Heterogeneous Reactions of Copper(II) Chloride with Toluene, *p*-Xylene, and Mesitylene

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Treatment of boiling toluene with copper(II) chloride yields a mixture of phenyltolylmethanes, and not bibenzyl as previously reported. Similar treatment of *p*-xylene gives 4-tolyl-2,5-xylylmethane and 2-chloro-*p*-xylene, and mesitylene yields 2-chloromesitylene. The decomposition of copper(II) chloride obeys first-order kinetics. The reactions are interpreted in terms of formation of a radical cation by removal of an electron from the aromatic π-system.

KHARASCH and SOSMORSKY[1] found that copper salts were effective catalysts for the oxidative coupling of diphenylacetonitrile, but this method of dimerisation has not been successfully applied to less highly activated molecules. Nonhebel[2] reported that, when toluene was heated under reflux in the presence of copper(II) chloride, hydrogen chloride was evolved and bibenzyl was formed.

Nonhebel did not isolate the bibenzyl, but identified the compound by gas chromatography. He also studied reactions of 9-alkoxy(or acyloxy)-10-methylanthracenes with copper(II) chloride to give diarylethanes, which were isolated.[3] Since copper(II) chloride can be regenerated from hydrogen chloride and copper(I) chloride by the action of air,[4] numerous catalytic dimerisations appeared possible, in which benzylic hydrogen atoms would be eliminated. We therefore attempted to repeat and extend Nonhebel's work with toluene.

EXPERIMENTAL

Materials.—Copper(II) chloride was dried at 120° for 24 hr. Hydrocarbons were dried over sodium. 2-Chloromesitylene was prepared by treatment of mesitylene with iron(III) chloride.[5]

General Procedure.—A mixture of copper(II) chloride and the hydrocarbon (500 g.) was heated under reflux. The system was swept with nitrogen, the effluent gases were passed through water, and the hydrogen chloride formed was estimated titrimetrically. Organic products were estimated by gas chromatography (2 m. column of 10% Apiezon L on Embacel). The copper contents of the inorganic residues were determined by atomic absorptiometry.

Autoclave Reactions.—Reactions of copper(II) chloride with toluene and *p*-xylene were carried out at 200°, under autogenous pressures, in an enamel-lined autoclave.

RESULTS

The organic products of the mesitylene reaction and of the autoclave reactions were filtered from the inorganic residues, isolated by fractional distillation, and identified as follows.

Toluene. After removal of unchanged toluene, a fraction (5 g.), b.p. 110°/2 mm., was collected; M^+ 182, τ 3·1 (9H, m, aromatic), 6·3 (2H, s, CH_2Ar_2), and 8·0 (3H, d, CH_3Ar). This fraction showed a single peak on g.l.c. which could be cleanly resolved from added bibenzyl. Comparison with standard i.r. spectra[6] confirmed that the fraction was a mixture of phenyltolymethanes, and absorption in the region 700—800 cm.$^{-1}$ indicated an approximate $o:p:m$ ratio of 4 : 1 : 0. The doublet in the n.m.r. spectrum at τ 8·0 is in agreement with this.

p-*Xylene.* Unchanged *p*-xylene was removed and a fraction (5 g.) was collected, b.p. 184°, i.r., n.m.r., and mass spectra identical with those of authentic 2-chloro-*p*-xylene. A further fraction (20 g.) was collected, b.p. 158°/5 mm., M^+ 210, τ 3·2 (7H, m, aromatic), 6·3 (2H, s, CH_2Ar_2), 8·0 (9H, m, CH_3Ar). This fraction was cleanly resolved by g.l.c. from added 1,2-bis-(*p*-tolyl)ethane.[7]

Mesitylene. A fraction (30 g.) was collected (b.p. 112°/10 mm.), the i.r., n.m.r., and mass spectra of which were identical to those of authentic 2-chloromesitylene.

The products isolated from the autoclave reactions served as standards for identifying (by combined g.l.c. and mass spectrometry) and estimating (by g.l.c.) the products of the atmospheric pressure reactions.

The results are shown in the Table. The rate of evolution of hydrogen chloride, during reactions performed at atmospheric pressure, obeyed first-order kinetics and rate constants (k) for the decomposition of copper(II) chloride, based on hydrogen chloride evolution, are tabulated. The overall decomposition of copper(II) chloride was also calculated from the copper contents of the inorganic residues. This method was not applicable to the atmospheric pressure toluene reaction, when only a very low conversion was achieved. For the atmospheric pressure *p*-xylene reaction, however, the final conversion of copper(II) chloride, indicated by the copper content of the inorganic residue, corresponded closely with the total hydrogen chloride evolved. This is as expected since the major organic product (*ca.* 80%) was non-chlorinated. Following this observation, the tabulated rate constants for the autoclave reactions were each calculated from the copper contents of residues formed in three reactions of evenly spaced durations. In the mesitylene reaction, half the chlorine lost from the copper chloride appeared in hydrogen chloride and nearly all the remainder in 2-chloromesitylene.

DISCUSSION

Since the decomposition of copper(II) chloride, during reactions at atmospheric pressure, obeyed first-order kinetics, the retardation by copper(I) chloride, observed in solution,[8] does not occur in these heterogeneous

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[1] M. S. Kharasch and G. Sosmorsky, *Tetrahedron*, 1958, **3**, 97.

[2] D. C. Nonhebel, *J. Chem. Soc.*, 1963, 1216.

[3] A. D. Mosnaim, D. C. Nonhebel, and J. A. Russell, *Tetrahedron*, 1970, **26**, 1123.

[4] H. Nord, *Acta Chem. Scand.*, 1955, **9**, 430.

[5] P. Kovacic and C. Wu, *J. Org. Chem.*, 1961, **26**, 759.

[6] The Sadtler Standard Spectra, Midget Edition, Prism Collection, Heyden and Son Ltd., London.

[7] C. Moritz and R. Wolffenstein, *Ber.*, 1899, **34**, 3531.

[8] A. Lorenzini and C. Walling, *J. Org. Chem.*, 1967, **32**, 4008.

Hydrocarbon	PhMe		$C_6H_3Me_3$
Molar ratio of hydrocarbon to $CuCl_2$	20	10	20
T (°C)	110	200	165
Reaction period (hr.)	240	18	96
Conversion of $CuCl_2$ (%)	0·37 *	23 †	48 * 95 †
10^5k (sec.$^{-1}$)	0·0006	0·40	9·2
Product yield (%) ‡	$PhCH_2 \cdot C_6H_4Me$		$ClC_6H_2Me_3$
	90	90	90

Hydrocarbon	p-MeC_6H_4Me	
Molar ratio of hydrocarbon to $CuCl_2$	20	10
T (°C)	137	200
Reaction period (hr.)	168	18
Conversion of $CuCl_2$ (%)	16 * 18 †	64 †
10^5k (sec.$^{-1}$)	0·029	1·7
Product yield (%) ‡	$MeC_6H_4 \cdot CH_2 \cdot C_6H_3Me_2$	
	80	80
Product yield (%) ‡	ClC_6H_3Me	
	20	20

* Based on HCl evolved. † Based on copper content of residue. ‡ Based on $CuCl_2$ converted.

reactions. An Arrhenius plot of the data from the Table does not give a single straight line. The rate of decomposition of copper(II) chloride depends on the organic reactant and, at a given temperature, increases along the series toluene, *p*-xylene, mesitylene. This suggests that free chlorine atoms are not involved.

The apparent absence of phenyl-*m*-tolylmethane from the products of the toluene reaction is consistent with an electrophilic intermediate, and the temperature independence of the distribution of products from *p*-xylene suggests that nuclear chlorination and diarylmethane formation may involve a common, rate-determining step. A reasonable reaction sequence is shown in the Scheme. Side-chain chlorination and dimerisation can also be interpreted in terms of this scheme.

$$\mathrm{HArMe} \xrightarrow{CuCl_2} [\mathrm{HArMe}]^{+\cdot}$$

$$[\mathrm{HArMe}]^{+\cdot} \xrightarrow{CuCl_2} \mathrm{ClArMe}$$

$$[\mathrm{HArMe}]^{+\cdot} \xrightarrow{-H^+} \mathrm{HArCH_2^{\cdot}}$$

$$2\mathrm{HArCH_2^{\cdot}} \longrightarrow \mathrm{HArCH_2 \cdot CH_2ArH}$$

$$\mathrm{HArCH_2^{\cdot}} \xrightarrow{CuCl_2} \mathrm{HArCH_2^{+}} \text{ or } \mathrm{HArCH_2Cl}$$

$$\mathrm{HArCH_2^{+}} \xrightarrow[-H^+]{HArMe} \mathrm{HArCH_2 \cdot ArMe}$$

SCHEME

$Ar = \cdot C_6H_4\cdot, \cdot C_6H_3Me\cdot, \text{ or } \cdot C_6H_2(Me_2)\cdot.$

We propose a common, initial, rate-determining step, in which the aromatic molecule loses an electron from its π-system to form a radical cation, probably in intimate contact with the surface of the copper chloride. The cation either undergoes nuclear chlorination or loses a side-chain proton. Proton loss yields a radical which undergoes further oxidation or, if sufficiently stable, either dimerises or becomes chlorinated. Thus, toluene yields a benzyl radical which is further oxidised and phenyltolylmethane is formed. The more stable radicals produced from 9-methylanthracenes, however, are sufficiently long-lived to dimerise[3] or to undergo chlorination.[9] The observed increased in reactivity and in the degree of nuclear chlorination, along the series toluene, *p*-xylene, mesitylene, is as expected on the basis of the inductive effect of the methyl group. The activation entropies of the toluene and *p*-xylene reactions are of the order of −30 e.u. This indicates a distinctive orientation of the hydrocarbon molecule at the copper chloride surface during the initial, one-electron oxidation step.

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[9] S. Gibson, A. D. Mosnaim, D. C. Nonhebel, and J. A. Russell, *Tetrahedron*, 1969, **25**, 5047.