

inducer in *Ps. fluorescens*.⁹ In the present investigation, too, the 2-oxo group may be essential for the induction of the enzyme, the length of carbon chain being probably less important in the induction process.

The strains of *Ps. fluorescens*, P-2 and UK-1, differ from each other in ability to utilize pantothenate. A diauxin of growth was observed in the strain UK-1 on pantothenate, because β -alanine was utilized very rapidly and pantoate after a lag of few hours. On the other hand,

the presence of valine, leucine, and isoleucine,¹⁰ no multivalent repression of 2-oxoisovalerate dehydrogenase was observed in *Ps. fluorescens*. The rates of enzyme synthesis were to some extent faster on valine + isoleucine, valine + leucine, and valine + isoleucine + leucine than on isoleucine + leucine.

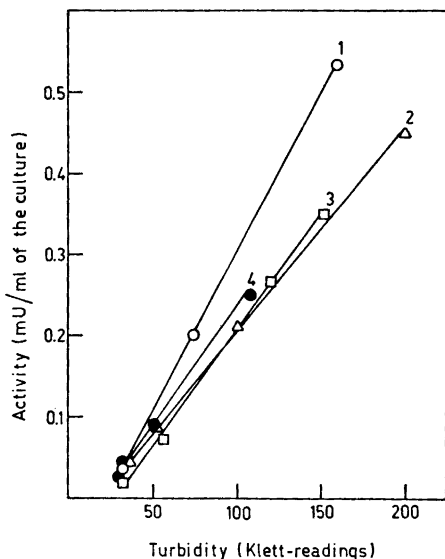


Fig. 2. The effect of mixtures of branched chain amino acids on the formation of 2-oxoisovalerate dehydrogenase in *Ps. fluorescens* UK-1. Other conditions were as described in the legend to Fig. 1.

1 = valine + isoleucine, 2 = leucine + isoleucine, 3 = valine + leucine, 4 = valine + leucine + isoleucine.

the generation times on valine were equal in the two strains, suggesting that the induction patterns of the utilization of valine closely resemble each other.

Fig. 2 shows the results of experiments in which the effects of the mixtures of branched chain amino acids were tested in the induction process in the strain UK-1. Although in *Salmonella typhimurium* and *E. coli* transaminase B was repressed in

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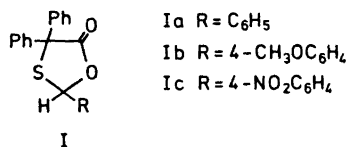
Reaction of 4,4-Diphenyl-2-aryl-1,3-oxathiolan-5-ones with Grignard Reagents

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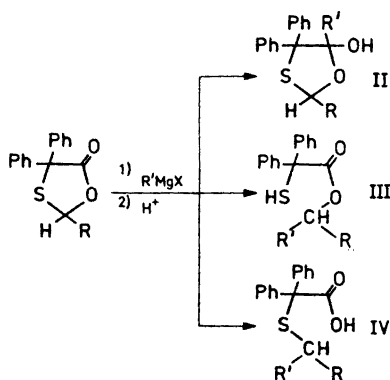
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The reaction of 1,3-oxathiolanones of type I with Grignard reagents presents an interesting problem because the reagent

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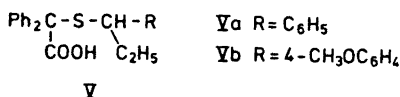
could attack either the carbonyl carbon or carbon-2, in analogy to the reaction between Grignard reagents and γ -lactones or oxathiolanes,¹⁻³ respectively (*cf.* Scheme 1).



Scheme 1.

As shown in Scheme 1 attack on carbon-5 will only give rise to one primary product II, which may react further, whereas attack on carbon-2 can give two primary products. If the carbon-sulfur bond is cleaved the reaction results in the formation of an ester (III). Cleavage of the carbon-oxygen bond will give a carboxylic acid (IV) as primary product.

We have observed that the reaction between I and phenylmagnesium bromide was incomplete, whereas no starting material was present after the reaction of I with ethylmagnesium bromide. The main product from the reaction of Ia with ethylmagnesium bromide was shown to be the acid Va, isolated in 59 % yield.



The reaction of Ib resulted in the formation of Vb in 49 % yield, whereas the reaction of Ic did not give rise to any acid of type V.

The acids isolated are the result of attack on carbon-2 and subsequent cleavage of the carbon-oxygen bond. We have not been able to isolate any compounds which could indicate that the other two modes of reaction were operative. The remaining part of the reaction mixtures consisted of benzophenone and diphenylacetic acid, which are often found as decomposition products of oxathiolanes.⁴

Our results are in accordance with results obtained by Cabiddu *et al.*¹⁻³ from the reaction of 1,3-benzoxathiolanes with Grignard reagents. These authors have in all cases identified *S*-alkylthiophenols as the only reaction products.

Experimental. ¹H NMR spectra were recorded on a Varian A60A spectrometer from ca. 5 % solutions in deuteriochloroform. Chemical shifts are given as δ -values.

Oxathiolanones were prepared as previously described.⁵

2,2-Diphenyl-2-(1'-phenylpropylthio)acetic acid (Va). A solution of 2,4,4-triphenyl-1,3-oxathiolan-5-one (0.02 mol) in a mixture of ether (100 ml) and benzene (100 ml) was added to a refluxing solution of ethylmagnesium bromide (0.04 mol) in ether (50 ml) over a period of 2 h. While the ether slowly distilled off an equal amount of benzene was added. The temperature was raised to 77°C and the refluxing continued for a further 2 h. The reaction mixture was poured into conc. sulfuric acid (2.5 ml) and ice water (500 ml), and the aqueous phase was extracted twice with benzene (100 ml). The combined benzene solutions yielded after evaporation 8.3 g of oil. The oil was stirred with 200 ml of 2 N sodium hydroxide for 10 h at room temperature. The base-insoluble products were removed by extraction with ether. After extraction with chloroform, the chloroform-soluble sodium salt of Va could be isolated by evaporation. On addition of 100 ml of 4 N hydrochloric acid to the sodium salt and subsequent extraction with chloroform the free acid was isolated as a pale yellow glass which crystallized during a month; yield 59 %. Recrystallized from benzene/hexane (1 : 7); m.p. 118–119°C. (Found: C 76.10; H 6.08; S 8.70. Calc. for C₂₃H₂₂O₂S: C 76.30; H 6.08; S 8.81). ¹H NMR spectrum in CDCl₃: 0.61 t (*J* = 7 Hz) (CH₃), 1.73 q (*J* = 7 Hz) (CH₂), 3.42 t (*J* = 7 Hz) (CH), 6.80–7.50 m (aromatic), 9.46 (COOH).

2,2-Diphenyl-2-(1'-(p-methoxyphenyl)propylthio)acetic acid (Vb). Oil purified by chromatography; yield 49 %. (Found: C 73.35; H 6.58; S 8.09. Calc. for $C_{24}H_{24}O_3S$: C 73.47; H 6.12; S 8.16.) 1H NMR spectrum in $CDCl_3$: 0.61 t ($J=7$ Hz) (CH_3), 1.73 q ($J=7$ Hz) (CH_2), 3.42 t ($J=7$ Hz) (CH), 3.70 s (OCH_3), 6.65–7.50 m (aromatic), 8.58 s (COOH).

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