subcutaneous and intravenous administration is approximately 450 mg./kg. More complete pharmacological investigations will be reported elsewhere. All preliminary tests indicate an enormous margin of safety and absence of serious side reactions in any but the highest doses.

When it is considered that the anhydrous sodium salt has the molecular weight of 422 as compared with the molecular weight of 172 for 2-methyl-1,4-naphthoquinone, the most active material (0.5 gamma) hitherto reported, it appears that this sodium salt represents probably the most active antihemorrhagic substance known when compared on a molecular basis with methylnaphthoquinone. It also encourages speculation as to whether the antihemorrhagic effects of 2-methyl-1,4-naphthoquinone, of its reduced form, and of like substances, are not mediated through a phosphoric ester.

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THE PHOTOCHEMICAL REACTIONS OF OXALYL CHLORIDE AND PHOSGENE WITH CYCLOHEXANE

Sir:

The occurrence of the hypothetical —COCl free radical has been postulated as an intermediate in certain photochemical reactions: notably in the formation of phosgene [Bodenstein, *et al.*, *Z. physik. Chem.*, **B3,** 459 (1929)] and in the photochemical decompositions of both phosgene and oxalyl chloride [Rollefson, *et al.*, THIS JOURNAL, **56,** 1089 (1934); **58,** 443 (1936)]. In line with the program under way in this Laboratory on chain reactions in solution involving atoms and free radicals, we have studied the photolysis of both phosgene and oxalyl chloride dissolved in cyclohexane. In both cases we have been able to isolate the acid chloride of cyclohexane carboxylic acid. The yields appear to be quantitative. The over-all reactions are

$$\begin{aligned} &C_6H_{12} + (COCl)_2 \longrightarrow C_6H_{11}COCl + HCl + CO \\ &C_6H_{12} + COCl_2 \longrightarrow C_6H_{11}COCl + HCl \end{aligned}$$

The following experiment with oxalyl chloride is typical of the procedure used. A 100-cc. flask (Pyrex glass) containing 25.2 g. of cyclohexane (0.3 m.) and 9.6 g. of oxalyl chloride (0.075 m.) was illuminated by a 300-watt tungsten lamp placed immediately below the flask. The heat from the lamp kept the reaction mixture refluxing gently. Gases were evolved. These were collected after passing through a trap at −80° and shown to consist of equal parts of carbon monoxide and hydrogen chloride. After twenty-four hours, the reaction mixture was fractionated and it was found that 4.2 g. of oxalyl chloride had reacted to form 4.1 g. of the acid chloride of cyclohexanecarboxylic acid (b. p. 99–101° at 52 mm.). The calculated yield is 4.8 g. The identification of the product was made by a determination of the neutralization equivalent and the preparation of the amide, m. p. 185–186°.

Phosgene reacts with cyclohexane in a similar manner. In this case quartz apparatus was used (a quartz reaction flask with a quartz mercury arc). In both cases the reaction takes place in the liquid phase as shown by identical results obtained in experiments in which care was taken to shield the vapor phase.

There can be little doubt that the reaction of phosgene and oxalyl chloride with cyclohexane in the light takes place through a free radical or atom mechanism in which the formation of the —COCl free radical plays a conspicuous rôle. In the gas phase the primary process in the photolysis of oxalyl chloride and phosgene has been postulated as follows

$$\begin{aligned} &(1) \quad COCl_2 \xrightarrow{h\nu} -COCl + Cl^- \\ &(2) \quad (COCl_2) \xrightarrow{h\nu} -COCOCl + Cl^- \\ &(\text{or } 2) \quad (COCl)_2 \xrightarrow{h\nu} 2\,-COCl \end{aligned}$$

In solution the absorption of light appears to be accompanied by the same primary step. This must be followed by reaction of the photolytic fragments with the hydrocarbon solvent. We hope to elaborate on the mechanism in our next publication.

The method of direct carboxylation appears to be fairly general and has been applied to a number of saturated hydrocarbons and their halogen derivatives. We are now engaged in studying the carboxylation of other types of organic compounds and the effect of various catalysts. It is of importance that means other than light of inducing the reaction have been found (*i. e.*, small quantities of organic peroxides are quite effective).

We are actively engaged in working out the details of this investigation and we hope to publish a full report shortly.

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