

Studies on Peroxy Compounds  
IX\*. The Introduction of Alkoxy  
Groups into Tetrahydrofuran

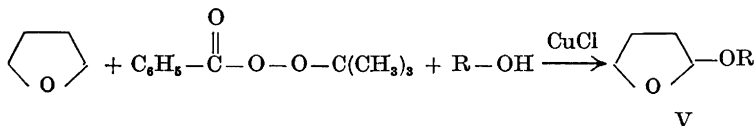
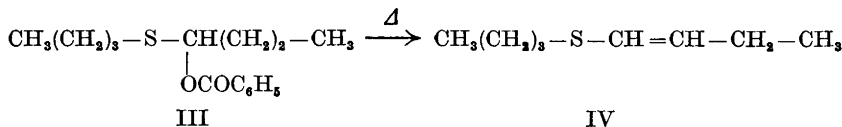
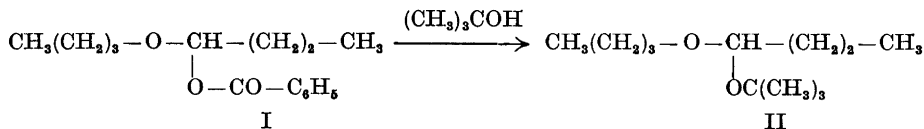
SVEN-OLOW LAWESSON and  
CURT BERGLUND

Department of Organic Chemistry, Chemical  
Institute, University of Uppsala,  
Uppsala, Sweden

When *t*-butylperbenzoate is decomposed in the presence of various types of substrates such as olefins<sup>1,2</sup>, benzyl ethers<sup>3</sup>, benzyl sulphides<sup>4</sup>, simple ethers and

sulphides<sup>5</sup> (catalytic amounts of cuprous salt being present) according to a method first described by Kharasch and Sosnovsky<sup>1</sup>, the benzyloxy group is introduced without rearrangement, fragmentation, dimerization or isomerisation of the substrate. No oxidation occurs when the substrate is a sulphide. In the case of tetrahydrofuran, tetrahydropyran and di-*n*-butyl ether, however, the *α*-*t*-butoxy compounds<sup>6,7</sup> are obtained. It is most probable that the benzyloxy compounds are first formed, which revert to the *t*-butoxy compound, since we have found<sup>5</sup> that when the benzyloxy compound I is heated under mild conditions with *t*-butanol, the *t*-butoxy compound II is formed.

The sulphur analogue III, however, gives an *α,β*-unsaturated sulphide IV<sup>5</sup> when heated with or without *t*-butanol.



V a: C<sub>2</sub>H<sub>5</sub>  
V b: *i*-C<sub>3</sub>H<sub>7</sub>  
V c: *t*-C<sub>4</sub>H<sub>9</sub>  
V d: *n*-C<sub>6</sub>H<sub>13</sub>

Product	Yield %	B.p. (°C)	mm Hg	n <sub>D</sub> <sup>20</sup>	Formula	Carbon, %		Hydrogen, %	
						Calc.	Found	Calc.	Found
V a	31	125	760	1.4149	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	62.04	62.05	10.41	10.50
V b	35	132	760	1.4147	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	64.58	64.37	10.84	10.89
V c	51	140-141*	760	1.4193	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	69.72	69.59	11.70	11.74
V d	36	87-88	10	1.4330					

\* by a mistake the boiling point was said to be 127°/760 mm Hg in an earlier paper<sup>7</sup>.

In further studies of the reaction between *t*-butyl perbenzoate and cyclic ethers and sulphides, we found, that if an alcohol (R-OH) is added to the substrate (tetrahydrofuran) before carrying out the reaction with *t*-butyl perbenzoate in the usual way, the alkoxy compound V is formed.

Yields cited are based on one series of experiment only and are not considered to be the maximum obtainable. A more detailed paper<sup>8</sup> on this subject will be published in the near future.

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## Analysis of Oxide Films on Copper by Coulometric Reduction

A. RÖNNQVIST

*Institute of Chemistry, University of Uppsala, Sweden*

Several methods have been used for analysing oxide films on copper<sup>1</sup>. The most attractive features of the coulometric method, originally developed by Evans and Bannister<sup>2</sup> and by Miley<sup>3,4</sup>, are its high sensitivity and the possibility of determining both cuprous and cupric oxide in the same run. When determining the two oxides the choice of a suitable electrolyte is important. Campbell and Thomas<sup>5</sup> pointed out that since copper oxide will dissolve in ammonium chloride, there is a possibility of error in earlier determinations

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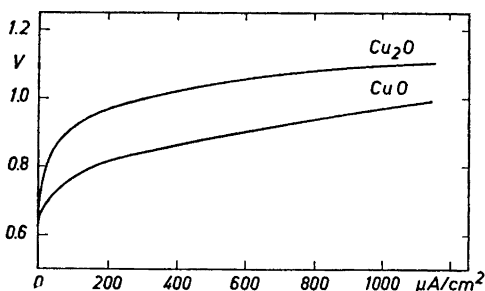


Fig. 1. Reduction potential of the two copper oxides, measured against an Ag-AgCl electrode in 0.1 M KOH, as a function of the current density.

made with  $\text{NH}_4\text{Cl}$  as electrolyte. KCl does not have this disadvantage, but it usually fails to give separation of the two oxides. Later Mills<sup>6</sup> suggested a phosphate buffer of pH 6.9 as a suitable electrolyte for separate determinations of the two oxides. To improve the coulometric method Lambert and Trevoy<sup>7</sup> recently demonstrated the importance of the complete elimination of dissolved oxygen and also of plateable cations from the electrolyte. This can be achieved by pre-electrolysis. The present paper demonstrates the possibility of using KOH (0.1 M) as electrolyte in the analysis

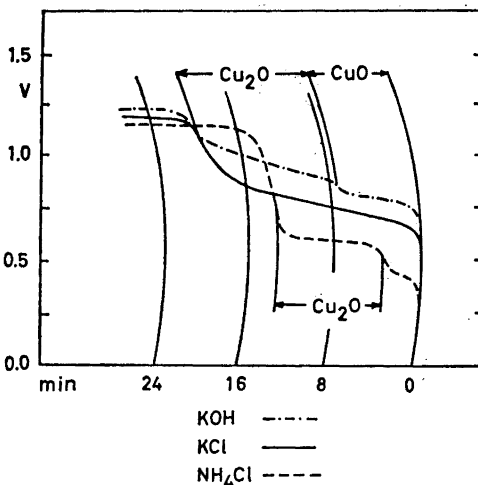


Fig. 2. Time-potential curves of coulometric runs.