

CHEMISTRY

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ABSTRACTS

Iodine Trichloride as a Chlorinating Agent. E. CAMPAIGNE and WAYNE E. THOMPSON, Indiana University.—This is a preliminary report, describing some remarkable results obtained when iodine trichloride is allowed to react with certain aliphatic and aromatic organic compounds, and tentatively suggesting a possible explanation of these results. Crystalline iodine trichloride reacts violently with an equimolar portion of benzene in carbon tetrachloride to produce 61% of the theoretical amount of o-dichlorobenzene, and only 9% of the expected monochlorobenzene. No p-dichlorobenzene was obtained. Even when a ten-fold excess of benzene was used, the principle product was o-dichlorobenzene. In addition, some pure 1,2,4,5-tetrachlorobenzene, uncontaminated by other tetrachloro-derivatives, was found, and also a small amount of hexachlorobenzene. Anisole reacted with iodine trichloride to give as the principle product 3,4-dichloroanisole. Butanoyl chloride yielded 2,3-dichlorobutanoyl chloride as the only chlorination product.

The stoichiometry of this reaction seems to be:



The abnormal products obtained in these studies can be explained by assuming that the attacking reagent holds two chlorine atoms rigidly at such a distance that each attacks an adjacent carbon atom simultaneously. This is probably brought about by the existence of a transitory unstable cyclic intermediate. We have tentatively termed this phenomenon "Simultaneous ortho-dichlorination", and propose that the attacking reagent is probably I_2Cl_6 . Experimental details and arguments for the mechanistic interpretation will be given.