Titanium Tetrachloride as a Catalyst in the Friedel–Crafts Reaction. Part III. Alkylation.*

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Titanium tetrachloride has been successfully used as a catalyst for the alkylation of benzene, toluene, and anisole by, *e.g.*, tertiary alkyl chlorides, primary, secondary, and tertiary alcohols, and 2-methylbut-2-ene.

With the alkyl chlorides small proportions of the titanic halide sufficed to promote reaction, but with the alcohols at least an equivalent amount was required for the most satisfactory results.

With benzene, in addition to monosubstitution some disubstitution also occurred in some cases, the second group entering the *para*-position exclusively; with toluene and anisole *para*-substitution was the invariable rule.

Moreover, while *sec.*-butyl alcohol gave *sec.*-butyl derivatives *iso*butyl alcohol tended to yield *tert.*-butyl derivatives.

Alkylations with alkyl chlorides in the presence of titanic chloride appear to have been described only by Stadnikov and Kashtanov (*J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1117; *Ber.*, 1928, **61**, 1389), who prepared in this way diphenylmethane and *m*- and *p*-dibenzylbenzene from benzene and benzyl chloride.

While titanium tetrachloride is not as active catalytically as aluminium chloride, certain advantages over the latter were noted: owing to its solubility in organic solvents reactions could be carried out in homogeneous media, and solvents such as carbon disulphide could be dispensed with. Also noteworthy was the absence of much polyalkylation; all disubstituted products were *para* only, and not mixed *para* and *meta* as frequently obtained with the aluminium halide.

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Early experiments with benzene showed that methyl and ethyl chloride did not react easily; however *tert.*-amyl and *tert.*-butyl chloride readily formed alkyl derivatives of benzene, toluene, and anisole. The reaction between *tert.*-butyl chloride and benzene yielded *p*-di-*tert.*-butylbenzene, accompanied by a small amount of the mono-*tert.*-butyl derivative; *tert.*-amyl chloride gave appreciable quantities of mono- as well as *p*-di-*tert.*-amylbenzene.

Somewhat discordant results are reported in the literature for the action of *tert.*-butyl chloride on toluene. Shoesmith and McGechen (*J.*, 1930, 2231) claimed that with aluminium or ferric chloride a mixture of *meta*- and *para*-substituted products resulted; on the other hand Baur (*Ber.*, 1891, **24**, 2833), Buu-Hoï and Cagniant (*Bull. Soc. chim.*, 1942, **9**, 887), and Larner and Peters (*J.*, 1952, 680) found that with aluminium chloride the chief product was the *meta*-isomer, and the last-named authors, and Bialobrzeski (*Ber.*, 1897, **30**, 1773), obtained *para*-substitution only with ferric chloride. Buu-Hoï and Cagniant explained Shoesmith and McGechen's results as being due to the use of concentrated sulphuric acid for isomer separation; this induced the reversible isomerisation *m*-*tert.*- $\rightleftarrows$ *p*-*tert.*-butyltoluene, yielding an equilibrium mixture of the two.

In our experiments the proportion of catalyst used had no pronounced effect on yields in alkylations with *tert.*-butyl or *tert.*-amyl chloride. The sole product isolated in each case was the *para*-compound. We found that the *tert.*-butyltoluene was most readily oxidised to *p*-*tert.*-butylbenzoic acid with dichromate and sulphuric acid. When anisole was treated with *tert.*-butyl and *tert.*-amyl chlorides *p*-*tert.*-derivatives only were produced, variation in temperature having very little effect on the yields obtained.

Alkylations with alcohols in the presence of titanic chloride have not been previously described in the literature. In our experiments satisfactory yields were usually obtained, and it was noted that while *iso*butyl alcohol gave tertiary-alkyl derivatives, *sec.*-butyl alcohol gave secondary derivatives. Moreover the ease of reaction was in the order tertiary > secondary > primary alcohol, though with methyl and ethyl alcohol reaction was usually slight. With *tert.*-butyl and *tert.*-amyl alcohol yields comparable to those given by the corresponding alkyl chlorides were obtained provided that the ratio of catalyst to alcohol was not less than 1 : 1 (raising this proportion had very little effect). This may be due, partly at least, to the loss of some titanium salt by reaction with the alcohol (cf. Cullinane *et al.*, *J. Appl. Chem.*, 1952, **2**, 250), *e.g.*, $TiCl_4 + 2ROH = TiCl_2(OR)_2 + 2HCl$.

With *tert.*-butyl alcohol and benzene both mono- and *p*-di-*tert.*-butylbenzene were formed, as with aluminium chloride (Huston, Fox, and Binder, *J. Org. Chem.*, 1938, **3**, 251; cf. Norris and Sturgis, *J. Amer. Chem. Soc.*, 1939, **61**, 1413). McKenna and Sowa (*ibid.*, 1937, **59**, 470) found that boron trifluoride gave in addition a small amount of the *o*-di-derivative.

tert.-Amyl alcohol yielded the mono- and *p*-di-*tert.*-derivative of benzene, low temperatures favouring formation of the latter. The former compound was obtained with aluminium chloride (Huston, Fox, and Binder, *loc. cit.*) and ferric chloride (Inatome *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 292). Both toluene and anisole reacted smoothly with *tert.*-butyl and *tert.*-amyl alcohol, variations in time or temperature having very little effect on the yields obtained. *p*-Alkyl derivatives were the sole products.

tert.-Amylene gave the same products as *tert.*-amyl alcohol with benzene, toluene, and anisole.

Rather high temperatures were needed to ensure the best yields in the reaction between *sec.*-butyl alcohol and benzene. No isomerization of the *sec.*-butyl group was detected, in agreement with the results obtained with aluminium chloride (Huston and Hsieh, *ibid.*, 1936, **58**, 439) and boron trifluoride (McKenna and Sowa, *loc. cit.*), the sole product being *sec.*-butylbenzene. Similarly no isomerization took place with toluene, and as with aluminium chloride (Tsukervanik and Tokareva, *J. Gen. Chem. Russia*, 1935, **5**, 764) *p*-*sec.*-butyltoluene was obtained.

Benzene and *iso*propyl alcohol reacted to give cumene, as with aluminium chloride (Huston and Hseih, *loc. cit.*; Tsukervanik and Taveeva, *Zhur. Obshchey Khim.*, 1952, **22**, 966); boron trifluoride yielded mono- and di-*iso*propylbenzene (McKenna and Sowa, *loc. cit.*). Toluene gave *p*-cymene only, also obtained by Tsukervanik and Tokareva (*loc. cit.*) with aluminium chloride, though Pajeau (*Bull. Soc. chim.*, 1948, 59) isolated both *m*- and *p*-cymene with the latter catalyst, whereas with sulphuric acid or ferric chloride all three *iso*propyltoluenes resulted.

The last-named author found that the action of aluminium chloride on *iso*propyl alcohol and anisole gave only *p*-*iso*propylanisole, but with titanium tetrachloride we obtained in addition *p*-*iso*propylphenol, formed by scission of the ether linkage.

No marked alkylation of benzene occurred with *iso*butyl alcohol; with toluene, isomerization to *p*-*tert.*-butyltoluene took place; Pajeau, using aluminium chloride, isolated both the *m*- and the *p*-*tert.*-butyl derivative. Anisole formed the *p*-tert.-butyl ether which was also given with aluminium chloride (Pajeau); in addition we obtained *p*-*tert.*-butylphenol. Somewhat high temperatures were needed in these experiments.

EXPERIMENTAL

A large number of experiments were carried out under varying conditions; some typical examples are described below and further results are given in the Table. The yields, while only approximate, were confirmed by repetition in many cases; all are based on the alkylating agent. All materials were purified before use and precautions taken to exclude moisture.

Alkylation with Alkyl Chlorides.—The usual procedure consisted in adding the catalyst to the other reactants in a vessel fitted with a reflux condenser, and as heat was normally evolved cooling was applied during the addition, with continuous agitation. At the end of each alkylation the cooled product, which usually contained a little tar, was decomposed cautiously with dilute hydrochloric acid, and the organic layer separated, washed successively with dilute hydrochloric acid and water, and dried ($CaCl_2$). The products formed were fractionally distilled through a column.

Action of tert.*-Butyl Chloride on Benzene.*—Fractionation of the product gave a portion, b. p. 165—168°, consisting almost entirely of *tert.*-butylbenzene, b. p. 167° (cf. Norris and Sturgis, *loc. cit.*; McKenna and Sowa, *loc. cit.*; Tsukervanik, *J. Gen. Chem. Russia*, 1935, **5**, 117), which was identified by the following derivatives: (*a*) *p*-acetamido-, m. p. 171—172° (Ipatieff and Schmerling, *J. Amer. Chem. Soc.*, 1937, **59**, 1050; Potts and Carpenter, *ibid.*, 1939, **61**, 663; Malherbe, *Ber.*, 1919, **52**, 322); (*b*) 2 : 4-dinitro-, m. p. 61—62° (Baur, *Ber.*, 1894, **27**, 1710; Malherbe, *loc. cit.*); (*c*) the *p*-sulphonamide, m. p. 136° (Huntress and Autenrieth, *J. Amer. Chem. Soc.*, 1941, **63**, 3446). A higher fraction, *p*-di-*tert.*-butylbenzene, b. p. 230—235°, solidified on cooling, then having m. p. and mixed m. p. 77° (cf. McKenna and Sowa, *loc. cit.*).

Action of tert.*-Amyl Chloride on Benzene.*—Two fractions resulted. One, b. p. 189—192°, composed of *tert.*-amylbenzene, b. p. 191° (cf. Ipatieff and Schmerling, *loc. cit.*), was identified by the following derivatives: the *p*-sulphonamide, m. p. 85—86° (Legge, *J. Amer. Chem. Soc.*, 1947, **69**, 2079; Huntress and Autenrieth, *loc. cit.*); *p*-acetamido-, m. p. 138° (Anschütz and Beckerhoff, *Annalen*, 1903, **327**, 22; Ipatieff and Schmerling, *loc. cit.*; Legge, *loc. cit.*); the second fraction, b. p. 262—266°, was almost entirely *p*-di-*tert.*-amylbenzene, b. p. 264° (cf. Simons and Archer, *J. Amer. Chem. Soc.*, 1938, **60**, 2952). This fraction (4 g.) was heated with chromic oxide (14 g.), water (60 c.c.), and concentrated sulphuric acid (66 c.c.) at 70°. When the reaction had subsided more chromic oxide (32 g.) was added gradually and the mixture was further heated at 100° for 30 min., then poured into water; terephthalic acid (1·5 g.) (dimethyl ester, m. p. 139—140°) was precipitated.

Action of tert.*-Butyl Chloride on Toluene.*—The product, b. p. 188—191°, consisted almost exclusively of *p*-*tert.*-butyltoluene, b. p. 191° (cf. Larner and Peters, *loc. cit.*), and was characterized by the following derivatives: 2-benzamido-, m. p. 142° (Battegay and Haeffely, *Bull. Soc. chim.*, 1924, **35**, 981); 2 : 6-dinitro-, m. p. 94—95° (Brady and Lahiri, *J.*, 1934, 1954); *sulphonamide*, colourless plates, m. p. 138—140° (Found: C, 58·6; H, 7·8; N, 6·1; S, 14·0. $C_{11}H_{17}O_2NS$ requires C, 58·1; H, 7·5; N, 6·2; S, 14·1%).

p-tert.*-Butylbenzoic Acid.*—Larner and Peters failed to oxidize *p*-*tert.*-butyltoluene by Bialobrzeski's chromic acid–acetic acid method, but secured a 35% yield of the acid by oxidation with potassium permanganate in aqueous pyridine. We obtained a 55% yield by heating the hydrocarbon (5 g.) with sodium dichromate (20 g.), water (90 c.c.), and concentrated sulphuric acid (75 c.c.) gradually to 45°; the reaction tended to become violent, but the temperature was not allowed to exceed 50°. After this reaction had subsided more sodium dichromate (25 g.) was added in small portions, the temperature being still kept at 50°, and the mixture was then

Alkylations (quantities in moles; the heading Cpd. refers to the amount of the aromatic reactant. When two values are given for the yield, the first refers to the mono- and the second to the di-alkyl product; single figures refer to monoalkyl derivatives).

$TiCl_4$	Cpd.	Temp.	Time (hr.)	Yield (%)	Note
	Benzene and tert.*-butyl chloride.*				
0·1	0·28	10°	3	9 + 69	—
0·1	0·28	10	6	4 + 84	1
	Benzene and tert.*-amyl chloride.*				
0·1	0·28	60	3	14 + 57	2
0·1	0·28	20	18	27 + 52	—
	Toluene and tert.*-butyl chloride.*				
0·025 or 0·05	0·24	10	1	73	—
0·1	0·24	10	1 or 3	77	—
	Toluene and tert.*-amyl chloride.*				
0·05	0·24	20	3	61	3
0·1	0·24	20	1	58	4
0·1	0·24	40	3	69	—
	Anisole and tert.*-butyl chloride.*				
0·1	0·2	10	0·5	64	—
0·1	0·2	0 or 10	1	71	5
	Anisole and tert.*-amyl chloride.*				
0·1	0·2	20 or 60	1	67	6
	Benzene and tert.*-butyl alcohol.*				
0·2	0·55	60	1	74 + 4	7
0·2	0·55	60	2	71 + 8	8
0·2	0·55	80	1	66 + 7	—
0·2	0·55	40	3	36 + 46	9
	Benzene and tert.*-amyl alcohol.*				
0·2 or 0·1	0·55	60	1	74	—
0·2	0·55	80	1	60 + 11	10
0·2	0·55	18	18	41 + 28	11
	Toluene and tert.*-butyl alcohol.*				
0·2	0·47	10	3	74	12
0·2	0·47	25	6	74	—
0·1	0·47	10	3	74	13
	Toluene and tert.*-amyl alcohol.*				
0·2	0·47	18	3	64	14
0·2	0·47	18	6	70	15
0·2	0·47	40	3	68	—
	Anisole and tert.*-butyl alcohol.*				16
0·2	0·2	10	1	67	17
0·1	0·2	10	1	67	18
	Anisole and tert.*-amyl alcohol.*				16
0·2	0·2	20	0·25	61	19
0·2	0·2	0	1	57	20
0·1	0·2	20	1	61	—
	Benzene and sec.*-butyl alcohol.*				
0·1 or 0·2	0·55	B. p.	6	61	—
	Benzene and iso*propyl alcohol.*				
0·1 or 0·2	0·55	B. p.	6	61	—
	Toluene and sec.*-butyl alcohol.*				
0·1	0·24	100	3	68	21
0·2	0·47	60	4·5 or 3	74	—
0·2	0·24	60	3	66	—
	Toluene and iso*propyl alcohol.*				
0·2	0·47	100	3	68	22
0·1	0·47	100	0·5	59	23
	Anisole and iso*propyl alcohol.*				24
0·1 or 0·2	0·2	100	3	44 (14)	—
0·2	0·2	140	1	53 (22)	—
	Toluene and iso*butyl alcohol.*				
0·2	0·47	B. p.	6	62	25
	Anisole and iso*butyl alcohol.*				
0·1	0·2	160	3	75	26
	Benzene and 2-methylbut-2-ene.				
0·1	0·55	60	9	13 + 42	27
0·1	0·55	80	6	40	—
	Toluene and 2-methylbut-2-ene.				
0·1	0·24	20	1	18	28
0·05	0·24	20	3	16	29
	Anisole and 2-methylbut-2-ene.				30
0·1	0·2	0	1	61	31
0·1	0·2	20	0·25 or 0·5	67	

Notes : With other conditions throughout as stated, further yields obtained were as follows: (1) With 0·55 mole of benzene 19 and 66%. (2) After 6 hr. 29 and 56%. With 0·55 mole of benzene 23 and 28%. (3) With 0·1 or 0·2 mole of titanic chloride 68%. (4) After 6 or 13 hr. 70%. (5) When anisole was added to the other ingredients at 10° 64%. (6) With 0·05 or 0·2 mole of titanic chloride at 20°, the yield was the same. (7) With 0·1 mole of titanium tetrachloride 71 + 8%, and with 0·05 mole 49 + 29%. (8) With 0·2 mole of benzene 63 + 16%. (9) With 0·2 mole of benzene 20 + 66%. (10) After 3 hr. at 60° 69 + 12%. (11) After 48 hr. 47 + 33%. (12) After 6 hr. 74, 48 hr. 77%. (13) With 0·05 mole of titanium tetrachloride 35%. (14) With 0·3 mole of titanium tetrachloride 64%, with 0·1 mole 57%. (15) After 18 hr. same yield. (16) The catalyst was added to the alcohol and anisole, mixed with carbon disulphide (30 c.c.). (17) After 2 hr. same yield; after 1 hr. at 40° 66%. (18) With 0·05 mole of catalyst 53%; with 0·3 mole 67%. (19) After 1 or 3 hr. same yield. (20) At 40° 61%. (21) At 80° same, at 60° 65%, at 40° 28%. (22) At 80° 62%, at 60° 61%, at 40° 57%, at 20° 19%. (23) After 1 hr. 61%, 3 hr. 67%. (24) Figures in parentheses give the yields of *p-iso*propylphenol. (25) After 3 hr. 11%, 9 hr. 55%. (26) At 140° 60%, 120° 19%, 100° or 50° no yield. The products contained in all cases about equal amounts of *p-tert.*-butylanisole and *p-tert.*-butylphenol. (27) After 6 hr. 13 + 31%, 3 hr. 23 + 8%. (28) After 3 hr. 33%, 6 hr. 30%. (29) With 0·2 mole of titanium tetrachloride 33%. (30) Yields are of *p-tert.*-amylanisole. (31) At 20° 67%, 40° 65%, 60° 67%.

heated at 100° for 15 min. The cooled product was poured into water, and the solid collected and extracted with dilute sodium hydroxide solution from which the acid was precipitated. Recrystallization from ligroin yielded colourless needles, m. p. 163—164°. Larner and Peters give m. p. 162—164°.

Action of tert.*-Amyl Chloride on Toluene.*—The product, b. p. 212—214°, was composed almost exclusively of *p-tert.*-amyltoluene (cf. Hennion and Kurtz, *J. Amer. Chem. Soc.*, 1943, **65**, 1001). Oxidation by the method used for di-*tert.*-amylbenzene gave terephthalic acid, and the *sulphonamide* crystallized from hot water in fine white needles, m. p. 113—114° (Found : C, 59·5; H, 7·8; N, 5·7; S, 13·5. $C_{12}H_{19}O_2NS$ requires C, 59·7; H, 7·9; N, 5·8; S, 13·3%).

4-tert.*-Amyl-2-benzamidotoluene.*—A mixture of nitric acid (*d* 1·42; 6 c.c.) and concentrated sulphuric acid (6 c.c.) was added gradually to *tert.*-amyltoluene (8 c.c.) at 15—20°, stirring being continued for a further 30 min. The product was poured into water, and the nitro-compound (6·7 g.) extracted with ether; it distilled at 125—130°/4 mm. Reduction followed by benzoylation yielded 4-tert.*-amyl-2-benzamidotoluene*, colourless plates (from alcohol), m. p. 122—123° (Found: C, 80·6; H, 8·0; N, 5·1. $C_{19}H_{23}ON$ requires C, 81·1; H, 8·2; N, 5·0%).

The methyl group in the above nitro-compound, dissolved in acetic anhydride and acetic acid, was oxidized with chromium trioxide to aldehyde diacetate. Hydrolysis of this product with hydrochloric acid yielded a compound which gave a strong positive Baeyer–Drewson indigo test (*Ber.*, 1883, **16**, 2205) for *o*-nitrobenzaldehydes.

4-tert.*-Amyl-2 : 6-dinitrotoluene.*—*p-tert.*-Amyltoluene (30 g.) in glacial acetic acid (30 c.c.) was cooled in ice-salt, and fuming nitric acid (*d* 1·5; 60 c.c.) and oleum (66 c.c.) containing 20% of free sulphur trioxide were added slowly below 5° with stirring. After being kept in the bath for a further 30 min., the mixture was heated at 40° for 3 hr. The cooled mixture was then poured on crushed ice, and the precipitated solid washed with aqueous sodium carbonate and water. Crystallization from alcohol afforded colourless crystals of 4-tert.*-amyl-2 : 6-dinitrotoluene*, m. p. 61—62° (Found : C, 57·7; H, 6·4; N, 10·9. $C_{12}H_{16}O_4N_2$ requires C, 57·1; H, 6·3; N, 11·1%).

3 : *5-Dinitro-*p*-toluic Acid* (CO_2H = 1).—The above solid (3 g.) was boiled under reflux with fuming nitric acid (*d* 1·5; 75 c.c.) for 120 hr., then the product was poured into water. After a few days pale yellow needles appeared and a further quantity was obtained from the mother-liquor. Recrystallization from hot water afforded 3 : 5-dinitro-*p*-toluic acid (1·5 g.), m. p. 158—159°, also obtained by oxidation of 2 : 6-dinitro-*p*-cymene by Wheeler and Harris (*J. Amer. Chem. Soc.*, 1927, **49**, 494).

4-tert.*-Amyl-2-nitro-6-benzamidotoluene.*—The *tert.*-amyl-dinitrotoluene (5 g.) was reduced with ammonium sulphide (16% solution; 30 c.c.) in ethanol (50 c.c.); the *amine hydrochloride* (4·1 g.) crystallized from dilute hydrochloric acid in pale yellow needles, m. p. 220° (decomp.) (Found : *M*, by titration, 256·9. $C_{12}H_{19}O_2N_2Cl$ requires *M*, 258·5%). The *benzoyl* derivative formed colourless plates (from dilute alcohol), m. p. 135° (Found : C, 69·7; H, 6·6; N, 8·7. $C_{19}H_{22}O_3N_2$ requires C, 69·9; H, 6·7; N, 8·6%).

Action of tert.*-Butyl Chloride on Anisole.*—The product, b. p. 222—225° (mostly 222—223°), m. p. 19°, was *p-tert.*-butylanisole (cf. Olsen *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 2451). The 2 : 6-dinitro-derivative had m. p. 100° (Baur, *Ber.*, 1894, **27**, 1618).

Action of tert.*-Amyl Chloride on Anisole.*—*p-tert.*-Amylanisole, b. p. 239—240°, was the sole product. Fischer and Grützner (*Ber.*, 1893, **26**, 1648) give b. p. 240—241°; Kreysler (*Ber.*, 1885, **18**, 1711) gives 216—217°.

4-tert.*-Amyl-2 : 6-dinitroanisole.*—To the ether (2 g.) in glacial acetic acid (10 c.c.), cooled in ice, fuming nitric acid (*d* 1·5; 4 c.c.) in acetic acid (10 c.c.) was added dropwise, followed by concentrated sulphuric acid (4 c.c.) in the same solvent (5 c.c.). The product was then heated at 70° for 30 min., cooled, and poured on ice. The precipitated oil solidified slowly and after recrystallization from alcohol or dioxan gave yellow needles (1 g.), m. p. 38°. Anschütz and Rauff (*Annalen*, 1903, **327**, 213), who prepared the compound by methylation of the phenol, give m. p. 39°.

Alkylation with Alcohols.—Similar procedures were adopted to those used with alkyl chlorides. The products obtained by treatment of benzene, toluene, and anisole with *tert.*-amyl and *tert.*-butyl alcohol were isolated and identified by the methods already described, and the results are summarized in the Table.

Action of sec.*-Butyl Alcohol on Benzene.*—The fraction, b. p. 170—175°, was almost all *sec.*-butylbenzene, b. p. 173° (cf. Birch, Dean, Fidler, and Lowry, *J. Amer. Chem. Soc.*, 1949, **71**, 1362), which was identified by the *p*-acetamido-derivative, m. p. 123° (Harrison, Kenyon, and Shepherd, *J.*, 1926, 659). A small quantity of a higher-boiling fraction was also formed.

Action of sec.*-Butyl Alcohol on Toluene.*—The liquid, b. p. 192° (cf. Welsh and Hennion, *J. Amer. Chem. Soc.*, 1941, **63**, 2603), was *p-sec.*-butyltoluene, which was oxidized in the usual way to terephthalic acid. Its mononitro-derivative had b. p. 110—112°/3 mm. and the corresponding amine 100—102°. The benzoyl derivative, presumably 2-*benzamido*-4-sec.-*butyltoluene*, crystallized from alcohol in colourless needles, m. p. 139—140° (Found: C, 80·5; H, 8·0; N, 5·0. $C_{18}H_{21}ON$ requires C, 80·9; H, 7·9; N, 5·2%), depressed on admixture with 2-benzamido-4-*tert.*-butyltoluene.

Action of iso*Propyl Alcohol on Benzene.*—The product consisted of *iso*propylbenzene (cumene), b. p. 152° (cf. Potts and Carpenter, *loc. cit.*), together with a very small quantity of a higher-boiling fraction. The 4-sulphonamide, colourless plates, had m. p. 105—106° (cf. Huntress and Autenrieth, *loc. cit.*).

Action of iso*Propyl Alcohol on Toluene.*—The sole product was *p*-cymene, b. p. 177°, oxidized to terephthalic acid. 2-Methyl-5-*iso*propylacetanilide was prepared as colourless plates, m. p. 71° (cf. Goldschmidt, *Ber.*, 1893, **26**, 2086).

Action of iso*Propyl Alcohol on Anisole.*—The product collected at 200—230° was divided into alkali-soluble and alkali-insoluble portions. The former yielded *p-iso*propylphenol, b. p. 228° (cf. Huston *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 899) [benzoate, colourless plates, m. p. 71° (Tsukervanik and Nazarova, *J. Gen. Chem. Russia*, 1937, **7**, 623; Huston *et al.*, *loc. cit.*)]; the latter consisted almost completely of *p-iso*propylanisole, b. p. 213° (cf. Klages, *Ber.*, 1904, **37**, 3996).

Action of iso*Butyl Alcohol on Toluene.*—The product contained mainly *p-tert.*-butyltoluene, identified as described above. In addition some *p-iso*butyltoluene appeared to be present; oxidation gave some terephthalic acid, which was not formed from the former hydrocarbon under the same conditions.

Action of iso*Butyl Alcohol on Anisole.*—The resultant oil was shaken with 5% sodium hydroxide solution, and the insoluble portion taken up in ether, from which *p-tert.*-butylanisole, identified as already described, was obtained. The portion soluble in alkali was almost all *p-tert.*-butylphenol, white needles (from light petroleum), m. p. 97—98° [benzoate, m. p. 79—80° (cf. Henry and Sharp, *J.*, 1926, 2434)]. Nitration yielded bright yellow needles, m. p. 94°. Studer (*Ber.*, 1881, **14**, 1474) gives 93° and Henry and Sharp 97—98° as the m. p. of 4-*tert.*-butyl-2 : 6-dinitrophenol.

Treatment of *p-tert.*-butylphenol (1 g.) in acetic acid (8 c.c.) with nitric acid (*d* 1·42; 8 c.c.) at 0°, followed by heating to 80° for 1 hr., gave picric acid as sole product (cf. Jedlicka, *J. prakt. Chem.*, 1893, **48**, 98).

Action of 2-*Methylbut*-2-*ene on Benzene.*—*tert.*-Amyl and *p*-di-*tert.*-amylbenzene were formed and identified as described above.

Action of 2-*Methylbut*-2-*ene on Toluene.*—In addition to the main product, *p-tert.*-amyltoluene, b. p. 212—214°, a small amount of a product, b. p. 262—266°, which was probably *p*-di-*tert.*-amylbenzene (cf. Simons and Archer, *J. Amer. Chem. Soc.*, 1940, **62**, 1623) was isolated.

Action of 2-*Methylbut*-2-*ene on Anisole.*—*p-tert.*-Amylanisole was the chief product, but a small quantity of material, boiling above 250°, was also obtained.

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