Pyromellitic dianhydride is a difficult to make but a well known starting material for synthesizing polyimide polymers with excellent heat and oxidative stability. A related monomer which might be equally as good is p-benzoquinone dianhydride (1). Several attempts at making (1) resulted in low yields of the desired monomer.
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HEAT AND HYDROLYTICALLY STABLE POLYMERS FOR FABRICABLE FILMS
AND LAMINATES

G. S. Marvel
H. K. Hall, Jr.

C. S. Marvel Laboratories
Chemistry Department
University of Arizona
Tucson, AZ 85721
Results

Pyromellitic dianhydride 1 is a well-known component of polymers with excellent heat and oxidative stability such as Kapton®. p-Benzquinone dianhydride 2 might be equally good. Brief literature reports already describe its roundabout synthesis (1) and its incorporation into polyimides (2). We have tried to devise a synthesis route which would make this interesting monomer readily available.

![Chemical Structures]

1

2

Various attempts to improve the base-induced coupling of acetonedicarboxylic ester by iodine (1,3) failed to give more than traces of the desired tetraester:

\[ 	ext{CH}_3	ext{OC} \overset{0}{\underset{\text{COOCH}}{\text{COOCH}}} \xrightarrow{\text{I}_2} \overset{\text{THF} 	ext{ or } \text{Cu}_2} \text{C}_4\text{H}_2 \text{OC} \overset{\text{COOCH}}{\text{COOCH}} \]

3

Coupling attempts using the dibromo derivative of acetonedicarboxylic ester also failed.

Next, Claisen self-condensation of tetraethyl 1,1,2,2-ethane-tetracarboxylate was found to give very low yields of the tetrahydro derivative corresponding to 3.

In the final phase of our work, the readily available 4 was converted to three derivatives 5-7 by reaction with alkali or thallium salts:
These were considered as possible intermediates for new thermally stable polymers.

![Chemical structures](image)

Yields were low, probably because of the unusual chemistry of these electrophilic quinones, as known for tetracyano-p-benzoquinone (4) and also because the aqueous work-up of the synthesis led to the dihydroxy quinone dicarboxylate (5).

This area does not seem promising for practical syntheses of thermally stable polymers.

References

Personnel

H. K. Hall, Jr.
A. B. Padias
M. Tomida

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