77. *Chlorination of Toluene in Presence of* (a) *Activated Charcoals and* (b) *Iron-impregnated Silica Gel. Production of Side-chain Substitution, Nuclear Substitution, and Tolan Derivatives.*

By JAMES B. FIRTH and TREVOR A. SMITH.

THE chlorination of boiling toluene in the dark and in presence of catalysts has been investigated. Two types of catalyst were used: (*a*) activated and impregnated charcoal, (*b*) silica gels containing a small amount of iron.

From the results obtained (see table), the presence of activated sugar charcoal accelerates the formation and increases the yield of side-chain substitution products. The activity in this respect appears to be slightly increased by previous sorption of iodine. With blood charcoal, the catalytic effect is much greater, the chlorination of the side chain being practically complete after 8 hours (No. 6); and chlorination for **16** hours gives rise to 2 : 2′-*dichlorotolan dichloride*. The formation of this compound is probably due to the chlorination of benzotrichloride to *o*-chlorobenzotrichloride, which under the influence of the catalyst condenses to form 2 : 2′-dichlorotolan tetrachloride; this on distillation decomposes with the formation of dichlorotolan dichloride.

The activity of the catalyst deteriorates on "activating" at higher temperatures. The introduction of iron into sugar carbon does not materially affect the catalytic activity.

Iron-impregnated silica gel induces nuclear substitution. It also induces condensation, with the result that, when the time of chlorination exceeds about 3 hours, the product includes tarry matter, the amount increasing with the duration of chlorination.

In the experiments with iron-impregnated silica gel as catalyst, glue-like products were obtained, probably owing to condensation of simpler chlorination products. In order to test this view the action of the catalyst alone on benzyl chloride was tried; after a lag of 2—3 minutes a violent reaction occurred, and dense clouds of hydrogen chloride were evolved. The reaction appeared to be complete in about 1 minute. The product was a reddish-brown glue with a blue fluorescence. The reaction was brought under control by dissolving the benzyl chloride in half its weight of light petroleum. The glue-like product was soluble in petroleum, acetone, benzene, and chloroform, all the solutions being highly fluorescent; but from them and many other solvents tried, a glue invariably resulted; no crystalline product could be obtained.

EXPERIMENTAL.

Preparation of Catalysts.—Series (a). *Sugar charcoal* was prepared by carbonising cane sugar, the resulting carbon being finely ground, washed with hot water, and dried at 100°.

Iodised sugar charcoal. Sugar charcoal was treated with $N/10$-iodine in chloroform for 24 hours, separated by filtration, gently warmed to remove most of the iodine, washed with alcoholic caustic potash and then with water, and dried at 100° (cf. Firth and Watson, J., 1923, **123**, 1219).

Blood charcoal. " Mercks " blood charcoal, which contained 0·24% of iron, was used.

" *Artificial* " *blood charcoal* was prepared by adding a solution of ferrous oxalate to a concentrated solution of cane sugar, followed by excess of aqueous ammonia; the liquid was evaporated to dryness and the residue was carbonised at as low a temperature as possible, washed with water, and dried at 100°.

Series (b). *Silica gel impregnated with iron.* 20 G. of ferric chloride were dissolved in 100 c.c. of hydrochloric acid (*d* 1·140) and 100 c.c. of sodium silicate solution (*d* 1·156) were slowly added with vigorous stirring to prevent local precipitation. In about ½ hour, the mixed solutions set to a firm clear gel. This was broken up and dried on a water-bath; sodium chloride which crystallised on the surface was removed from time to time by washing with water, this treatment being continued until there was no appreciable separation of salt (about 3 days). The product was thoroughly washed, dried by gradual heating to 200°, ground, again washed, and dried at 200°. The activity of the catalyst was liable to vary over quite a wide range, and in order to obtain concordant results the above procedure should be carried out as quickly as possible. The activity of the catalyst was considerably diminished (1) when the preliminary removal of sodium chloride was carried out by rapid heating to a relatively high temperature, and (2) after several days' storage. The average iron content of the final gel was 3·5 ± 0·5%. The portion of catalyst to be used in an experiment was activated by heating in a vacuum at the required temperature.

Chlorination.—Toluene was chlorinated in the dark at its boiling point in presence of a known weight of catalyst for a definite period. The weight, volume, and density of the product were determined. It was then steam-distilled; in some experiments, benzoic acid separated. The dried distillate was fractionated several times; the fraction collecting up to 180° was weighed, and its density determined. This fraction contained unchanged toluene, *o*- and *p*-chlorotoluenes, benzyl chloride, and, in some experiments, benzaldehyde. The benzyl chloride was determined by boiling a known weight of the distillate with alcohol and solid silver nitrate and weighing the silver chloride produced (cf. Silberrad, Silberrad, and Parke, J., 1925, **127**, 1726). The other constituents were determined by the method of Cohen, Dawson, Blockley, and Woodmansey (J., 1910, **97**, 1623).

In some experiments benzylidene chloride was a product (benzaldehyde obtained on steam-distillation). In these experiments the steam distillate was divided into two fractions, (*a*) up to 120° (unchanged toluene), (*b*) 120—185° (chlorinated products). The composition of (*b*) was determined as before, the density of benzaldehyde being substituted for that of toluene in the formula. A summary of typical results is set forth in the following tables.

The dark-coloured, neutral, high-boiling product obtained in experiment 10 probably contained cis- and trans-2 : 2'-*dichlorotolan dichloride*, since on fractional distillation and recrystallisation from acetone, the fraction, b. p. *ca.* 220°/30 mm., yielded about 7 g. of yellow crystalline substance. The first crop had m. p. 170°, and the last m. p. 139°. The different crops gave similar analytical results and were therefore probably isomeric forms of the same substance (Found: C, 53·4; H, 2·5; Cl, 43·4. $C_{14}H_8Cl_4$ require C, 52·8; H, 2·5; Cl, 44·7%). Boiling with pyridine furnished a compound (yellow needles) having the m. p. of 2 : 2'-dichlorotolan.

Series (*a*). Activated Charcoals. 100 G. of Toluene in each Experiment.

			Fractionated product.						
No.	Catalyst and temp. of activation.	Hours of chlorination.	W., g.	*d.*	Benzyl chloride, %.	Chloro-toluenes, %.	Toluene, %.	Benzal-dehyde, %.	Benzoic acid, g.
1	Nil	8	76	1·050	42	37	21	—	—
2	1 G. sugar charcoal, 600°	8	82	1·087	73	24	3	—	—
3	1 G. sugar charcoal, iodised, 600°	8	87	1·085	90	8	2	—	—
4	1 G. sugar charcoal, 900°	8	61	1·082	89	5	6	—	—
5	1 G. sugar charcoal, iodised, 900°	8	80·5	1·081	88·5	4·5	7	—	—
6	Blood charcoal, 600°	8	—	—	—	—	—	—	126
7	,, ,,	4	9·0	1·068	87	3	8	2	nil
8	,, ,, 800°	8	35·5	1·077	30	7	7	56	32
9	,, ,, 900°	8	70	1·074	68	22	10	—	nil
10	,, ,, 600°	16	—	—	—	—	—	—	33
11	Artificial blood charcoal, 600°	8	98	1·086	81	11	8	—	nil

Series (*b*). Iron-impregnated Silica Gel. 100 G. of Toluene in each Experiment.

1	1 G., 600° for 2 hours	4	64	0·998	trace	63	37
2	1 G., 120° for 12 hours	4	64	1·053	nil	89	11
3	1 G., 600° for 2 hours	8	49	1·035	19·5	61	19·5
4	2 G., 600° for 2 hours	8	(Crude product, black brittle solid)				

In series (*b*), a brown glue remained after steam-distillation, the amount being greater in experiment 3 than in 1 and 2. This glue, distilled under 12·15 mm., gave a pale yellow fraction, b. p. 210—220°. Chlorine was given off and a carbonaceous residue remained. The distillate became semi-solid on cooling, and on recrystallisation from alcohol–acetone (1 : 3) deposited yellow crystals, m. p. 145° [Found : (i) C, 67·2; H, 4·1; Cl, 28·4; (ii) C, 67·6; H, 4·0; Cl, 28·5. $C_{14}H_{10}Cl_2$ requires C, 67·5; H, 4·0; Cl, 28·5%] (cf. Onufrowicz, *Ber.*, 1884, **17**, 883).

Experiment 4 [series (*b*)]. Repeated extraction with acetone yielded a glue, from which no pure crystalline product could be isolated. Another portion, distilled at 2 mm., gave off chlorine, leaving a carbonaceous residue. A few drops of yellow liquid distilled at 300—340°, which set to a hard glue. Several solvents were tried, but no pure crystalline product could be obtained. To reduce glue formation, experiment 3 [series (*b*)] was repeated, the time of chlorination being reduced to 3 hours. The product on distillation yielded a fraction, b. p. 230—260°, from which a white solid deposited on cooling; recrystallised from acetone, this gave needles, m. p. 82°, b. p. 230°/715 mm. On boiling with alcoholic silver nitrate, no turbidity was produced, showing the absence of side-chain substitution products [Found : (i) C, 43·0; H, 2·1; Cl, 54·9; (ii) C, 42·85; H, 2·6; Cl, 54·55. Calc. for $C_7H_5Cl_3$: C, 43·0; H, 2·6; Cl, 54·5%].

In three experiments in which portions of the same catalyst material were used (*a*) as soon as possible after preparation, (*b*) after 14 days, (*c*) after 28 days, the yields of this product were 38 g., 28 g., and 14·5 g., respectively. From the above data it was concluded that the product was probably 2 : 4 : 5-trichlorotoluene (cf. Seelig, *Annalen*, 1897, **237**, 129).

University College, Nottingham.

[*Received, December* 31*st*, 1935.]