is made in the literature[3] is the bromo-methylation of bromobenzene.

A yield of 66% of a pure product is obtained when the photo-bromination is carried out under similar conditions (but with less bromine) as described for the preparation of *p*-bromobenzal bromide.[4] One hundred and two grams (0.60 mole) *p*-bromotoluene, in a three-necked Pyrex flask, mounted with a mercury-sealed stirrer, a dropping funnel and a reflux condenser with gas-trap, is heated in an oil-bath at 120° (bath temperature) and exposed to the light of a 100-watt lamp. With constant agitation, 102 g. of bromine (0.64 mole) is added during three hours, and the stirring is continued for another thirty minutes. By this time, the evolution of hydrogen bromide has come to a standstill. The product solidifies, upon standing, to a brownish crystalline mass and is filtered by suction from the adhering oil and washed three times with 30 cc. of ethyl alcohol. The yield is 80 g. From the mother liquor, upon cooling with an ice–salt mixture, a second crystallizate (18–20 g.) is obtained. The yield is 66%; m. p. of both crops 61° sharp without further recrystallization. The product was identical with one prepared according to Schramm,[1] and gave the correct analysis. Calcd. for $C_7H_6Br_2$: Br, 64.0. Found: Br, 63.7.

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[3] Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 524 (1920).

[4] "Organic Syntheses," Vol. XVII, p. 20.

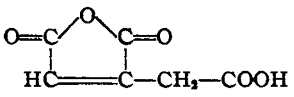
DEPARTMENT OF ORGANIC CHEMISTRY
HEBREW UNIVERSITY
JERUSALEM, PALESTINE

RECEIVED AUGUST 11, 1945

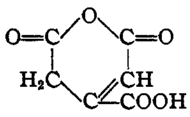
Adduct of Anthracene with *cis*-Aconitic Anhydride

BY JESSE WERNER AND PAUL NAWIASKY

In connection with a research program being carried out in this Laboratory, it was found necessary to prepare the Diels–Alder adduct of anthracene with *cis*-aconitic anhydride. Malachowski, *et al.*,[1] have investigated the chemistry of the so-called *cis* and *trans* forms of aconitic anhydride and found decided differences in chemical behavior. The *cis* anhydride has quinonoidal properties since it adds to dimethylaniline and hydroquinone, whereas the *trans* does not.[2] From this and other evidence, they deduced that the two anhydrides are structural rather than geometrical isomers. The structure which they arrived at for the *cis* form is (I). That for the *trans* form is (II), with a probable equilibrium existing between the keto and enol forms. Schönberg and Ismail[3] have found that the *cis* anhydride gives a red color with triphenyl phosphine, whereas the *trans* form gives no color at all, thus providing further evidence that the *cis* isomer possesses quinonoidal properties, whereas the *trans* does not. The *cis* structure is that of a substituted maleic anhydride. Pfeiffer and Böttler[4] regard maleic anhydride as the quinone of furan, and as such it shows many of the reactions attributed to the quinone structure.



I



II

On refluxing with anthracene in xylene, the *cis* form was found to react very rapidly and in good yield in the Diels–Alder condensation. However, the *cis* form is rather difficult to obtain in a pure state, in contrast to the *trans* form. Since the *trans* form is slowly converted to the *cis* on melting or keeping in solution above its melting point, it was of interest to determine the relative dienophilic reactivities of the non-quinonoidal *trans* form and the quinonoidal *cis* form by refluxing the *trans* form with anthracene in xylene. The reaction in this case was quite slow, but the product obtained was identical with that from the *cis* isomer. This indicates that the mechanism involved a slow conversion of the *trans* to the *cis* form and a subsequent condensation of the *cis* isomer with anthracene.

It is of interest to note that both forms of aconitic anhydride contain the dienophilic C=C—C=O grouping. However, the dienophilic reactivities of the two are quite different, the quinonoidal nature of the *cis* form evidently enhancing its dienophilic properties.

Procedure.—Six grams of anthracene (Eastman Kodak Company) and 5.2 g. of either *cis* or *trans* aconitic anhydride (prepared according to Malachowski, *et al.*,[1] and melting at 72–73° and 135–136°, respectively) were mixed with 50 cc. of xylene. With the *cis* isomer the mixture was heated rapidly to reflux for one-half hour; with the *trans* isomer the mixture was heated to reflux during one hour and refluxed for four hours. In both cases the mixture was allowed to crystallize at room temperature overnight, after which the crystals were filtered off, washed with 100 cc. of xylene and dried on the steam-bath. The yield of pale yellow plates was 7.0 g. (63%) with the *cis* and 6.7 g. (60%) with the *trans*. Two recrystallizations from ethyl acetate gave pure white crystals, m. p. 262–263° (dec.) in each case.

Anal. Calcd. for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: (for *cis*), C, 71.72; H, 4.28; for *trans*, C, 71.60; H, 4.37.

Mixtures of the two adducts showed no change in melting point.

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[1] Malachowski, Giedroyć and Jerzmanowska, *Ber.*, **61**, 2525 (1928).

[2] *Cf.* Norton, *Chem. Rev.*, **31**, 468 (1942).

[3] Schönberg and Ismail, *J. Chem. Soc.*, 1374 (1940).

[4] Pfeiffer and Böttler, *Ber.*, **51**, 1819 (1918).

PROCESS DEVELOPMENT DEPARTMENT
GENERAL ANILINE WORKS DIVISION
GENERAL ANILINE & FILM CORPORATION
GRASSELLI, NEW JERSEY

RECEIVED SEPTEMBER 11, 1945

2-(4-Homosulfanilamido)-quinoxaline

BY FRANK J. WOLF, RUSSELL M. WILSON, JR., AND MAX TISHLER

Owing to the recent interest in marfanil,[1] the preparation of the corresponding homosulfanila-

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[1] J. Klarer, *Klin. Wochschr.*, **20**, 1250 (1941).