in CD_3OD at 60 Mc./sec τ-Values relative to internal tetramethylsilane are shown on the formulas. As required for a tricyclic indole derivative the n.m.r. signals show the presence of three aromatic protons, one of which is typical for the singlet of a proton in the α-position of 3-substituted indoles and tryptamines.[7] The other two aromatic protons form an AB quartet characteristic of 2 *ortho* protons($J_{6,7}$, 9 cps.).[8] Position 4 of the indole ring must therefore be substituted and formula IV is excluded.

The assignment of the upfield pair of the quartet to the signal from the C-6 proton follows from the shielding influence of the adjacent oxygen, and from the corresponding peaks in bufotenine which show both *ortho* ($J_{6,7}$, 9 cps.) and *meta* ($J_{4,6}$, 2 cps.) coupling.[9] The position of the singlet for two equivalent N-methyl groups changes from τ 7.70 in bufotenine (*cf.* $N_{(b)}$-methyltryptamines[7]) to 6.30 in dehydrobufotenine, a shift which agrees with their attachment to an anilinium-type nitrogen in III. Chemical shifts for methylene hydrogens are given at the center of bands in which the fine structure is obscured because of overlapping either with each other or with solvent and N-Me peaks. The comparative evaluation of the n.m.r. data of bufotenine with those of dehydrobufotenine fully support structure III, whose synthesis and biosynthesis are under investigation.

(7) L. A. Cohen, J. W. Daly, H. Kny and B. Witkop, *J. Am. Chem. Soc.*, **82**, 2184 (1960).

(8) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

(9) *para* coupling ($J_{4,7}$, 0.5 cps.) also was resolved in the signals from the protons on C-4 and C-7 in bufotenine.

(10) Visiting Associate of the USPHS.

NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH
BETHESDA 14, MD.
F. MÄRKI[10]
A. V. ROBERTSON[10]
B. WITKOP

RECEIVED JUNE 22, 1961

THE RELATIVE REACTIVITY OF THIOACYL AND SELENOACYL ANALOGS[1]

Sir:

The high reactivity of acyl derivatives of coenzyme A and of thiol esters in general has been attributed to polarization of the type R-C(=O)-SR[1] activating the carbon of the carbonyl group to attack by nucleophilic reagents.[2]

Since polarization increases in passing from carbamyl to thiocarbamyl to selenocarbamyl analogs,[3,4,5] it seemed likely that selenoacyl compounds should be more highly polarized and more reactive than their thioacyl analogs.

(1) This work was supported, in part, by a grant (CY-3937) from the United States Public Health Service.

(2) F. Lynen, *J. Cell. Comp. Physiol.*, **54**, suppl. 1, 33 (1959).

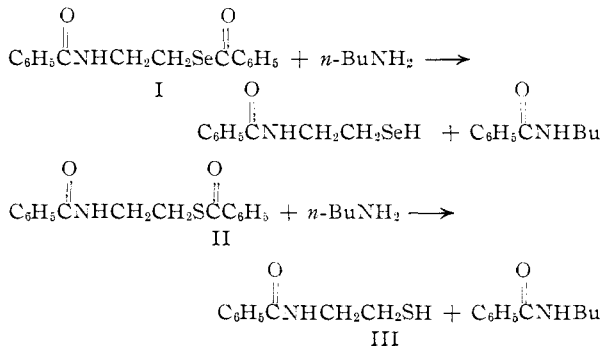
(3) H. G. Mautner and W. D. Kumler, *J. Am. Chem. Soc.*, **78**, 97 (1956).

(4) H. G. Mautner, *ibid.*, **78**, 5292 (1956).

(5) H. G. Mautner and E. M. Clayton, *ibid.*, **81**, 6270 (1959).

It was found that selenopantethine[6] could fully replace its sulfur analog in *Lactobacillus helveticus*,[7] a microörganism requiring preformed pantethine for growth. On the other hand, selenopantethine inhibits the utilization of pantethine[8] as a precursor of coenzyme A in a pigeon liver system.[9,10] These observations coupled with the recent finding that for certain animals selenium is an essential trace element,[11,12] and the claim[13] that selenocoenzyme A is formed when selenite is administered to rats, raised further interest in the relative reactivity of thioacyl and selenoacyl analogs.

To study transacylation rates this test system was used



N,Se-Dibenzoylselenocysteamine (I) was prepared by the reaction of benzoyl chloride with selenocysteamine and then recrystallized from 50% methanol. A yield of 90% of analytically pure, crystalline product melting at 99–100° was obtained.

Ultraviolet Spectrum.—Absolute ethanol: λ_{max} 240, 285, 305 mμ (inflect.); E_{max} 21,630, 5,520, 4,390.

The corresponding sulfur analog (II) was prepared by the method of Fry.[14] When N,Se-dibenzoylselenocysteamine (I) and N,S-dibenzoylcysteamine (II) were permitted to react with an excess of *n*-butylamine in ethanol, the selenium compound was found to react much more rapidly than its sulfur analog:

	Concn. acyl compound, M	Concn. amine, M	$k_{obs.}$, sec.$^{-1}$	Temp., °C.
Compd. I	8.76×10^{-5}	3.38×10^{-1}	2.73×10^{-3}	29.8
Compd. II	8.76×10^{-5}	3.38×10^{-1}	2.31×10^{-5}	29.8

The reaction rates were followed by observing the disappearance of the ultraviolet thiobenzoyl peak at 264 mμ or the selenobenzoyl peak at 285 mμ.

(6) W. H. H. Günther and H. G. Mautner, *ibid.*, **82**, 6270 (1960).

(7) H. G. Mautner and W. H. H. Günther, *Biochim. Biophys. Acta*, **36**, 561 (1959).

(8) H. G. Mautner and W. H. H. Günther, unpublished data.

(9) N. O. Kaplan and F. Lipmann, *J. Biol. Chem.*, **174**, 37 (1948).

(10) O. Brenner-Holzach, R. Adler and F. Leuthardt, *Helv. Chim. Acta*, **39**, 1790 (1956).

(11) K. Schwarz and C. M. Foltz, *J. Am. Chem. Soc.*, **79**, 3292 (1957).

(12) E. L. Patterson, R. Milstrey and E. L. R. Stokstad, *Proc. Soc. Exptl. Biol. Med.*, **95**, 617 (1957).

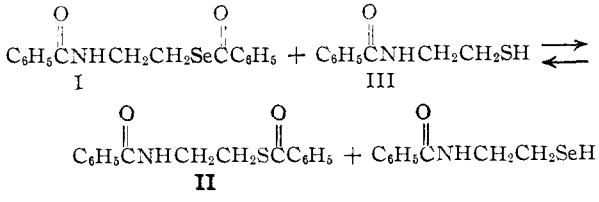
(13) K. W. Lam, M. Riegl and R. E. Olson, *Fed. Proc.*, **20**, 229 (1961).

(14) E. M. Fry, *J. Org. Chem.*, **15**, 802 (1950).

For both compounds repetition of the reactions in synthetic amounts, then air oxidation, gave rise to quantitative yields of *n*-butylbenzamide and N,N′-dibenzoylcystamine or N,N′-dibenzoylselenocystamine, respectively.

Similar ratios of reactivity were seen when other selenoacyl and thioacyl analogs were permitted to react with amines.

It then seemed of interest to investigate the reaction of a selenoacyl compound with a mercaptan to form the corresponding thioacyl compound



Reaction of N,Se-dibenzoylselenocysteamine (I) with N-benzoylcysteamine[15] (III) in equimolar amounts ($1.50 \times 10^{-4} M$) in absolute ethanol at reflux temperature resulted in disappearance of the selenobenzoyl ultraviolet absorption and appearance of the corresponding thiobenzoyl peak at 265 mμ ($k_{obs.}$ 4.26×10^{-4} sec.$^{-1}$). Spectroscopic evidence suggests a quantitative yield of N,S-dibenzoylcysteamine (II).

Repetition of the reaction on a larger scale in 50% ethanol, followed by chromatography on alumina with tetrahydrofuran as eluent, allowed isolation of the thiol ester (II) in 70% yield. Infrared spectrum and mixed melting points showed the product to be authentic N,S-dibenzoylcysteamine.

The high activation of selenol esters may make them useful tools for the acylation of amines and thiols under mild conditions.

(15) A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, 1919 (1948).

DEPARTMENT OF PHARMACOLOGY
YALE UNIVERSITY HENRY G. MAUTNER
SCHOOL OF MEDICINE WOLFGANG H. H. GÜNTHER
NEW HAVEN, CONNECTICUT

RECEIVED JUNE 19, 1961

ETHYLENE–BUTENE-2 ALTERNATING CRYSTALLINE COPOLYMERS

Sir:

The aliphatic olefins containing an internal double bond do not yield high molecular weight homopolymers with the catalytic systems acting by an anionic coördinated mechanism, active for the α-olefins polymerization.

However, using many homogeneous or heterogeneous catalysts, able to polymerize ethylene through an anionic coördinated mechanism, we succeeded in preparing linear high-molecular weight copolymers of these monomers with ethylene.

As appears in Table I, the over-all copolymerization rate and the composition of the copolymers obtained, depend on the type of catalysts employed. This is in agreement with the ionic

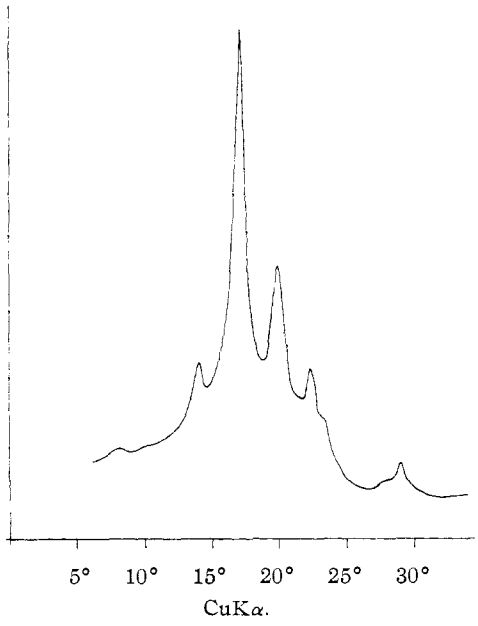
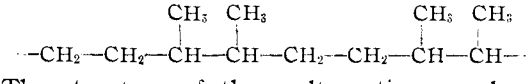


Fig. 1.—Geiger-counter registration of the X-ray spectrum of ethylene–*cis*-butene-2 alternating copolymer.

mechanism of these copolymerizations.[1] Copolymers having a high content of monomeric units deriving from a monomer containing an internal double bond are obtained only when operating with high concentrations of the latter and with very low ethylene concentrations. On the contrary, when operating under high ethylene pressure, the polymer obtained practically consists only of polyethylene. When comparing the copolymerization of ethylene with *cis*-butene-2 or, respectively, with *trans*-butene-2, a higher copolymerization rate with the *cis* isomer is observed.

Taking into account that with all the catalysts of the anionic coördinated type used by us no homopolymerization of butene-2 occurs, it also could be expected that in the copolymerization two butene-2 monomeric units never can be bound directly one to the other, as has been confirmed by the results reported here.

When employing sufficiently low ethylene concentrations, we prepared ethylene–butene-2 alternating copolymers, or at least copolymers containing long sequences with the chemical structure



The structure of these alternating copolymers was demonstrated by the experimental results: (1) Even decreasing as much as possible the concentration of ethylene present in the liquid phase in which the copolymerization occurs, neither crude copolymers nor their fractions having a butene-2 molar content higher than 50% have ever been obtained. (2) The analysis of the infrared absorption spectrum of copolymers containing about 50 mole % of butene-2 shows an intense absorption band at 13.2 μ, which is to be attributed to sequences of two methylenic groups. Absorption

(1) G. Natta, G. Mazzanti, A. Valvassori and G. Sartori, *La Chimica e l'Industria*, **40**, 717 (1958).