

author, these conditions may result in the production of some unsaponifiable matter. In the calculating procedure employed⁶, this again may give rise to a considerably higher content of eicosenoic acid than that actually present. No attempts were made to isolate and identify the acid.

Experimental. The kernels (16.1 g) from filbert nuts were extracted with ethyl ether for 8 h in a Soxhlet apparatus as described⁷; extraction was repeated until completeness (40 % oil). After saponification with ethanolic potassium hydroxide and acidification with sulphuric acid the fatty acids were isolated by extraction with ether and converted into methyl esters by refluxing with methanol containing a little sulphuric acid.

A Perkin-Elmer gas chromatograph (Fraktometer model 116 E), equipped with a katharometer detector and 4 mm-columns was used for the separation. Silicone elastomer (E 301) and silicone grease on Celite⁸ in 1 m and 2 m columns, respectively, were used as unpolar stationary phases. Reoplex 400 on Celite (in the ratio 1:5), in a 2 m column, served as the polar phase. Helium was used throughout as a carrier gas, and the sample size varied between 1 and 5 mg.

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Copper(I) N,N-Dialkylthiocarbamates

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In a previous paper¹ the author has discussed the N,N-dialkylthiocarbamates of copper, silver and gold. They have all turned out to be polymeric, in solution as well as in the solid state, and many of them have given evidence of possessing interesting structures².

In order to throw light on the unique properties of these compounds, the investigations have been extended to include thiocarbamates as well.

In Table 1 there is a summary of some data describing the copper(I) dialkylthiocarbamates investigated. In a previous paper³ Fredga has reported that the diethyl compound seems to be hexameric (molecular weight determination in chloroform) and the investigations of the author also indicate that most of these compounds are hexameric. However, some of them also seem to be tetrameric. The degree of polymerity, amongst other things, depends on the method of preparation.

Some of the compounds show, as do the corresponding dithiocarbamates, a pronounced tendency to crystallize with solvents. Thus the copper(I) dipropylthiocarbamate crystallizes with a third of a mole of acetone. The "crystal solvent" can be

Table 1. Data for the salts $[R_2N-CO-SCu]_n$. The molecular weight determinations are made cryoscopically in benzene.

R	m.p. °C	n	Cu calc.	Cu found
Methyl	220 (decomp.)		37.89	37.29
Ethyl	220 (decomp.)	6	32.46	32.43
Propyl	180–183	6	28.39	28.40
Butyl	131–133 ^a 120–122	6 and 4?	25.23	25.06
Isobutyl	230 d.	6	25.23	25.24
Isoamyl	166–171	6	22.70	22.67

^a Polymorphism?

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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