fractions. Microanalyses showed an increasing chlorine content with increasing boiling point, but apparently separation of chlorinated material from bimesityl was incomplete. The pale yellow solid (dichlorobimesityl?) obtained from the mesitylene–ferric chloride–bromobenzene reaction was recrystallized from ethanol as colorless needles, m.p. 130.5–131.5°.

Anal. Calcd. for $C_{18}H_{20}Cl_2$: C, 70.36; H, 6.56; Cl, 23.08. Found: C, 70.51; H, 6.64; Cl, 22.80.

Ferric chloride and pentamethylbenzene. The reaction of ferric chloride (0.25 mole) and pentamethylbenzene (0.5 mole) started at 20° but proceeded very slowly even at higher temperatures. The reaction mixture was kept at 20–50° for 2 hr., at 65–70° for another 2 hr., then treated with dilute hydrochloric acid, and filtered. The solid organic material was taken up in ether, leaving 4 g. of black, infusible solid. Distillation of the organic material gave an 83% recovery of pentamethylbenzene. Crystallization of the pot residue from cyclohexane yielded 4 g. of colorless crystals, m.p. 181.5–182°. The analytical sample melted at 182.5–183.5°.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.80; H, 10.20; mol. wt., 270. Found: C, 89.82; H, 10.14; mol. wt., 271.

The presence of a single nuclear hydrogen was indicated by the infrared spectrum. The NMR spectrum revealed the presence of the following types of hydrogen in the indicated ratio: nuclear/methylene/methyl = 1/2/28.

This compound was inert to bromine in glacial acetic acid at room temperature in the presence of aluminum chloride; pentamethylbenzene yielded bromopentamethylbenzene readily under the same conditions. An attempt at nitration failed to yield the desired derivative.

Synthesis of 2,2′,3,3′,4,4′,5,5′,6-nonamethyldiphenylmethane. In 150 ml. of carbon disulfide were dissolved 4.4 g. (0.022 mole) of pentamethylchloromethylbenzene, m.p. 81.5–83° (prepared[24] by the method of Aitken, Badger, and Cook[25]), and 3 g. (0.022 mole) of 1,2,3,4-tetramethylbenzene (95% pure, Chemicals Procurement Co.). After introduction of 0.1 g. of aluminum chloride at 26°, the reaction mixture was allowed to stand for 17 hr. with occasional stirring. The organic layer was separated after addition of water, dried, and distilled to remove the solvent. The residue consisted of 0.7 g. of yellow crystals and 2 g. of brown oil which solidified on standing. The yellow crystals were crystallized twice from cyclohexane yielding colorless crystals, m.p. 179–180°. A mixture melting point with the crystalline product from the pentamethylbenzene–ferric chloride reaction was 180–181°. Their infrared spectra were identical. Isolation of pure material from the 2 g.-portion by attempted crystallization from cyclohexane was not successful.

Ferric chloride and 1,2,4,5-tetrachlorobenzene. The reaction of ferric chloride (0.25 mole) and the tetrachlorobenzene (0.5 mole) began at 185°. After being maintained at 185–198° for 2 hr., the hot reaction mixture was poured into dilute hydrochloric acid with stirring. The organic material was triturated repeatedly with dilute hydrochloric acid, and then distilled to remove unchanged tetrachlorobenzene. The majority of the distillation residue was dissolved in hot glacial acetic acid. About 1 g. of insoluble, gray crystals remained which was crystallized from methanol–acetic acid, m.p. 218–221°; lit.[5] hexachlorobenzene, m.p. 226°. The addition of aqueous alcohol to the original glacial acetic acid solution gave 13 g. of crude pentachlorobenzene, m.p. 70–80°. Recrystallization from glacial acetic acid and then from ethanol yielded colorless needles, m.p. 86.5–87°; lit.[5] m.p. 86°.

Acknowledgment. We gratefully acknowledge the support of this work by the National Science Foundation.

CLEVELAND 6, OHIO

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[24] Prepared by C. E. Stephan.

[25] R. R. Aitken, G. M. Badger, and J. W. Cook, *J. Chem. Soc.*, 331 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Reaction of Ferric Chloride with Xylenes[1]

PETER KOVACIC AND CHISUNG WU

Received June 29, 1960

The course of the ferric chloride–xylene reaction has been investigated. *p*-Xylene yielded 2,5,2′,5′,4″-pentamethyltriphenylmethane (I), in addition to chloro-*p*-xylene, (*p*-methylbenzyl)-*p*-xylene (II) and di(*p*-xylyl)methane (III). 4-Chloro-*m*-xylene and 2,2′,4,4′-tetramethylbiphenyl were obtained from *m*-xylene. The principal product from *o*-xylene consisted of polymer, along with 4-chloro-*o*-xylene in low yield. Yields of chloroxylene were in the order, *m*- $\gg$ *o*- > *p*-xylene. Aluminum chloride in catalytic amounts promoted the chlorination reaction. Correlations are drawn between the nature of the products and structure of the aromatic reactant.

Studies of the reaction of ferric chloride with simple aromatic compounds, such as benzene, halobenzenes, and monoalkylbenzenes,[2–4] have shown that a number of competing reactions may occur: nuclear chlorination, side-chain attack leading to diphenylmethane-type compounds, disproportionation, and polymerization. Among the aromatic hydrocarbons, mesitylene is thus far unique in that biaryl formation also occurs.[5]

The present investigation was aimed at obtaining further insight into the relationship between mode of reaction and aromatic structure by extending the reaction scope to the xylenes.

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[1] Part VIII in the series, *Reactions of Metal Halides with Organic Compounds;* this paper is abstracted in part from the Ph.D. thesis of C. Wu, Case Institute of Technology, 1960.

[2] P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

[3] P. Kovacic, C. Wu, and R. W. Stewart, *J. Am. Chem. Soc.*, **82**, 1917 (1960).

[4] P. Kovacic and C. Wu, unpublished work.

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

TABLE I[a]

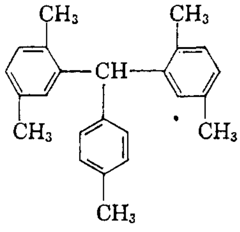
FERRIC CHLORIDE[b] AND XYLENES: EFFECT OF ALUMINUM CHLORIDE

					Chloroxylene		
Xylene	Moles	$AlCl_3$, mole	Time, hr.	Temp.	Yield, %	Isomer[c]	Residue,[d] g.
ortho	2	0	8	18–104	6	4-Cl	31
	2	0.02	6	27–128	59	4-Cl	12
meta	2	0	5.5	17–82	33	4-Cl	16
	2	0.02	3.5	47–71	77	4-Cl	3
para	1.6	0	6	14–100	<1	—	59
	2	0.02	7	11–78	32	2-Cl	28

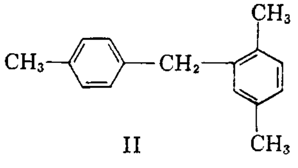
[a] R. W. Stewart, M. S. thesis, Case Institute of Technology, 1957, p. 28. [b] One mole. [c] Predominant isomer as indicated by infrared spectral analysis. [d] Residue from steam distillation of the reaction mixture; includes higher-boiling product and polymer.

RESULTS

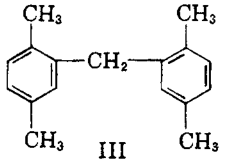
p-Xylene. The reaction of ferric chloride with *p*-xylene at 10–20° yielded 2,5,2′,5′,4″-pentamethyltriphenylmethane (I) as the main product, in addition to chloro-*p*-xylene, (*p*-methylbenzyl)-*p*-xylene (II), di(*p*-xylyl)methane (III), and polymeric material.



I



II



III

Structure I was assigned on the basis of elemental analysis, molecular weight, NMR spectrum, and comparison with identical material synthesized by condensation of *p*-tolualdehyde with *p*-xylene in the presence of concentrated sulfuric acid at room temperature. Before the structure of I was elucidated, unsuccessful attempts were made to prepare this compound by reaction of α-halo-*p*-xylene with either *p*-xylene or III.

Compounds II and III were identified by analysis, physical properties, infrared spectra and comparison with corresponding samples obtained from the Friedel-Crafts alkylation of *p*-xylene with α-halo-*p*-xylene. The identity of III was further confirmed by comparison with authentic samples obtained from other sources.[6]

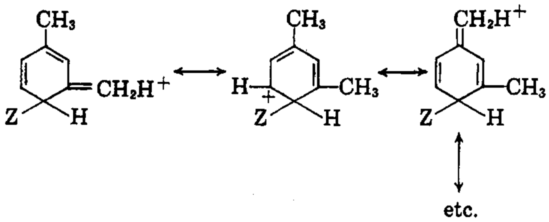
m-Xylene. From *m*-xylene and ferric chloride were obtained 23% of 4-chloro-*m*-xylene, 7% of 2,2′,4,4′-tetramethylbiphenyl and black, ether-soluble solid. The identity of 4-chloro-*m*-xylene was confirmed by oxidative conversion to 4-chloro-3-methylbenzoic acid, and the bi-*m*-xylyl by comparison with an authentic sample synthesized from 4-iodo-*m*-xylene by the Ullmann reaction.

o-Xylene. The *o*-xylene–ferric chloride reaction afforded only small quantities of 4-chloro-*o*-xylene and high-boiling oil in addition to a large amount of black, ether-soluble solid. 4-Chloro-*o*-xylene was identified by its infrared spectrum and by oxidation to 4-chloro-2-methylbenzoic acid.

Effect of aluminum chloride. Catalytic amounts of aluminum chloride increased the yield of chloroxylene in all cases and decreased the amount of higher molecular weight material (Table I). The promoting action of aluminum chloride on aromatic chlorination by ferric chloride has been noted previously.[2]

DISCUSSION

Nuclear chlorination. Less than 3% of chlorinated product was obtained from either *o*- or *p*-xylene whereas 23–33% yields were realized from *m*-xylene by the action of ferric chloride. This difference may be explained on the basis of hyperconjugative stabilization of the *m*-xylene–ferric chloride *sigma* complex which affords a more favorable energy level for the *meta* than for the other two isomers. The fact that mesitylene gave 28–30% yields of chloromesitylene[5] is in keeping with the above interpretation. A more favorable situation for side-chain attack with *o*- and *p*-xylene might also account for the low yields of their chloro derivatives.



(Z^+ = the attacking, electrophilic species)

Side-chain reaction. While some participation of the methyl group was observed[3] previously in the case of toluene and *p*-chlorotoluene, this type of

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(6) We are grateful to Dr. Louis Schmerling, Universal Oil Products Co., and Dr. B. S. Friedman, Sinclair Research Laboratories, for the samples of di(*p*-xylyl)methane.

reaction appears to be more predominant with *p*-xylene. The increased attack at the side-chain of *p*-xylene may be rationalized on the basis of hyperconjugative stabilization of a labile intermediate. The same interpretation can also be used for *o*-xylene provided the polymer, which constitutes the principal product, arises from side-chain involvement.

Formation of I from *p*-xylene is the first case in which a triphenylmethane-type compound has been isolated from the reaction of ferric chloride with alkylbenzenes. It is reasonable to designate II as a precursor in this reaction. (*p*-Methylbenzyl)-*p*-xylene (II) and di(*p*-xylyl)methane (III) have been reported[7,8] previously as products from alkylation of *p*-xylene. Schmerling and co-workers proposed[8] a reasonable mechanism for formation of II and III from certain alkyl halides and *p*-xylene in the presence of a Friedel-Crafts catalyst.

Biaryl formation. Biaryls have been identified as products from the reaction of ferric chloride with phenols[9] and naphthols.[10] Dichlorobinaphthyl (undetermined structure) is said[2] to arise from 1-chloronaphthalene. The discussion on biaryl formation from mesitylene[5] may also be applied with appropriate modifications to the case of bi-*m*-xylyl from *m*-xylene. The increase in yield of biaryl-type product in the order, toluene < *m*-xylene < mesitylene, correlates with the corresponding increase in steric factors associated with the aromatic reactant. On the other hand, the same type of correlation may be made in relation to basicity and the opportunity for hyperconjugative stabilization of an intermediate *sigma*-complex.

EXPERIMENTAL[11]

Materials. Reagent grade xylenes (99 mole % min. purity, Phillips Petroleum Co.) were used directly. α-Bromo-*p*-xylene and *p*-tolualdehyde were from Eastman Organic Chemicals, and α-chloro-*p*-xylene was from K & K Laboratories. Matheson Coleman and Bell ferric chloride, reagent, sublimed powder, was used.

General procedure. Ferric chloride (1 mole) was added to the xylene (2 moles) with cooling in an ice bath. After completion of the reaction, the reaction mixture was worked up as previously described.[3]

Ferric chloride and p-xylene. Ferric chloride and *p*-xylene were allowed to react at 10–20° for 3 hr. Distillation through a 12-in. helix-packed column gave a forerun fraction consisting of recovered *p*-xylene (1.2 moles), b.p. 135–137°. The second fraction, b.p. 179–180°, wt. 0.6 g. (1%), had an infrared spectrum identical with that of authentic chloro-*p*-xylene (Matheson Coleman & Bell).

The third fraction, b.p. 125–126° (1.33 mm.), b.p. 300° (743 mm., test tube), consisted of a colorless oil (3 g.), n_D^{20} 1.5655; lit.[7] for 2-(*p*-methylbenzyl)-*p*-xylene (II) of questioned purity, b.p. 302–308°, n_D^{20} 1.5491–1.5620. The infrared spectrum was identical with that of II synthesized by the Friedel-Crafts method (α-halo-*p*-xylene and *p*-xylene) and slightly different from that[12] of Friedman's sample.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63; mol. wt., 210. Found: C, 91.08; H, 8.54; mol. wt., 204.

The fourth fraction was collected at 140–150° (0.6 mm.) as a colorless oil (3 g.) which solidified on standing. Crystallization from ethanol afforded colorless needles of di(*p*-xylyl)methane (III), m.p. 63–64°, b.p. 310° (747 mm., test tube); lit.[8] m.p. 64–64.8°, b.p. 320° (760 mm., extrapolated). The mixture melting points with Schmerling's sample[8] and with Friedman's sample[7] were undepressed. In addition, the infrared spectra of all samples in carbon disulfide were identical.

The tarry residue from fractionation was distilled through a one-plate column *in vacuo*. There was obtained 25 g. of viscous, yellow oil which partly solidified on standing. The distillation residue consisted of 19 g. of brown, amorphous solid which gave a negative test for chlorine. Trituration of the yellow semi-solid with ethanol gave 14 g. of solid from which colorless crystals (I), m.p. 111.5–112°, were obtained on crystallization from ethanol. The NMR spectrum revealed the presence of the following types of hydrogen in the indicated ratio: tertiary:nuclear:primary = 1:10:15.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.67; H, 8.33; mol. wt., 314. Found: C, 91.59; H, 8.40; mol. wt., 315.

Oxidation with chromic anhydride in acetic acid gave only a trace amount of acidic product which remained unmelted at 300°, and no neutral material.

2,5,2',5',4''-Pentamethyltriphenylmethane.[13] The method was adapted from the procedure[14] used by Kliegl for the preparation of di-*p*-tolylphenylmethane.

A mixture of *p*-xylene (170 g., 1.6 moles), *p*-tolualdehyde (48 g., 0.4 mole), and concentrated sulfuric acid (60 g.) was shaken by machine in a stoppered flask under nitrogen for 40 hrs. at room temperature. After the addition of 50 ml. of ether and 200 ml. of water, the organic layer was separated, washed repeatedly with dilute sodium hydroxide solution and then with water, and dried. Removal of unchanged *p*-xylene and *p*-tolualdehyde by distillation gave a viscous, dark brown, oily residue which contained some white crystals. Short-path distillation of the residue at 1 mm. yielded a distillate (4.2 g.) consisting of white solid and pale yellow semi-solid. Two crystallizations from ethanol gave white crystalline solid, m.p. 109.5–111°. A mixture melting point with the corresponding *p*-xylene–ferric chloride product, m.p. 110–111.5° showed no depression. The infrared spectra of the two samples were identical.

p-Xylene and α-halo-p-xylene. (a). To a mixture of α-bromo-*p*-xylene (18.5 g., 0.1 mole) and *p*-xylene (47.7 g., 0.45 mole) was added portionwise 3.2 g. (0.02 mole) of ferric chloride during 30 min. with shaking in a water bath (5 ± 3°). After an additional 0.5 hr. of stirring at the same temperature range, the reaction mixture was extracted with water. Fractionation of the organic material yielded 6 g. of II, b.p. 109–110° (0.25 mm.), b.p. 127° (1.3 mm.), n_D^{21} 1.5654; 7 g. of III, m.p. 63.5–64°, b.p. 130–132° (0.25 mm.); 4 g. of yellow, viscous semisolid, b.p. 186° (0.2 mm.) which crystallized as colorless needles from ethanol, m.p. 156–157°.

Anal. Found: C, 91.41; H, 8.72.

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(7) B. S. Friedman, F. L. Morritz, C. J. Morrissey, and R. Koncos, *J. Am. Chem. Soc.*, **80**, 5867 (1958).

(8) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **81**, 2718 (1959).

(9) (a) K. Bowden and C. H. Reece, *J. Chem. Soc.*, 2249 (1950); (b) R. Majima and G. Takayama, *Ber.*, **53**, 1907 (1920).

(10) (a) I. S. Ioffe and B. K. Krichevtsov, *J. Gen. Chem. (U.S.S.R.)*, **9**, 1136 (1939), and earlier papers in the series, *Biaryls and Their Derivatives;* (b) C. N. Ionescu and A. Bardeanu, *Bul. soc. chim. România*, **17**, 297 (1935).

(11) Boiling points and melting points are uncorrected. Microanalyses were determined by Drs. Weiler and Strauss, Oxford, England, and the NMR spectrum by Dr. L. F. Johnson, Varian Associates, Palo Alto, Calif. Molecular weights were determined by the Rast method.

(12) Thanks are due to Dr. B. S. Friedman for providing the infrared spectrum of this material.

(13) Prepared by F. W. Koch.

(14) A. Kliegl, *Ber.*, **38**, 84 (1905).

The distillation residue consisted of a brown, viscous semisolid.

(b). *α*-Chloro-*p*-xylene (29 g., 0.2 mole) was added dropwise during 1 hr. to a mixture of *p*-xylene (10.6 g., 0.1 mole), carbon disulfide (100 ml.), and aluminum chloride (1.3 g., 0.01 mole) at room temperature. After completion of the addition, the reaction mixture was stirred for 2 hr. and worked up in the usual manner. Fractionation of the organic material yielded 1.3 g. of *p*-xylene, b.p. 55–57° (47 mm.), 5 g. of II, b.p. 127° (1.3 mm.), n_D^{20} 1.5654, and 5 g. of a yellow, viscous oil, b.p. 167–168° (0.5 mm.) which slowly crystallized on standing, m.p. 118–119° (from ethanol). The infrared spectrum was different from that of the solid, m.p. 111.5–112° from the *p*-xylene–ferric chloride reaction. The distillation residue (14.4 g.) was a brown, sticky semisolid.

Di(p-xylyl)methane and α-chloro-p-xylene. To a carbon disulfide (20 ml.) solution of III (0.9 g., 4 mmoles) was added 50 mg. of aluminum chloride and then 0.5 g. (4 mmoles) of *α*-chloro-*p*-xylene dropwise at room temperature. The reaction was allowed to continue at room temperature for 1 hr. After addition of water, the organic layer, containing suspended yellow solid, was separated and the solvent removed by evaporation. The yellow residue was extracted with hot methanol leaving 0.2 g. of highly insoluble (ether, carbon disulfide, chloroform), pale yellow solid which did not melt at 320°. From the methanol extract was recovered 0.25 g. of crude III, m.p. 54–56°.

Ferric chloride and o-xylene. The reaction, carried out at 20–30° for 5 hr., yielded 2.2 g. (3%) of 4-chloro-*o*-xylene, 2 g. of brown, high-boiling oil, and 24 g. of coal-like solid which did not contain chlorine. The 4-chloro-*o*-xylene, b.p. 192.5°, n_D^{20} 1.5226 (lit.[15] b.p. 191.5°) was characterized[16] by its infrared spectrum and oxidative derivative, 4-chloro-2-methylbenzoic acid, m.p. 169.5–170°; lit.[17] m.p. 171°.

Ferric chloride and m-xylene. Following the occurrence of an energetic reaction at 17°, the temperature was held at 26° for 1 hr. After the work-up, distillation of the product yielded 16 g. (23%) of 4-chloro-*m*-xylene, b.p. 186–187° (745 mm.), n_D^{20} 1.5226; lit.[18,19] b.p. 186.5° (767 mm.), n_D^{25} 1.5230. The infrared spectrum showed typical absorption bands for 1,2,4-substitution. Oxidation[16] with chromic anhydride in acetic acid gave 4-chloro-3-methylbenzoic acid, m.p. 208–209°; lit.[18] m.p. 209–210°.

A colorless liquid, wt. 8 g. (7.6%), b.p. 122–123° (1.1 mm.), b.p. 292° (746 mm., test tube), n_D^{20} 1.5651, d^{20} 0.9686, was also obtained. Upon cooling in the refrigerator overnight, it solidified to colorless crystals, m.p. 35–38°. The melting point was increased to 39–40° after two crystallizations from methanol.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63, mol. wt., 210. Found: C, 91.33; H, 8.42; mol. wt., 205.

The mixture melting point with authentic 2,2′,4,4′-tetramethylbiphenyl showed no depression, and the infrared spectra of the two samples were identical.

Treatment with 2:1 sulfuric acid–nitric acid yielded a tetranitro derivative, pale yellow crystals, m.p. 139–140° from chloroform.

Anal. Calcd. for $C_{16}H_{14}N_4O_8$: N, 14.35. Found: N, 14.42, 14.47.

The residue from fractional distillation was a black, amorphous solid (no chlorine), wt. 16 g.

2,2′,4,4′-Tetramethylbiphenyl. 4-Iodo-*m*-xylene was prepared as previously described.[20] After three distillations the product was obtained as a pale yellow liquid, b.p. 104° (10 mm.), b.p. 232° (745 mm.), $n_D^{16.5}$ 1.5990; lit.[21,22] b.p. 111° (14 mm.), b.p. 230° (742 mm.), $n_D^{16.3}$ 1.6008.

The method[21] of Ullmann and co-workers, involving specially treated[23] copper, was used for the conversion of 4-iodo-*m*-xylene to 2,2′,4,4′-tetramethylbiphenyl, m.p. 40–41° from methanol; lit.[21] m.p. 41°, b.p. 288° (722 mm.).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

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(15) A. Krüger, *Ber.*, **18**, 1755 (1885).

(16) Performed by F. J. Donat.

(17) F. Kunckell, *Ber.*, **41**, 2648 (1908).

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(20) R. L. Datta and N. R. Chatterjee, *J. Am. Chem. Soc.*, **39**, 435 (1917).

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(23) E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.*, **55**, 4219 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Reactions of Some Organic Compounds with Cupric Bromide

ARTHUR W. FORT

Received June 13, 1960

The reactions of isophorone, 3,4,5-trimethylanisole, 5,5-dimethylcyclohexane-1,3-dione and *β*-naphthol with cupric bromide in methanol or methanol-water are described.

The chlorination of acetone by cupric chloride has been described by Kochi,[1] who mentioned also the reactions of diethyl ketone and acetophenone with cupric chloride. That reactions of cupric halides with other active-hydrogen compounds might be unusual and have synthetic application seemed to be an attractive possibility, and experiments have been carried out using isophorone (I), 3,4,5-trimethylanisole (II), *β*-naphthol (III), and 5,5-dimethylcyclohexane-1,3-dione (IV) as active-hydrogen compounds.

Preliminary experiments with I in methanol showed that cupric bromide was a more active oxidizing agent than cupric chloride, and further work was limited to use of cupric bromide. All reactions reported below were carried out either in methanol or methanol-water.

Isophorone (I) reacted fairly slowly with cupric

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(1) J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).