[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

A Study of the Double Fries Rearrangement[1,2]

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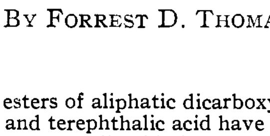
The di-*p*-tolyl esters of aliphatic dicarboxylic acids from succinic to sebacic acid, and the di-*p*-tolyl esters of the aromatic acids isophthalic and terephthalic acid have been successfully rearranged (Fries rearrangement) in the presence of aluminum chloride to their corresponding bis-(*o*-hydroxyketones). Attempted rearrangement of the di-*p*-tolyl esters of oxalic, malonic and phthalic acids did not result in the formation of bis-(*o*-hydroxyketones), but gave 2-hydroxy-5-methylbenzoic acid, 4-hydroxy-6-methylcoumarin and 1-hydroxy-4-methylanthraquinone, respectively.

For certain studies on coördination it was necessary to prepare a series of aromatic bis-(*o*-hydroxyketones) of the type



where X represents $(CH_2)_n$ or *m* or *p*-phenylene. The most practical approach to such a series of compounds appeared to be *via* a double Fries rearrangement of the diesters of dicarboxylic acids. However, a literature survey showed that no systematic study of the double Fries rearrangement had been undertaken. The few isolated examples found in the literature either did not state yields in the rearrangement or else gave a low yield for the purified rearranged product. As against usual yields of 70–90% in the mono Fries rearrangement,[3] the yields, where given for the double Fries rearrangement, were of the order of 20% or less. In the present study the di-*p*-tolyl esters were chosen in order to prevent any rearrangement to *p*-hydroxyketones.

Rearrangement of the Diesters of Succinic Acid and Higher Homologs.—The first successful attempt to rearrange diesters of aliphatic acids was made by Fries and Bartens,[4] who reported the rearrangements of di-*p*-tolyl succinate and di-(3,5-dimethylphenyl) succinate to 1,4-bis-(2-hydroxy-5-methylphenyl)-butane-1,4-dione and 1,4-bis-(2-hydroxy-4,6-dimethylphenyl)-butane-1,4-dione, respectively. However, no yields were given in this study. Schwenk and Priewe[5] reported the rearrangement of di-*m*-tolyl adipate to 1,6-bis-(2-hydroxy-4-methylphenyl)-hexane-1,6-dione, but again no yields were given. Huebner and Link[6] found that diphenyl glutarate rearranged to the extent of 60% with the formation of a mixture of the *ortho* and *para* isomeric hydroxyketones, from which they were able to isolate 1,5-bis-(2-hydroxyphenyl)-pentane-1,5-dione in 11% yield. The latest publication on the double Fries rearrangement is by Smith and Holmes,[7] who rearranged di-(2,3,5-trimethylphenyl) succinate. They used varying experimental conditions but were only able to obtain a relatively pure product, 1,4-bis-(2-hydroxy-3,4,6-trimethylphenyl)-butane-1,4-dione, in about 20% yield.

In the present work the di-*p*-tolyl esters of aliphatic dicarboxylic acids from succinic to sebacic were prepared from *p*-cresol and the respective acids by the action of phosphorus oxychloride. The yields were from 46% for the adipate to 87% for the sebacate ester.

Our first attempts at the rearrangement of the diesters of aliphatic acids involved essentially the mixing of the diester and aluminum chloride in the ratio of 1:2.5, respectively, and heating to about 130°. These conditions, tried in three different cases (see Table II), gave relatively low yields of 44% or less. It was subsequently found, however, that with chlorobenzene as solvent, the reaction proceeded much more satisfactorily, with yields up to 79% of the expected bis-(*o*-hydroxyketone). The only exception to this upward trend was the rearrangement of di-*p*-tolyl succinate which, with chlorobenzene as solvent, gave a yield of only 43% of the rearranged product.

Rearrangement of the Diesters of Aromatic Dicarboxylic Acids.—Blicke and Patelski,[8] working on esters of aromatic dicarboxylic acids, obtained the expected Fries rearrangement products 1,3-bis-(4-hydroxybenzoyl)-benzene and 1,4-bis-(4-hydroxybenzoyl)-benzene from diphenyl isophthalate and diphenyl terephthalate, respectively. However, attempted rearrangement of diphenyl phthalate[9] resulted in the formation of phenolphthalein and 1-hydroxyanthraquinone. The di-*p*-tolyl esters of the aromatic acids, phthalic, isophthalic and terephthalic acid, were prepared from *p*-cresol and the corresponding acid chloride.

The present work was in accordance with previous results, since rearrangement of the di-*p*-tolyl esters of isophthalic and terephthalic acids with aluminum chloride in chlorobenzene gave the expected bis-(*o*-hydroxyketones) in yields of 31.6 and 25.6%, respectively; but attempted rearrangement of di-*p*-tolyl phthalate gave 1-hydroxy-4-methylanthraquinone in 14% yield.

Rearrangement of the Diesters of Oxalic and Malonic Acid.—The rearrangements of the esters of oxalic and malonic acid fall in a special category, since in no case are bis-(*o*-hydroxyketones) obtained.

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(2) A portion of a thesis presented by Forrest D. Thomas II in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1958.

(3) A. H. Blatt, "Organic Reactions," Vol. I, chapter II, John Wiley and Sons, Inc., New York, N. Y., pp. 342–369.

(4) K. Fries and K. Bartens, *Ann.*, **442**, 270 (1925).

(5) E. Schwenk and H. Priewe, THIS JOURNAL, **56**, 2101 (1934).

(6) F. Huebner and K. P. Link, *J. Biol. Chem.*, **138**, 529 (1941).

(7) L. I. Smith and R. R. Holmes, THIS JOURNAL, **73**, 3847 (1951).

(8) F. F. Blicke and R. A. Patelski, *ibid.*, **60**, 2283 (1938).

(9) F. F. Blicke and O. J. Weinkauff, *ibid.*, **54**, 330 (1932).

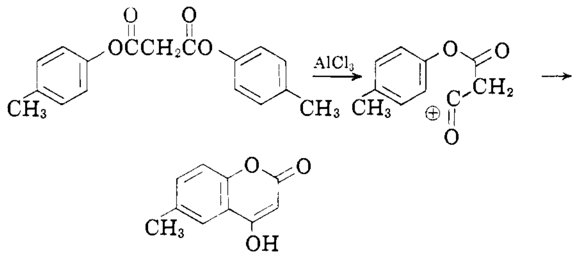
No reference to the rearrangement of diesters of oxalic acid could be found in the literature. However, Stollé and Knebel,[10] while studying the formation of coumarandiones, found that 4-methylphenyloxaloyl chloride, in the presence of aluminum chloride, gave 2-hydroxy-5-methylbenzoic acid and a small amount of 2-hydroxy-5-methylphenyloxoacetic acid instead of the expected 5-methylcoumarandione. Giua[11] obtained di-β-naphthyl malonate while attempting to prepare 4-hydroxy-6,7-benzocoumarin by condensing β-naphthol with malonoyl chloride in the presence of aluminum chloride. Ziegler and Junek have prepared several 4-hydroxycoumarins by the action of aluminum chloride on the appropriate malonic ester.[12]

In this study, the di-*p*-tolyl esters of oxalic and malonic acid were prepared under the same conditions used for the preparation of the esters of the higher aliphatic dicarboxylic acids. But neither of the two esters gave the corresponding bis-(*o*-hydroxyketones) when subjected to the conditions of the Fries rearrangement. Attempted rearrangement of di-*p*-tolyl oxalate resulted in the formation of a small amount of 2-hydroxy-5-methylbenzoic acid, while attempted rearrangement of di-*p*-tolyl malonate gave 4-hydroxy-6-methylcoumarin in 37.6% yield.

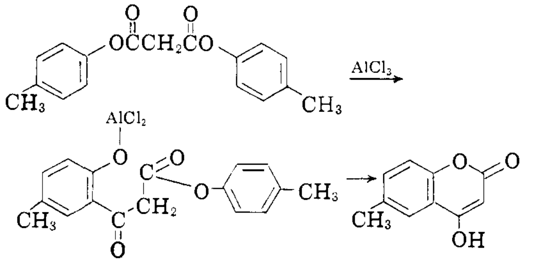
It is interesting to note that from a mechanistic viewpoint the hydroxycoumarin could have been produced by either of two paths. As shown in Chart I, route I involves initial cleavage of di-*p*-tolyl malonate to give an acyl cation which undergoes intramolecular cyclization to give the hydroxycoumarin. Route II, on the other hand, involves an initial mono Fries rearrangement followed by intramolecular cyclization to the 4-hydroxycoumarin in question.

CHART I

Route I



Route II



Infrared Spectra.—The infrared spectra of the bis-(*o*-hydroxyketones) show no absorption band in the region of 2.77–2.79 μ (3610–3584 cm.$^{-1}$), characteristic of a free phenolic hydroxyl group. Martin[13] observed that the infrared spectra of both salicylaldehyde and *o*-hydroxyacetophenone exhibit broad bands extending from 2.8 μ (3571 cm.$^{-1}$) to 3.6 μ (2778 cm.$^{-1}$) which were attributed to the absorption of the hydroxyl group hydrogen bonded to the carbonyl group and, in part, to the carbon–hydrogen stretching frequency. All of the bis-(*o*-hydroxyketones) derived from aliphatic acids have a strong band in the region of 3.28–3.53 μ (3049–2833 cm.$^{-1}$) which may be attributed partly to the hydroxyl group bonded to the *o*-carbonyl and partly to the carbon–hydrogen stretching frequency. As the chain length between the phenyl groups increases, the absorption bands become more narrow and are shifted to slightly longer wave lengths. Gordy[14] has obtained the infrared spectra of acetophenone and *o*-hydroxyacetophenone and found for acetophenone that the carbonyl frequency appeared at 5.96 μ (1678 cm.$^{-1}$), while in *o*-hydroxyacetophenone it was shifted to 6.17 μ (1621 cm.$^{-1}$). Absorption also occurred around 6.30 μ (1587 cm.$^{-1}$), which is characteristic of the benzene ring. In each bis-(*o*-hydroxyketone) there was no carbonyl absorption around 5.80–6.00 μ (1724–1667 cm.$^{-1}$), but there was strong absorption in the region of 6.02–6.30 μ (1661–1587 cm.$^{-1}$). In each case the band possessed three peaks, except for the isophthalic and terephthalic derivatives which had two peaks. These peaks would be characteristic of the shifted carbonyl group and of the benzene ring. In these compounds, the carbonyl frequency is not well separated from the frequency of the benzene ring, as was noted by Gordy for *o*-hydroxyacetophenone.

In a study of the infrared spectra of anthraquinone type compounds, Flett[15] observed that 1-hydroxyanthraquinone had no absorption around 2.98 μ (3350 cm.$^{-1}$) which would be associated with the hydroxyl group. However, two sharp bands appeared in the region of 6.0 μ (1667 cm.$^{-1}$). The first at 5.98 μ (1673 cm.$^{-1}$) was attributed to the conjugated carbonyl absorption and the second at 6.11 μ (1636 cm.$^{-1}$) to the carbonyl which was hydrogen-bonded to the hydroxyl group. The infrared spectra of 1-hydroxy-4-methylanthraquinone follows closely that reported for 1-hydroxyanthraquinone. There was no absorption around 2.98 μ (3350 cm.$^{-1}$), but there were three sharp bands in the 6.0 μ (1667 cm.$^{-1}$) region. The first at 5.99 μ (1669 cm.$^{-1}$) corresponds to the conjugated carbonyl absorption; the second at 6.09 μ (1642 cm.$^{-1}$) to the hydrogen-bonded carbonyl and the third at 6.11 μ (1637 cm.$^{-1}$) was probably due to benzene ring absorption.

Experimental[16]

A. Di-*p*-tolyl Esters.—All of the esters of aliphatic acids were prepared from the same molar proportions and in the same general way described below for di-*p*-tolyl succinate.

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[10] R. Stollé and E. Knebel, *Ber.*, **54B**, 1213 (1921).

[11] M. Giua, *Atti accad. Lincei*, [6] **2**, 343 (1925) [*C. A.*, **20**, 1233 (1926)].

[12] (a) E. Ziegler and H. Junek, *Monatsh.*, **86**, 29 (1955); (b) **86**, 506 (1955); (c) **87**, 212, 218 (1956); (d) E. Ziegler and H. Maier, *ibid.*, **89**, 143 (1958).

[13] A. E. Martin, *Nature*, **166**, 474 (1950).

[14] W. Gordy, *J. Chem. Phys.*, **8**, 516 (1940).

[15] M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948).

[16] All melting points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

TABLE I

DI-*p*-TOLYL ESTERS

Diester, di-*p*-tolyl	Yield, %	M.p., °C.	Recrystn. solvents	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Oxalate	43.7	148–149[18a]	Ethanol	71.10	71.11	5.22	5.49
Malonate	71.4	68–69[18b]	Ethanol	71.82	71.99	5.67	5.42
Succinate	63.4	119–120[17]	Ethanol	72.47	72.62	6.08	6.17
Glutarate	61.5	86–87	1:2 H_2O–EtOH	73.06	72.96	6.45	6.48
Adipate	46	98–99	Ethanol	73.60	73.46	6.79	6.92
Pimelate	69.4	82–83	1:2 H_2O–EtOH	74.09	73.83	7.11	6.99
Suberate	64.5	81–82	Ethanol	74.55	74.73	7.39	7.59
Azelate	62	69–70	1:4 H_2O–EtOH	74.97	75.09	7.66	7.75
Sebacate	87	76.5–77.5	Ethanol	75.36	75.34	7.81	7.73
Phthalate	71	85–86[19]	Methanol	76.28	76.18	5.24	5.06
Isophthalate	76.4	161–162	1:2 dioxane–EtOH	76.28	76.25	5.24	5.17
Terephthalate	75.5	197–198	Dioxane	76.28	76.23	5.24	5.38

TABLE II

BIS-(*o*-HYDROXYKETONES)

Bis-(*o*-hydroxyketones)	Yield, %	M.p., °C.	Recrystn. solvents	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Infrared bands, μ 3.25–3.60	Infrared bands, μ 6.00–6.50
1,4-Bis-(2-hydroxy-5-methylphenyl)-butane-1,4-dione	44[a] 43[b]	189[4]	Ethanol	72.47	72.62	6.08	6.19	3.33 3.40 3.45	6.11 6.18 6.30
1,5-Bis-(2-hydroxy-5-methylphenyl)-pentane-1,5-dione	66[b]	140–141	Ethanol	73.06	72.92	6.45	6.34	3.33 3.40 3.50	6.10 6.18 6.28
1,6-Bis-(2-hydroxy-5-methylphenyl)-hexane-1,6-dione	28[a] 72[b]	163–164	1:3 H_2O–dioxane	73.60	73.77	6.79	6.90	3.34 3.46	6.15 6.22 6.29
1,7-Bis-(2-hydroxy-5-methylphenyl)-heptane-1,7-dione	59.5[b]	100–101	Ethanol	74.09	73.99	7.11	6.94	3.42 3.46	6.10 6.20 6.28
1,8-Bis-(2-hydroxy-5-methylphenyl)-octane-1,8-dione	35[a] 72[b]	136–137	1:3 H_2O–dioxane	74.55	74.74	7.39	7.35	3.40 3.53	6.11 6.18 6.27
1,9-Bis-(2-hydroxy-5-methylphenyl)-nonane-1,9-dione	58[b]	79–80	Ethanol	74.97	74.99	7.66	7.78	3.43 3.52	6.08 6.17 6.27
1,10-Bis-(2-hydroxy-5-methylphenyl)-decane-1,10-dione	79[b]	126–127	1:2 dioxane–EtOH	75.36	75.37	7.91	7.83	3.45 3.53	6.10 6.18 6.28
1,3-Bis-(2-hydroxy-5-methylbenzoyl)-benzene	31.6[b]	190–191	1:2 dioxane–EtOH	76.28	76.29	5.24	5.13	3.30	6.11 6.25
1,4-Bis-(2-hydroxy-5-methylbenzoyl)-benzene	25.6[b]	190–190.5	1:1 dioxane–EtOH	76.28	76.57	5.24	5.08	3.31	6.12 6.17

[a] Prepared without use of solvent. [b] Prepared with chlorobenzene as solvent.

The esters of aromatic acids were all prepared in the same general way described below for di-*p*-tolyl terephthalate. Pertinent information is assembled in Table I.

Di-*p*-tolyl **Succinate.**—Succinic acid (11 g., 0.09 mole) and *p*-cresol (20 g., 0.18 mole) were placed in a 200-ml. round-bottom flask equipped with a thermometer and a reflux condenser protected by a drying tube. The flask and contents were heated to 115–120° by means of an oil-bath. Phosphorus oxychloride (16 g., 0.1 mole) was added dropwise to the hot mixture. Toward the end of the addition the vigorous bubbling due to the evolution of hydrogen chloride subsided, and on continued heating only a negligible amount of bubbling was observed. After heating for two to three hours at 115–120°, the dark reaction mixture was allowed to cool, whereupon a reddish-brown crystalline material formed on top of a black viscous material. The crystalline material was scraped away from the black resin and mixed with 250 g. of a 1:1 mixture of ice and water. The dark orange crystals were then filtered, dried, and recrystallized from ethanol to give 17 g. (63.4%) of a light orange crystalline material, m.p. 114–118°. This material was pure enough to be used in the Fries rearrangement. Three additional recrystallizations from ethanol afforded a white crystalline material, m.p. 119–120°, reported[17] 121°.

Di-*p*-tolyl **Terephthalate.**—Terephthaloyl chloride (10 g., 0.05 mole) and *p*-cresol (13 g., 0.12 mole) were mixed in an apparatus as described above for di-*p*-tolyl succinate and slowly heated to 100°. Heating was continued three to four hours or until the evolution of hydrogen chloride ceased. Then the mixture was cooled, extracted with 50 ml. of 10% sodium hydroxide, washed with water and dried. The tan powder was crystallized from dioxane to give white crystals, 13.1 g. (75.5%), m.p. 197–198°. An additional recrystallization from dioxane gave white crystals, m.p. 197–198°.

B. **Bis-(*o*-hydroxyketones).** **Rearrangement without Solvent.** **1,4-Bis-(2-hydroxy-5-methylphenyl)-butane-1,4-dione.**—Di-*p*-tolyl succinate (6.0 g., 0.02 mole), aluminum chloride (6.7 g., 0.05 mole) and carbon disulfide (50 ml.) were mixed in a flask and heated to reflux for 0.5 hour. The carbon disulfide was removed, and the light yellow solid

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[17] C. A. Bischoff and A. v. Hedenström, *Ber.*, **35**, 4080 (1902).

[18] (a) C. A. Bischoff and A. v. Hedenström, *ibid.*, **35**, 3443 (1902), reported m.p. 149°; (b) H. J. Backer and J. L. Lolkema, *Rec. trav. chim.*, **57**, 1237 (1938), reported m.p. 60°.

[19] R. Meyer, *Ber.*, **26**, 209 (1893), reported m.p. 83–84°.

remaining was heated to 130°. At 120° the solid began to melt and, after heating at 130°, a light brown, spongy mass had formed. After heating four hours at 130°, the material was cooled, then chipped loose and mixed with 250 g. of a 1:1 mixture of ice and concentrated hydrochloric acid. The yellow mixture which formed was filtered, the solid residue mixed with 100 g. of 1:1 mixture of ice and concentrated hydrochloric acid and the mixture stirred overnight. The next day the mixture was filtered and the residue extracted with 25 ml. of boiling ethanol. A light yellow residue remained which was dried at 110°. On drying, the material became black; yield 2.61 g. (44%). A 0.5-g. sample of the crude product was chromatographed over 30 g. of silicic acid and eluted with chloroform to give 0.5 g. of a light brown solid, m.p. 184–186°, reported[4] m.p. 187°.

Rearrangement with Solvent.—All runs were made with the same molar proportions and in the manner described for 1,4-bis-(2-hydroxy-5-methylphenyl)-butane-1,4-dione. For the rearrangement of the isophthalate and terephthalate esters heating was continued for 33 and 38 hr., respectively. Pertinent information is assembled in Table II.

1,4-Bis-(2-hydroxy-5-methylphenyl)-butane-1,4-dione.—Di-*p*-tolyl succinate (6 g., 0.02 mole), aluminum chloride (6.7 g., 0.05 mole) and chlorobenzene (50 ml.) were mixed in a 200-ml. flask equipped with a thermometer and a reflux condenser. The condenser was fitted with a calcium chloride tube leading to a water trough, which acted as a trap to absorb the hydrogen chloride evolved during the reaction. When the mixture was refluxed for six hours, a blackish residue had formed in the flask. After cooling, the mixture was added to 250 g. of a 1:1 mixture of ice and concentrated hydrochloric acid and stirred overnight. A clear yellow aqueous layer and a gray organic layer formed. The chlorobenzene was removed from the reaction mixture by steam distillation. A clear yellow aqueous solution containing some black solid remained in the flask. The mixture was cooled overnight, then filtered. The black solid which collected was then ground to a paste, mixed with water, and again filtered. The material gathered on the filter was air-dried, then extracted with two 25-ml. portions of boiling ethanol. A light greenish crystalline material remained; yield 2.9 g. (48.5%). A 0.5-g. sample of the crude product was chromatographed over 30 g. of silicic acid and eluted with chloroform to give 0.44 g. (43%) of a dark yellow crystalline material, m.p. 186–188°. A sample of the crude product was crystallized three times from ethanol to give white needles, m.p. 189°, reported[4] 187°.

2-Hydroxy-5-methylbenzoic Acid.—An attempted rearrangement of di-*p*-tolyl oxalate (2.7 g., 0.01 mole) was carried out as described above for the rearrangement of di-*p*-tolyl succinate. The temperature was increased from 60 to 120° during one hour, then held at 120° for two hours until the evolution of hydrogen chloride ceased. After the chlorobenzene was removed by steam distillation a dark oil remained in the distillation flask. This oil was extracted with 50 ml. of 10% sodium hydroxide. The hot alkali solution was made acidic with hydrochloric acid and upon cooling, 2-hydroxy-5-methylbenzoic acid separated as long white needles; yield 0.27 g. (17.7%), m.p. 150.5–151.5°, reported[20] m.p. 151°.

4-Hydroxy-6-methylcoumarin.—An attempted rearrangement of di-*p*-tolyl malonate (2.8 g., 0.01 mole) was carried out as described above for di-*p*-tolyl succinate. After the chlorobenzene was removed by steam distillation a light yellow solid remained in the distillation flask. This product was recrystallized from methanol to give long white needles; yield 0.66 g. (37.6%), m.p. 247–248° (dec. about 235–240°), reported 240°,[12a] 241° (dec. about 238°).[21]

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.17; H, 4.58. Found: C, 68.20; H, 4.56.

1-Hydroxy-4-methylanthraquinone.—An attempted rearrangement of di-*p*-tolyl phthalate (3.5 g., 0.01 mole) was carried out as described above for di-*p*-tolyl succinate, except that the temperature was held at 100° for 16 hours. After the chlorobenzene was removed by steam distillation, a red-brown solid remained in the distillation flask. This solid was collected and recrystallized from glacial acetic acid to give 1-hydroxy-4-methylanthraquinone as red-brown needles; yield 0.53 g. (14%), m.p. 171–172°. A further recrystallization of a sample of this crude product from ethanol gave bright orange-yellow needles, m.p. 173°, reported[22] m.p. 175–176°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.47; H, 4.20.

Infrared Spectra of Bis-(*o*-hydroxyketones).—The infrared spectra of all the bis-(*o*-hydroxyketones) and 1-hydroxy-4-methylanthraquinone were obtained as potassium bromide pellets. A Perkin–Elmer, model 21 spectrophotometer, was used. Important absorption bands are listed in Table II.

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(20) W. J. Pavaotović, *J. prakt. Chem.*, [2] **33**, 65 (1885).

(21) R. Anschütz, *Ann.*, **367**, 251 (1909).

(22) O. Fischer and A. Sapper, *J. prakt. Chem.*, **83**, 207 (1910).

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[CONTRIBUTION FROM SINCLAIR RESEARCH LABORATORIES, INC.]

The Alkylation of *p*-Xylene[1]

BY B. S. FRIEDMAN, F. L. MORRITZ, C. J. MORRISSEY AND R. KONCOS

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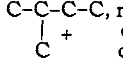
As reported by others, considerable steric hindrance is encountered in introducing a *t*-alkyl group *ortho* to a methyl group. While *p*-xylene can be *t*-butylated in low yield, attempts to accomplish the *t*-pentylation of *p*-xylene by reaction with isoamylenes in the presence of sulfuric acid, boron fluoride, ferric chloride or aluminum chloride–nitromethane result in formation of polymer or of small amounts of by-product *t*-butyl-*p*-xylene. With certain catalysts, *e.g.*, aluminum chloride or hydrogen fluoride, a secondary C_5-alkylate, 2-*p*-xylyl-3-methylbutane (II), is formed in good yield, but *t*-pentyl-*p*-xylene (I) was absent in all cases. Aluminum chloride–nitromethane also produces II in high yield when *t*-pentyl chloride is the alkylating agent. The evidence favors a mechanism involving formation of II *via* direct reaction with a secondary carbonium ion,  $\mathrm{C{-}\underset{\underset{C}{|\;+}}{C}{-}C{-}C}$, rather than the mechanism postulating initial formation of I and subsequent isomerization to II. Aluminum chloride ± nitromethane produces sizeable amounts, and hydrogen fluoride somewhat less, of by-product condensation products of *p*-xylene. These consist of diphenylmethane derivatives, a major component being di-*p*-xylylmethane. A mechanism is presented for these condensation reactions.

p-Xylene is alkylated[2] readily with unbranched olefins, alcohols and alkyl halides but resists alkylation by the more branched members of these groups. This resistance is especially characteristic of reactions employing catalysts (*e. g.*, sulfuric acid and ferric chloride[3]) which strongly favor

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(1) Presented at the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957.

(2) See chapter on "The Alkylation of Aromatic Compounds by the Friedel-Crafts Method," by C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946.

(3) D. Nightingale and J. R. Janes, THIS JOURNAL, **66**, 154 (1944).