

peroxide and sodium salts of malonic ester derivatives. In that case it was found that in inert solvents the O—O-bond was split with ease and the benzyloxy group introduced into the malonic ester derivatives in good yields. The new products were then also characterized by hydrolyzing them to tartronic acids.

As a full paper will soon be submitted for publication in this Journal we include here only one experiment. Additional work is under way to test more fully this reaction especially with derivatives of ethyl cyanoacetate³, malononitrile³, β -diketones⁴, β -ketoesters⁵ and other active methylene compounds.

Experimental. The sodium compound of diethyl ethylmalonate was prepared from 2.4 g of NaH and 18.8 g of diethyl ethylmalonate in 150 ml of dry benzene. Then 18 g of benzoylperoxide in 150–200 ml of dry benzene was added to the sodium compound, cooled in an ice-water bath. After standing over night the reaction mixture was worked up in the usual way. Distillation gave diethyl O-benzoylethyltartronate with b. p. 137°/0.15 mm Hg. Yield 75 % n_D^{20} 1.4890. (Found: C 62.23; H 6.50. Calc for $C_{16}H_{20}O_6$: C 62.32; H 6.54.)

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Tetrahydrofuran as a New Solvent in Condensation Reactions

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Inspired by the work of H. Normant *et al.*^{1,2} who succeeded in preparing Grignard reagents from aryl chlorides and vinyl

halides by running the reaction in tetrahydrofuran (THF) we have just begun to study the usefulness of this solvent in certain condensation reactions. We now want to report very shortly some of our preliminary results. A full paper will be published at a later date.

It is known that potassium or sodium salts (enolates) of active methylene compounds in general are insoluble in such inert solvents as benzene, toluene, xylene, *etc.* Under these conditions further reactions are often very sluggish because of the inhomogeneous system. As magnesium ethoxide is soluble in inert solvents Lund's well-known method³ offers some advantage in this case. An excellent review⁴ has recently been published on this subject concerning these matters.

We have found that diethyl malonate reacts very vigorously with sodium hydride in THF and the corresponding sodium compound formed is completely soluble. Reactive halogen compounds as benzoylchloride, acetylchloride and ethylchloroformate react instantaneously and give diethyl benzoylmalonate, diethyl acetylmalonate and tricarbetoxymethane, respectively, in excellent yields. In the same way ethyl acetoacetate whose sodium compound is also soluble in THF, gives ethyl 2-benzoylacetoacetate and diethyl acetylsuccinate when treated with benzoylchloride and ethyl bromoacetate, respectively. The yields were in all cases higher than 70 % although we have not attempted to work out the conditions for maximum yields.

Experimental. All experiments were carried out in nitrogen atmosphere and in the usual type of apparatus. Preparation of diethyl benzoylmalonate may be taken as a typical example.

To sodium hydride (0.2 mole) covered with 200 ml of THF, was added 0.21 mole of diethylmalonate. In less than one hour the evolution of hydrogen had ceased and a clear solution was formed. The flask was cooled in ice-water and then 0.2 mole of redistilled benzoylchloride was added all at once. Stirring was continued for another 5–10 min and then the mixture was poured into water and acidified. The aqueous solution was separated and extracted twice with ether. The organic layers were combined and washed with sodium bicarbonate solution and then with water, and finally dried over sodium sulphate. Distillation gave the main fraction at a b.p. of 137°C/0.5 mm Hg. Yield 72 %.

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Preparation and Properties of Glucoconringiin, the Precursor of the Thyreostatic 5,5-Dimethyl-2-Oxazolidinethione

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The mustard oil glucoside glucoconringiin is present according to Kjær *et al.*¹ in several *Cochlearia* spec. which are rather common in the Finnish flora. In the course of investigations with goitrogens in plants it seemed therefore of interest to isolate this glucosidic precursor of the thyreostatic and probably also goitrogenic 5,5-dimethyl-2-oxazolidinethione.

Some years ago Kjær *et al.*¹ and Schultz and Wagner² prepared and characterized glucoconringiin as its tetraacetyl derivative from seeds of *Conringia orientalis* (L.) Andr. and showed that the deacetylated glucoside which they obtained in amorphous form is split by myrosinase into sulphate, glucose and 5,5-dimethyl-2-oxazolidinethione. This heterocyclic compound, isolated and identified by Hopkins³ twenty years ago from *C. orientalis* seeds, is formed by spontaneous cyclization from an intermediate 2-hydroxy-2-methylpropyl isothiocyanate. Its thyreostatic effect was established by Astwood *et al.*⁴ and was found comparable to that of (-)-5-vinyl-2-oxazolidinethione (goitrin).

The purpose of this paper is to report briefly the method for preparation and some properties of crystalline glucoconringiin, which unlike its tetraacetyl deriva-

tive has the advantage of being split readily by myrosinase and is therefore more suitable for physiological investigations.

Glucoconringiin was prepared by ion exchange on Dowex 2-X 4 of an extract from seeds of *Conringia orientalis* (L.) Andr. Upon elution with K_2SO_4 solution it was obtained as a colourless syrup which crystallized upon long standing in the refrigerator. Two recrystallizations from 90 % ethanol yielded pure glucoconringiin as anhydrous potassium salt in white, short needles. Elementary analysis agreed with the composition $C_{11}H_{20}NO_{10}S_2K$. F 168°C (decomp., uncorr.), $[\alpha]_D^{25} -10.87^\circ$ in H_2O . In agreement with earlier results^{1,2} the formation of glucose, sulfate and 5,5-dimethyl-2-oxazolidinethione could be observed during enzymatic cleavage. The enzymatic process could be followed by UV spectroscopy: with increasing cleavage the maximum absorbance shifts from 230.5 $m\mu$ to 240 $m\mu$ ($\epsilon = 15\ 400$), the maximum of 5,5-dimethyl-2-oxazolidinethione.

Spectrophotometric assay of the enzymatic cleavage of glucoconringiin: 0.0155 g of glucoconringiin was dissolved in 2 ml of a mixture of equal parts of myrosinase solution and phosphate buffer pH 6.8. In certain intervals 0.1 ml portions were taken off, diluted to 50 ml with water and the UV absorption measured between 220 $m\mu$ and 260 $m\mu$ against an equal blank dilution of myrosinase solution and phosphate buffer solution.

<i>t</i> min	UV- maximum <i>mμ</i>	Optical density	Mol.* extinction, ϵ
1	230.5	0.245	6 760
20	233	0.258	7 140
90	235	0.310	8 560
180	237	0.430	11 900
270	238	0.516	14 250
360	239	0.562	15 500

* based on the initial substrate concentration.

By treatment of glucoconringiin with hydrochloric acid hydroxylamine was formed which was detected by the method of Blom⁵. These results indicate that glucoconringiin is of the same structural type as the other known mustard oil glucosides⁶, and has the following structure (p. 1719).

85 g of finely ground seeds of *Conringia orientalis* (L.) Andr. were defatted by petro-