream of nitrogen. Within 2 min the suspended lead dioxide coagulated and fell to the bottom of the flask while a fine white solid deposited from solution. Decantation and filtration of the reaction mixture gave 4-(2,6-di-*tert*-4-methyl-phenoxy)-2,6-di-*tert*-butyl-4-methyl-2-cyclohexadien-1-one (2), 0.185 g (19%), mp 85–90° (lit.[2] mp 85–90°).

Oxidation of 4,6-Di-*tert*-butyl-*o*-cresol with Manganese Dioxide in Methanol.—A mixture of 1.0 g (0.0045 mol) of the *o*-cresol and 2.4 g of the oxidant was stirred at 25° in 35 ml of methanol for 216 hr. The mixture was filtered and the filtrate evaporated to an oil (0.558 g). This product was shown to be a 2:1 mixture of 4,6-di-*tert*-butyl-α-methoxy-*o*-cresol and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde dimethyl acetal by the following nmr data (CCl₄): τ 5.42 (s, 4, ArCH₂OCH₃), 4.53 [s, 1, CH-(OCH₃)₂].

Oxidation of 4,6-Di-*tert*-butyl-*o*-cresol with Lead Dioxide in Methanol.—A mixture of 0.72 g (0.0032 mol) of the *o*-cresol and 2.38 g (0.0096 mol) of lead dioxide in 50 ml of methanol was stirred at 25° for 46 hr. The reaction mixture was filtered and the filtrate evaporated to an oil which was dissolved in hexane and treated with charcoal. Filtration and evaporation of the hexane solution gave the pure 3,5-di-*tert*-butyl-2-hydroxybenz-aldehyde dimethyl acetal: 0.193 g (21%); $\nu_{cm^{-1}}^{neat}$ 3350, 1600, 1235, 1105, 1055, 1040; nmr (CCl₄) τ 8.72 (s, 9, *tert*-Bu), 8.62 (s, 9, *tert*-Bu), 6.68 (s, 6, –OCH₃), 4.52 [s, 1, CH(OCH₃)₂], 3.2 and 2.8 (AB system, 2), 2.15 (s, 1, –OH).

Anal. Calcd for C₁₇H₂₈O₃: C, 72.81; H, 10.06. Found: C, 72.99; H, 10.23.

Preparation of Dimethyl Acetals. A. Of 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde (4).—A mixture of 11.7 g (0.05 mol) of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 41 g (0.38 mol) of trimethyl orthoformate, 30 ml of absolute methanol, and 0.5 g of

(9) D. A. Bolon, *J. Org. Chem.*, **35**, 3666 (1970).

(10) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. N. Evans, B. A. Heins, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

ammonium chloride was refluxed for 3.5 hr. The reaction mixture was cooled and filtered, and the filtrate evaporated to a solid. The solid was recrystallized from hexane (5°) to give white needles of the acetal 4, 7.0 g (57%), mp 84–86°. The ir and nmr spectra of this product were identical with corresponding spectra of the acetal isolated in the oxidation reactions.

B. Of 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde.—A mixture of 0.39 g (0.0016 mol) of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 5 g (0.04 mol) of trimethyl orthoformate, 3 ml of absolute methanol, and 0.05 g of ammonium chloride was refluxed for 36 hr. The reaction mixture was cooled and filtered, and the filtrate evaporated to the liquid acetal, 0.436 g (97%). The ir and nmr spectra of this product were identical with the corresponding spectra of the acetal isolated from the oxidation of 4,6-di-*tert*-butyl-*o*-cresol.

Preparation of 2,6-Di-*tert*-butyl-4-methoxymethylidene Quinone Methide (3a).—A mixture of 11.7 g (0.05 mol) of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (5), 30 ml of trimethyl orthoformate, 30 ml of absolute methanol, 30 ml of xylene, and 0.5 g of ammonium chloride was refluxed 1 hr. Approximately 0.5

the total volume of the reaction mixture was removed by distillation. The residual solution was refluxed for an additional 2 hr. Filtration of the cooled reaction mixture and evaporation of the filtrate in vacuum gave an orange solid. Crystallization of the product from petroleum ether (bp 60–110°) gave orange needles of the quinone methide (3a), 7.5 g (60%), mp 136–138° (lit.[11] mp 136–138°).

Reaction of 3a with Methanol.—A solution of 0.86 g (0.0034 mol) of 3a in 15 ml of absolute methanol was stirred at 25° for 1 hr. The characteristic orange color of this quinone methide was instantaneously discharged upon dissolving in methanol and a colorless solution resulted. Evaporation of the solvent gave a quantitative yield of the dimethyl acetal 4, mp 81–83°.

(11) E. Muller, R. Mayer, U. Heilmann, and K. Scheffler, *Justus Liebigs Ann. Chem.,* **645,** 66 (1961).

New Friedel–Crafts Chemistry. XXIII. The Mechanism of the Aluminum Chloride Catalyzed Rearrangement of *tert*-Pentylbenzene to 2-Methyl-3-phenylbutane

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Transalkylations between *tert*-pentylbenzene (1a) and toluene and between *p-tert*-pentyltoluene (1b) and benzene have been effected by AlCl₃–CH₃NO₂ without significant isomerization of the *tert*-pentyl group. When transalkylations between 1a and toluene were repeated, but with the addition of a molar equivalent of isopropyl chloride, extensive isomerization of the *tert*-pentyl group occurred. Treatment of 2-chloro-3-methyl-3-phenylbutane (10a) with AlCl₃–CH₃NO₂ and methylcyclohexane produced a mixture of 1a and 2-methyl-3-phenylbutane (2a). Reaction of 1,2-dibromo-2-methylpropane (13, X = Br) with benzene and AlCl₃–CH₃NO₂ yields a mixture of two diphenylbutanes, whereas 1,3-dichloro-3-methylbutane, under similar conditions, gives no diphenylpentane. Treatment of 1-chloro-2-methyl-2-phenylpropane (14, X = Cl) with AlCl₃–CH₃NO₂ and methylcyclopentane gave isobutylbenzene but no *sec*-butylbenzene. On the basis of the transalkylation results and of the behavior of 10a, 13, and 14, we conclude that the rearrangement of 1a to 2a takes place by a hydride abstraction process concerted with phenyl participation, producing a phenonium ion intermediate, followed by a second hydride transfer to the phenonium ion from the side chain of another arene molecule.

Alkylations of benzene with *tert*-pentyl chloride,[2–4] isopentyl bromide,[3] 1-chloro-2-methylbutane,[5] and 2-chloro-3-methylbutane[5] have been found to give mixtures of *tert*-pentylbenzene (1a) and 2-methyl-3-phenylbutane (2a). When aluminum chloride was used as catalyst, the pentylbenzene isomers were produced in an apparent equilibrium proportion of 15–18% 1a and 85–82% 2a. However, when the reactions were catalyzed by only trace amounts of aluminum chloride[4] or by weaker alkylation catalysts such as BF₃,[3] ZrCl₄,[3] AlCl₃–CH₃NO₂,[2,5] or FeCl₃,[2] *tert*-pentylbenzene was the sole or major product. These results have been explained in terms of initial alkylation by *tert*-pentyl cation (which is produced by rapid ionization and/or isomerization of the isomeric pentyl halides) to give *tert*-pentylbenzene (1a), followed by a slower rearrangement of 1a to 2-methyl-3-phenylbutane (2a) brought about by the stronger catalysts.[3,5,6] In a recent paper,[5]

we described two plausible mechanisms for the subsequent isomerization of 1a to 2a, but we concluded that the data available at that time did not allow a choice between the two possibilities.

The alternative mechanisms for rearrangement of 1a to 2a may be presented as shown in Scheme I. The first, which may be referred to as an *intermolecular* mechanism, involves the dealkylation–rearrangement–realkylation sequence 1a → 3 → 4 → 2a.[7–9] The second, which may be referred to as an *intramolecular* mechanism (since the rearranging side chain never becomes separated from the aromatic ring) involves a hydride abstraction, which may or may not be concerted with phenyl participation *via* a phenonium ion, 5a,[5] or with methyl participation *via* a methyl-bridged cation, 6a. If the hydride abstraction is not a concerted process, the classical ions 7a, 8a, and 9a may be involved. We have now obtained additional experimental data which we believe constitute definitive. evidence for the most probable pathway for the rearrangement of 1a to 2a.

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(3) L. Schmerling and J. P. West, *ibid.,* **76,** 1917 (1954).

(4) B. S. Friedman and F. L. Morritz, *ibid.,* **78,** 2000 (1956).

(5) R. M. Roberts and S. E. McGuire, *J. Org. Chem.,* **35,** 102 (1970).

(6) L. Schmerling, J. P. Luvisi, and R. J. Welch, *J. Amer. Chem. Soc.,* **81,** 2718 (1959).

(7) B. S. Friedman, F. L. Morritz, C. J. Morrisey, and R. Koncos, *ibid.,* **80,** 5867 (1958).

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(9) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 450.