

neutralized with sodium carbonate, and extracted with ether. The residue, obtained after evaporation of the ether solution, was identified as phenanthraquinone (melting point and mixed melting point determinations).

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## Synthesis of 2-Trifluoroacetylpyrrole<sup>1</sup>

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The reaction of pyrrole and trifluoroacetic anhydride in benzene at near zero temperatures occurred readily and 2-trifluoroacetylpyrrole was obtained in good yield. At higher temperatures a black tar formed rapidly. In contrast, the reaction of the weaker acid, acetic anhydride, and pyrrole was reported by Ciamician and Dennstedt<sup>3</sup> to require heating to give 2-acetylpyrrole.

2-Trifluoroacetylpyrrole was also prepared by treating pyrrole magnesium bromide with trifluoroacetyl chloride at low temperatures but the yield was low. This route was first reported by Oddo<sup>4</sup> who obtained 2-acetylpyrrole from the reaction of pyrrole magnesium bromide and acetyl chloride. More recently Portnoy and Gisser<sup>5</sup> prepared 2-heptafluorobutylthiophene by the reaction of thiophene magnesium bromide and heptafluorobutyl chloride.

Although the fully fluorinated acyl chlorides have been reported to be acylating agents for aromatic compounds in a Friedel-Crafts type reaction,<sup>6</sup> when trifluoroacetyl chloride was added to pyrrole the characteristic "pyrrole red" color formed immediately, then a black tar separated. This occurred with and without aluminum chloride when near zero temperatures were used and either carbon tetrachloride or ether was used as diluent.

### EXPERIMENTAL

**2-Trifluoroacetylpyrrole. Method 1.** A solution of 35 ml. trifluoroacetic anhydride in 300 ml. dry benzene was cooled to about 0°. While the anhydride solution was stirred vigorously, 15 g. pyrrole in 40 ml. benzene was added dropwise

(1) This investigation was made at the Fluorine Research Center, University of Florida, Gainesville, Fla., under a grant from Minnesota Mining & Manufacturing Co., St. Paul, Minn.

(2) Present address: Celanese Corp. of America, Petroleum Chemicals Research and Development Dept., Clarkwood, Tex.

(3) G. Ciamician and M. Dennstedt, *Gazz. chim. ital.*, **13**, 445 (1883).

(4) B. Oddo, *Gazz. chim. ital.*, **39**, 649 (1910).

(5) S. Portnoy and H. Gisser, *J. Org. Chem.*, **22**, 1752 (1957).

(6) J. H. Simons, W. T. Black, and R. F. Clark, *J. Am. Chem. Soc.*, **75**, 5621 (1953).

over a 2-hr. period. After the addition, the reaction mixture was maintained at about 0° for an additional 4 hr. The reaction mixture was washed with water then dried with anhydrous sodium sulfate. The benzene was removed by distillation and the residue was steam distilled. Trifluoroacetylpyrrole was recovered from the steam distillate by ether extraction: (24 g., 66 wt. % on pyrrole). The crude product was purified by vacuum sublimation and melted 46–47° (uncorr.).

*Anal.*<sup>7</sup> Calcd. for C<sub>6</sub>F<sub>3</sub>H<sub>4</sub>ON: F, 35.9; N, 8.59; mol. wt., 163. Found: F, 34.3; N, 8.67; mol. wt., 163.

*Method 2.* A solution of 7 g. freshly distilled pyrrole in 50 ml. dry ether was cooled to 3–5° in a flask equipped with stirrer, thermometer, addition funnel, and Dewar-type condenser. Twenty-five ml. of 4M methyl magnesium bromide in ether (Arapahoe Special Products, Inc.) was added dropwise during a 1-hr. period while the reaction mixture was stirred and maintained at 3–5°. After the addition of the Grignard reagent, the stirred reaction mixture was maintained cold for 1 hr.

The condenser was filled with an acetone–Dry Ice mixture and the pyrrole magnesium bromide reaction mixture was gassed with 15 g. trifluoroacetyl chloride (10 wt. % excess). The acid chloride addition was completed within 30 min. and the reaction mixture was allowed to warm to room temperature. After the ether was distilled off, the residue was washed with 5 wt. % aqueous NaOH, then steam distilled. The product, recrystallized from ethyl alcohol–water, melted at 45–47° (uncorr.).

The product prepared by both methods was a white solid with a phenol-like odor and was soluble in benzene, ether, and carbon tetrachloride. An infrared spectrogram of a carbon tetrachloride solution of 2-trifluoroacetylpyrrole showed absorptions at 2.91 microns (NH), 3.03 microns (CH), and 6.0 microns (CO). The phenylhydrazone, prepared by the standard procedure,<sup>8</sup> was a dark liquid which decomposed on heating.

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(7) Micro-nitrogen determination by Peninsular Chemical Research, Gainesville, Fla. Mol. wt. determined by the melting point depression of *d*-camphor at one arbitrary dilution.

(8) R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, 2nd ed., Wiley and Sons, New York, 1940, p. 139.

## Preparation of Indazoles and Quinazolines by Catalytic Dehydrogenation

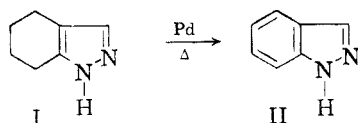
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In a previous publication<sup>1</sup> it was reported that 4,5,6,7-tetrahydroindazole (I) was readily converted to indazole (II) by heating with palladium-on-carbon in decalin. A search of the literature revealed only a few other references<sup>2</sup> to this type of

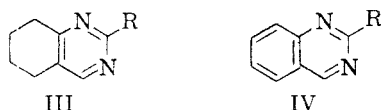
(1) C. Ainsworth, *J. Am. Chem. Soc.*, **79**, 5242 (1957).

(2) E. C. Horning, M. G. Horning, and G. N. Walker, *J. Am. Chem. Soc.*, **70**, 3935 (1948); H. Adkins and L. G. Lundsted, *J. Am. Chem. Soc.*, **71**, 2964 (1949) and A. Treibs and D. Dinelli, *Ann.*, **517**, 152 (1935).



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>

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(3) K. von Auwers, W. Buschmann, and R. Heidenreich, *Ann.*, **435**, 277 (1924).

(4) W. Borsche and K. Diacont, *Ann.*, **510**, 287 (1934).

(5) E. Benary, *Ber.*, **63**, 2601 (1930).

(6) A. K. Macbeth and H. J. Rodda, *Nature*, **156**, 207 (1945).

(7) P. C. Mitter and A. Bhattacharya, *Quart. J. Indian Chem. Soc.*, **4**, 149 (1927); [*Chem. Abstr.*, **21**, 3198 (1927)].

(8) M. T. Bogert and F. P. Nabenhauer, *J. Am. Chem. Soc.*, **46**, 1932 (1924).

(9) K. von Auwers, T. Bahr, and E. Frese, *Ann.*, **441**, 54 (1925).

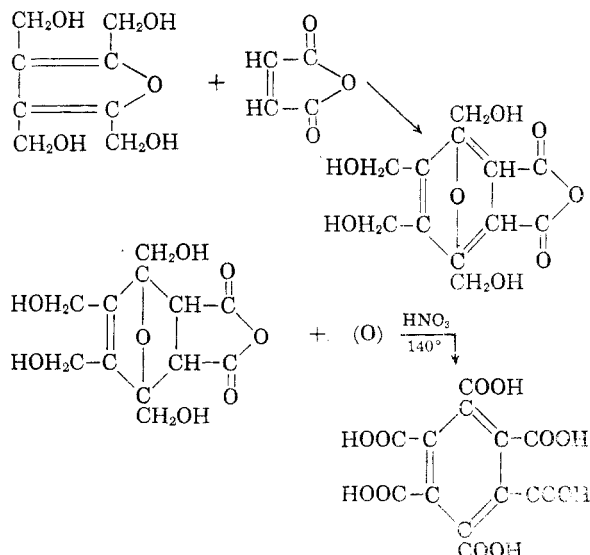
## Heterocyclic Tetramethylol Derivatives in the Diene Synthesis

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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).