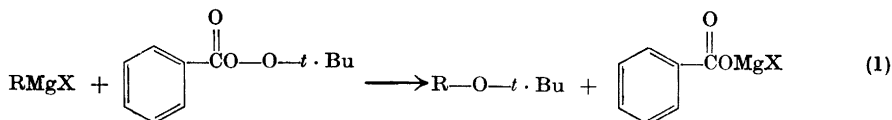


Studies of Peroxycompounds  
 II. \* The Preparation of Diethyl-  
*t*-butoxy-malonate and Ethyl-  
*t*-butoxy-acetoacetate

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In the first paper of this series<sup>1</sup> a new  
 method of preparing *t*-butylethers was  
 described:



The reaction is very smooth and gives excellent yields in general, and seems further, at least in the laboratory scale, to be the best method to prepare aromatic *t*-butylethers.

It was then felt that a perester might react with sodium compounds of diethylmalonate or ethyl acetoacetate for instance. Earlier, Milas *et al.*<sup>2</sup> reacted *t*-butylperbenzoate with sodium methoxide in excess of methanol and obtained methylbenzoate and the sodium salt of *t*-butylhydroperoxide. In analogy with eqn. 1, the —O—O—bond could be split by certain types of organosodium compounds in inert solvents and an ether group introduced. We have now managed to introduce the *t*-butoxy-group into diethyl malonate and ethyl acetoacetate *via* the corresponding sodium compound. The perester used was *t*-butylperacetate, as the perbenzoate was difficult to separate from the new alkoxy-compound.

Experimentally the sodium compound was made in benzene from sodium hydride and the corresponding ester and to the preheated mixture *t*-butylperacetate was added dropwise. The reaction was exothermic but after the heat evolution ceased, the reaction flask was heated for some time. Diethyl-*t*-butoxy-malonate was isolated in a yield of 27% (C 56.93; H 8.78. Calc. C 56.88; H 8.68) and the corresponding

barbituric acid, m. p. 187—189°C, was also prepared (C 47.96; H 6.04. Calc. C 47.99; H 6.04). The sedative effect of the barbiturate was tested and found to be negligible. Compare the similar neopentylbarbituric acid prepared by Brändström<sup>3</sup>. Ethyl-*t*-butoxy-acetoacetate (C 59.47; H 8.85. Calc. C 59.38; H 8.97) was prepared in a similar way in a yield of 31%.

Further research is planned in this field especially with peresters derived from stronger acids. Acknowledgement is expressed to *The Swedish Natural Science Research Council* for a grant and to Dr. R. Dahlbom (*AB Astra*) for the physiological test.

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3. Brändström, A. *Acta Chem. Scand.* **13** (1959) 615.

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Studies of Peroxycompounds  
 III. The Introduction of the Benzoyloxygroup into Diethylmalonate

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In the reaction between *t*-butylperbenzoate and a Grignard reagent the O—O—bond is easily split and the corresponding *t*-butylether is formed<sup>1</sup>. Also in the case of benzoylperoxide<sup>1</sup> the O—O—bond is first attacked by a Grignard reagent but here the mechanism is probably not yet quite understood. When a *t*-butyl perester was treated with the sodium compound of diethylmalonate or ethyl acetoacetate<sup>2</sup> a very sluggish reaction took place and the *t*-butoxygroup was introduced into the corresponding esters, although in low yields. It was then quite natural to investigate the reaction between benzoyl-

\* Ref.<sup>1</sup> is considered as Part I of this series.