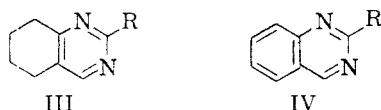


reaction, namely, the transformation of a tetrahydrobenzo heteroaromatic compound to a benzo heterocyclic material. Two successful related dehydrogenations were recorded,<sup>1</sup> and we now report other examples.

It was found that 1-phenyl-4,5,6,7-tetrahydroindazole was converted in low yield to 1-phenylindazole. When the reaction was applied to the tetrahydroquinazoline system III, the transformation to IV took place in good yield where R was amino and in lower yield where R was aliphatic or aromatic.



The method was not successful when applied to 2-phenyl-4,5,6,7-tetrahydroindazole, 1-*p*-nitrophenyl-4,5,6,7-tetrahydroindazole, and 4,5,6,7-tetrahydrobenzo isoxazole.

#### EXPERIMENTAL

**Dehydrogenation—General Procedure.** A mixture of 10 g. of the tetrahydro compound, 5 g. of 5% palladium-on-carbon, and 100 ml. of dry decalin was heated under reflux for 2 days. The catalyst was removed by filtration, and the filtrate was concentrated by heating under reduced pressure on a steam bath. The residue was recrystallized from alcohol or petroleum ether.

In this manner 1-phenyl-4,5,6,7-tetrahydroindazole<sup>3</sup> gave 1-phenylindazole,<sup>4</sup> m.p. 80°, yield 20%; 2-amino-5,6,7,8-tetrahydroquinazoline<sup>5</sup> yielded 2-aminoquinazoline,<sup>6</sup> m.p. 200°, yield 45%; 2-phenyl-5,6,7,8-tetrahydroquinazoline<sup>7</sup> formed 2-phenylquinazoline,<sup>8</sup> m.p. 100°, yield 30%; 2-methyl-5,6,7,8-tetrahydroquinazoline (prepared by the general method reported in ref. 7, picrate, m.p. 135°. *Anal.* Calcd. for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>7</sub>: C, 47.75; H, 4.01; N, 18.56. Found: C, 47.42; H, 4.36; N, 18.77) gave 2-methylquinazoline,<sup>3</sup> m.p. 40°, yield 10%.

The dehydrogenation procedure was not successful when applied to 2-phenyl-4,5,6,7-tetrahydroindazole,<sup>3</sup> 1-*p*-nitrophenyl-4,5,6,7-tetrahydroindazole (prepared by the general method reported in ref. 3, m.p. 112°. *Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 64.18; H, 5.39; N, 17.28. Found: C, 64.38; H, 5.39; N, 17.34) and 4,5,6,7-tetrahydrobenzoisoxazole.<sup>9</sup>

THE LILLY RESEARCH LABORATORIES  
ELI LILLY AND Co.  
INDIANAPOLIS, IND.

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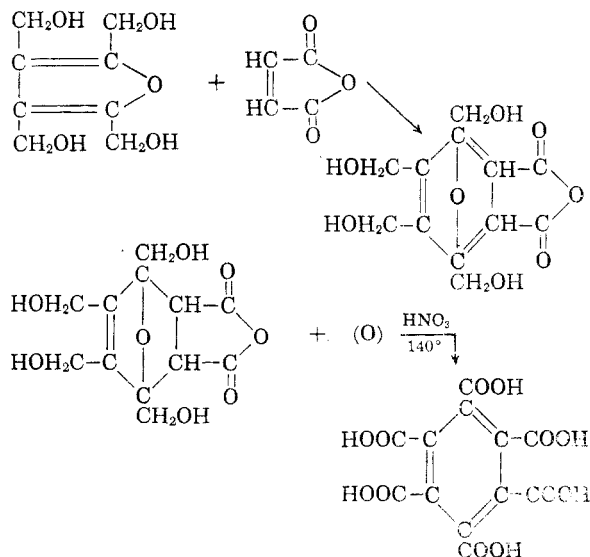
## Heterocyclic Tetramethylol Derivatives in the Diene Synthesis

E. C. WINSLOW, J. E. MASTERSON, AND D. A. CAMPBELL

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As a new approach to the laboratory preparation of mellitic acid by the diene synthesis, an attempt was made in this laboratory to add maleic anhydride as a dienophile to the diene system of tetraethyl furantetracarboxylate. The adduct of such a reaction could be hydrolyzed and oxidized to remove the oxygen bridge and produce mellitic acid. Accordingly tetraethyl furantetracarboxylate was prepared by the method of Sutter.<sup>1</sup> Several attempts to bring about the addition of maleic anhydride to this ester were unsuccessful. Attempts were also made to force tetraethyl furantetracarboxylate to react as a diene in the diene synthesis by using different dienophiles. Fumaronitrile, maleonitrile, and dimethylacetylenedicarboxylate were used as dienophiles but no reaction was observed. It was postulated that the dienic character of the tetraester was reduced by pi electron withdrawal from the diene structure of the ring because of the juxtaposition of four ester groupings. If such were the case, the replacement of the four ester groupings on the furan ring by four methylol groups should give some hope of enhancing the dienic character of the ring. The positive inductive effect of the four methylol groups could be relied upon to enhance the pi electron density of the diene system, thus improving its dienic character.

In order to test this theory tetraethyl furantetracarboxylate was reduced to tetramethylolfuran by the use of lithium aluminum hydride. The product, when purified, reacted with maleic anhydride in a



(1) H. Sutter, *Ann.*, **499**, 47 (1932).

typical diene synthesis. The adduct formed by this reaction was subjected to oxidation with concentrated nitric acid to produce mellitic acid.

Because thiophene and its simple derivatives do not react as dienes in a diene synthesis, an attempt was made to see if the positive inductive effect of four methylol groups on the thiophene ring could enhance the dienic character of thiophene sufficiently to enable it to react in a diene synthesis. Tetramethyl thiophenetetracarboxylate was prepared by a method employed by Michael.<sup>2</sup> This was reduced to tetramethylolthiophene by the use of lithium aluminum hydride. This compound failed to react with either maleic anhydride or dimethyl acetylenedicarboxylate in a diene synthesis.

### EXPERIMENTAL<sup>3</sup>

*Tetramethylolfuran.* The tetraethyl ester of furan tetracarboxylic acid was reduced with lithium aluminum hydride to produce tetramethylolfuran. Eleven grams of lithium aluminum hydride were pulverized in a mortar and then suspended in 200 ml. of anhydrous ether in a 1000-ml., three-neck, round-bottom flask, fitted with a reflux condenser and a mechanical stirrer. Thirty-four grams of the tetraethyl ester of furan tetracarboxylic acid were warmed in a water bath to liquefy the ester and a few milliliters of ether were added to keep it in the liquid state. The ester was placed in a small separatory funnel and added drop-wise with caution to the hydride suspension which was cooled in an ice water bath. The rate of ester addition was adjusted to gentle reflux of the reaction mixture. After the ester had reacted, enough water was cautiously added to decompose the excess hydride, after which a large volume of water was added. The resulting aqueous layer contained a thick orange solid in suspension. The water layer was filtered to remove the aluminum and lithium salts and the filtrate, now strongly basic, was adjusted to a pH of approximately nine with phosphoric acid. The solution was again filtered, removing lithium and aluminum phosphates, and then evaporated on a steam bath to a volume of about 200 ml. The solution was allowed to go to virtual dryness at room temperature. The residue was treated with 95% ethyl alcohol to extract preferentially the organic portion. The ethyl alcohol was evaporated to 17 g. of a dark brown sirup, representing crude tetramethylol furan. Crystal formation occurred very slowly at a temperature of 0°. These crystals were removed mechanically and recrystallized from water using decolorizing charcoal to yield 8 g. (45%) of white crystals which melted at 123–124°.

*Anal.* Calcd. for  $C_8H_{12}O_5$ : C, 51.08%; H, 6.39%. Found: C, 50.93%; H, 6.46%.

*Mellitic acid.* Mellitic acid was prepared by addition of maleic anhydride to tetramethylol furan followed by oxidation of the adduct with nitric acid. About 5 g. of crude tetramethylol furan were placed in an 8-inch test tube. Four grams of finely ground maleic anhydride were added in the dry state to the test tube. About 5 ml. of dry benzene at a temperature of 23° was added and shaken gently to obtain a homogeneous mixture. During the next 5 min. the reaction temperature rose to 33°. The mixture was allowed to stand for 1 hr. after it returned to room temperature. The mixture was removed as a water suspension and added dropwise through a reflux condenser to 70 ml. of a boiling 1:1 by volume mixture of concentrated nitric and fuming nitric acid. Boiling was maintained for 1 hr. after addition and then the clear yellow solution was evaporated to dryness on a steam bath. The yellow residue was crystallized once from con-

centrated nitric acid and then from water using decolorizing carbon. White crystals melting at 284–286° were obtained. The yield was not determined because of subdivision of the diene adduct in other purification attempts.

*Tetramethylolthiophene.* A modification of the reduction technique for the production of tetramethylolfuran was required in the preparation of tetramethylolthiophene because the ester which was used as starting material is relatively insoluble in ether. Lithium aluminum hydride (2.75 g., 0.07 mole) was pulverized and suspended in 300 ml. of absolute ether in a 500-ml. round-bottom flask which was attached to a Soxhlet extraction tube containing tetramethyl thiophenetetracarboxylate (10.0 g., 0.03 mole). The reduction was run at reflux temperature for 12 hr. until no solid remained in the extraction thimble. Water was added to decompose the excess hydride. The reaction mixture was poured into ice water and the ether layer separated from the aqueous mixture. The aqueous portion was filtered with suction, the filtrate was evaporated on a steam bath to dryness, and the residue was extracted with 95% alcohol. The resulting brown solution was evaporated at room temperature to a viscous mass.

The product was isolated by use of Permutit Q cation exchange resin and Dowex 2 anion exchange resin.

Twenty ml. of an aqueous solution of the reaction mixture (5% by volume) was adjusted to a pH of approximately four with hydrochloric acid. This solution and the washes were allowed to run through the cation column at the rate of 2.5 ml./minute. After the solution had passed over the resin the column was washed with 50 ml. of distilled water, 20 ml. of 95% ethyl alcohol, and again with 150 ml. of distilled water. The filtrate obtained from the cation column was passed through the anion column at the rate of 2.5 ml./minute. The column was then washed, at the same rate of flow, with 20 ml. of distilled water and 100 ml. of distilled water saturated with carbon dioxide. The filtrate was colorless. The deionized filtrate was evaporated on a steam bath to a volume of 25 ml. and allowed to go to dryness at room temperature. The residue, two grams (33%), was a white substance which melted at 102–103°.

*Anal.* Calcd. for  $C_8H_{12}O_2S$ : C, 47.06; H, 5.88; S, 15.69. Found: C, 46.94; H, 5.97; S, 15.98.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF RHODE ISLAND  
KINGSTON, R. I.

## Attempts to Copolymerize Pyrene with 1,3-Butadiene and with *p*-Chlorostyrene<sup>1</sup>

C. S. MARVEL AND B. D. WILSON

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Some preliminary experiments on the copolymerization of pyrene with 1,3-butadiene in an emulsion system were reported by Marvel and Anderson.<sup>2</sup> The polymers obtained showed ultraviolet absorption maxima at 342, 301.5, and 260  $m\mu$  and on this basis it was concluded that copolymerization had occurred. In this further work on the problem with

(1) The work discussed herein was performed under contract number AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. L. E. Coleman and Lt. Paul D. Shaw, project engineers.

(2) C. S. Marvel and W. S. Anderson, *J. Am. Chem. Soc.*, **76**, 5434 (1954).

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