

removed quite easily without any appreciable destruction of the outer shape of the crystals but their optical properties are totally changed. It would thus seem to be a case of pseudomorphism. The true molecules may be written as $[(n-C_3H_7)_2N-C-SCu]_6$



The copper(I) dimethylthiocarbamate behaves in an analogous manner when recrystallized from chloroform. It also crystallizes with a third of a mole of solvent. The crystals are red but after removing the chloroform they become yellow.

The copper(I) dialkylthiocarbamates are now being investigated using X-rays and the research programme is continuing with these, together with the mercaptides and xanthates of copper, silver and gold. Preliminary results indicate the silver(I) *tert*-amylmercaptide to be built up from six simple units and the copper(I) *tert*-amylmercaptide from six or eight simple units.

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Studies on Peroxy Compounds XXV*. 2-Benzoyloxycyclohexanone-1

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A method for introducing the benzoyloxy group into a so-called active methylene compound as diethyl malonate is to react the sodium compound of diethyl malonate in benzene with benzoyl peroxide. Thereby the oxygen-oxygen bond of the peroxide is attacked by the nucleophile giving diethyl O-benzoyl-tartronate in high yields¹. Other active methylene compounds react in the same way (for pertinent references, see Lawesson *et al.*²)

Our interest in developing methods for the introduction of acyloxygroups into

organic molecules directed our attention to the enamine chemistry. Enamines may in many cases react as sodium derivatives of active methylene compounds³ and we now want to report that enamines in an inert solvent react smoothly with benzoyl peroxide. An enamine reacts as a nucleophilic agent attacking the oxygen-oxygen bond whereby the benzoyloxy group is introduced. After mild hydrolysis of the enamine, a new carbonyl compound is isolated with a benzoyloxy-grouping at the α -carbon. This novel method for the formation of carbon-oxygen bonds offers new synthetic routes to a wide variety of organic compounds and a broad investigation is under way to test this reaction both with enamines derived from simple aldehydes and ketones as well as from more complicated carbonyl compounds.

Experimental. 2-Benzoyloxycyclohexanone-1. In a three-necked flask, equipped with a mechanical stirrer, a reflux condenser and a dropping funnel, is placed 20 g (0.12 mole) of 1-morpholino-1-cyclohexene⁴ dissolved in 50 ml of anhydrous benzene. 24.2 g (0.1 mole) of recrystallized benzoyl peroxide dissolved in 175 ml of benzene, is added dropwise during 45 min to the enamine, cooled in ice-water to 0–4°C. After stirring for another 30 min, 40 ml of conc. hydrochloric acid and 40 ml of water are added and stirred at room temperature for one hour. The benzene layer is separated from the aqueous layer, and the organic phase is washed once with water. Then the organic phase is extracted twice with sodium hydroxide solution, washed neutral with water and dried over sodium sulphate. After the benzene and some cyclohexanone are distilled off, the residue solidifies and is recrystallized from ethanol to give colourless needles of 2-benzoyloxycyclohexanone-1, m.p. 86–87°C (Lit.⁵ m.p. 87°C). Yield 17 g (78 %). No attempts have yet been made to obtain optimal yields.

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