

Quantitative relation between the reactants and products expected from equation (6) is in good accord with our observation. Equation (1) can be derived from the assumption that reaction (2) determines the overall rate, but similar result is also derived from reaction (3). Therefore, it cannot be decided which is the rate determining step. However, according to our observation, *p*-nitrotoluene is somewhat soluble in aqueous alkali, and from the latter the nitrotoluene is reversibly recovered by adding mineral acid. This fact supports the assumption that equilibrium (2) is rapidly set up and the radical type decomposition of the salt, i. e., reaction (3) does determine the rate.

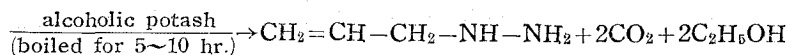
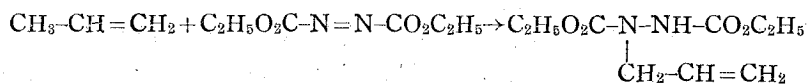
The authors are grateful to Professor Ryhei Oda for his suggestive discussion and encouragement in this work, to Professors Shinzo Okada and Shiro Yoshizawa and Mr. Fumio Hine, Department of Industrial Chemistry, Kyoto University, for their helpful discussions and laboratory experiments in the electrochemistry.

14. Studies on the Reaction of Ethyl Azodicarboxylate and Ethyl Oleate

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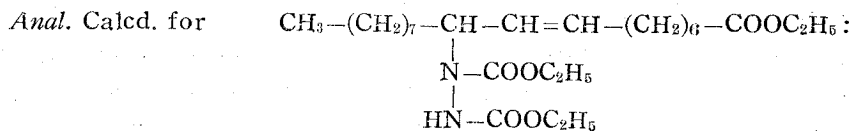
It has already been known that N-allphylhydrazo-N,N'-dicarboxylic ester is produced when olefin is reacted with azodicarboxylic ester at room temperature and the product is saponified with alcoholic potash (E. Müller : Z. angew. Chem., 63, 18).



The authors have attempted this reaction with ethyl oleate. The azodicarboxylic ester was synthesized according to the method of Org. Synth. 82, 58.

The results are summarised in the following:

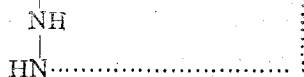
(1) The reaction product from azodicarboxylic ester and oleic ethyl ester (yield; quantitative).



N, 5.77; Found: N, 5.45.

(2) The saponified product (Yield; quantitative).

Anal. Calcd. for $(\text{CH}_3-(\text{CH}_2)_7-\text{CH}-\text{CH}=\text{CH}(\text{CH}_2)_7-\text{CO}):$



N, 9.56; Found: N, 10.12.

15. Syntheses of Antioxidants. (III)

Polynuclear Alkylphenol Antioxidants Containing *p*-hydroxyanisole Nuclei and Relations between Molecular Weight and Potencies

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In the preceding report, we have described polynuclear alkylphenol antioxidants containing *p*-cresol nuclei and found some excellent, high molecular, active compounds with good solubility to fatty oils. In view of the recent publication that mono-*t*-butyl-*p*-hydroxyanisole is an effective and nontoxic antioxidant, we have now prepared some similar polynuclear alkylphenol antioxidants containing *p*-hydroxyanisole and found some effective ones, one of them was superior to commercial 2,5-di-*t*-butyl-*p*-cresol.

p-Hydroxyanisole was dimethylolated as follows. A mixture of 31 g. of *p*-hydroxyanisole, 100. of 10 % aqueous NaOH and 37 g. of 40 % formalin was kept at 15-16°C in the period of three days and neutralized with dilute sulfuric acid. After standing overnight in a refrigerator the precipitated crystals were filtered, yield 22 g. Repeated recrystallizations from ethyl acetate afforded pure dimethylol-*p*-hydroxyanisole, m. p. 127-128°C, which was a new compound.

Condensations with various phenols were carried out according to the description of our preceding report. From the condensation product with phenol a crystalline compound was isolated with the aid of hot water and was recrystallized from a mixture of benzene and acetic acid, m. p. 192-193°C. The acetate, m. p. 99-100°C, molecular weight, 454. This is considered to be the acetate of a trinuclear compound bis-(*p*-hydroxybenzyl)-*p*-hydroxyanisole with calculated molecular weight 452. The condensation with *p*-cresol afforded beside resinous product crystals, m. p. 179-181°C, whose acetate, m. p. 120-121°C, had molecular weight of 493. This was assumed to be the acetate of trinuclear bis-(2-hydroxy-5-methylbenzyl)-*p*-hydroxyanisole. *o*-Cresol, *m*-cresol, thymol, eugenol, *p*-bromophenol, *o*-bromophenol, *p*-*t*-butylphenol, mono-*t*-butyl-*p*-cresol, mono-*t*-butyl-*o*-cresol and mono-*t*-butyl-*m*-cresol gave resinous products.