

ml. of water containing 8 ml. of 12 *N* hydrochloric acid was cooled to 0°. A 10% aqueous solution of sodium nitrite was added until a starch-iodine test indicated an excess of nitrous acid. A solution of 0.56 g. (0.005 mole) of glutamic anhydride in 25 ml. of water containing 0.2 g. of sodium carbonate was cooled to 0° and added to the diazotized amine to precipitate the crude product. Recrystallization from ethyl acetate gave 0.89 g., 87% of the theoretical amount, of γ -ketoglutaconic anhydride phenylhydrazone as orange plates, m.p. 165°.

Anal. Calcd. for $C_{11}H_9O_3N_2$: C, 61.11; H, 3.73. Found: C, 61.15; H, 3.75.

γ -Ketoglutaconic Anhydride *o*-Tolylphenylhydrazone (III, Ar = *o*-Tolyl).—This compound was prepared by the procedure given for the phenyl analog using diazotized *o*-toluidine. Recrystallization from ethyl acetate gave 0.66 g., 57.3%, of γ -ketoglutaconic anhydride *o*-tolylphenylhydrazone as orange crystals, m.p. 174–175°.

Anal. Calcd. for $C_{12}H_{10}O_3N_2$: N, 12.17. Found: N, 12.43.

γ -Ketoglutaconic Anhydride *p*-Tolylphenylhydrazone (III, Ar = *p*-Tolyl).—This compound was prepared by the procedure given for the phenyl analog using diazotized *p*-toluidine. Recrystallization from ethyl acetate gave 0.91 g., 79.3%, of γ -ketoglutaconic anhydride *p*-tolylphenylhydrazone, yellow crystals, m.p. 201°.

Anal. Calcd. for $C_{12}H_{10}O_3N_2$: N, 12.17. Found: N, 12.14.

γ -Ketoglutaconic Anhydride *o*-Methoxyphenylhydrazone (III, Ar = *o*-Methoxyphenyl).—This compound was prepared by the procedure given for the phenyl analog using diazotized *o*-anisidine. Recrystallization from ethyl acetate gave 0.69 g., 56%, of γ -ketoglutaconic anhydride *o*-methoxyphenylhydrazone, red crystals, m.p. 169°.

Anal. Calcd. for $C_{12}H_{10}O_4N_2$: C, 58.53; H, 4.09. Found: C, 58.51; H, 4.21.

γ -Ketoglutaconic Anhydride β -Naphthylhydrazone (III, Ar = β -Naphthyl).—This compound was prepared by the procedure given for the phenyl analog using diazotized β -naphthylamine. Recrystallization from ethyl acetate gave 1.15 g., 86.5%, of γ -ketoglutaconic anhydride β -naphthylhydrazone as orange crystals, m.p. 252–253°.

Anal. Calcd. for $C_{15}H_{13}N_2O_3$: C, 67.66; H, 3.79. Found: C, 67.66; H, 3.96.

γ -Ketoglutaconic Anhydride α -Naphthylhydrazone (III, Ar = α -Naphthyl).—This compound was prepared by the procedure given above for the phenyl analog using diazotized α -naphthylamine. Recrystallization from ethyl acetate gave 1.13 g., 85.5%, of γ -ketoglutaconic anhydride α -naphthylhydrazone as orange crystals, m.p. 163–165°.

Anal. Calcd. for $C_{15}H_{13}N_2O_3$: C, 67.66; H, 3.79. Found: C, 68.06; H, 3.83.

γ -Ketoglutaconic Anhydride *o*-Carboxyphenylhydrazone (III, Ar = *o*-Carboxyphenyl).—This compound was prepared by the procedure given above for the phenyl analog using diazotized 2-anthranilic acid. Recrystallization from acetic acid gave 1.06 g., 80%, of γ -ketoglutaconic anhydride *o*-carboxyphenylhydrazone as yellow crystals, m.p. 268–270°.

Anal. Calcd. for $C_{12}H_9N_2O_5$: C, 55.39; H, 3.10. Found: C, 55.48; H, 3.22.

γ -Ketoglutaconic Anhydride *p*-Dimethylaminophenylhydrazone (III, Ar = *p*-Dimethylaminophenyl).—This compound was prepared by the procedure given above for the phenyl analog using diazotized *N,N*-dimethylphenylenediamine. Recrystallization from ethyl acetate gave 0.81 g., 64%, of γ -ketoglutaconic anhydride *p*-dimethylaminophenylhydrazone, deep blue needles, m.p. 200–201°.

Anal. Calcd. for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.05. Found: C, 60.33; H, 4.83.

1-Phenyl-3-carboxy-6-pyridazone (IV, Ar = Phenyl).—A mixture of 0.5 g. (0.0024 mole) of γ -ketoglutaconic anhydride phenylhydrazone and 25 ml. of 10% aqueous potassium hydroxide was refluxed for two hours. During this time the anhydride dissolved and the color was discharged. The cooled reaction mixture was extracted with ether to remove unreacted starting materials and acidified. The acid solution was then extracted with several 25-ml. portions of ether which were dried over anhydrous potassium sulfate and evaporated to dryness to yield the crude product. Recrystalliza-

tion from ethyl acetate gave 0.14 g., 28% of the theoretical amount, of 1-phenyl-3-carboxy-6-pyridazone, m.p. 210–212°.

Anal. Calcd. for $C_{11}H_9O_3N_2$: N, 12.96. Found: N, 12.74.

1-(*o*-Tolyl)-3-carboxy-6-pyridazone (IV, Ar = *o*-Tolyl).—This compound was prepared by the procedure given for the β -naphthyl analog from 0.5 g. of the *o*-tolylhydrazone. The crude product precipitated on acidification. There was obtained 0.21 g., 42%, of 1-(*o*-tolyl)-3-carboxy-6-pyridazone, m.p. 236°, recrystallized from ethyl acetate.

Anal. Calcd. for $C_{12}H_{10}O_3N_2$: N, 12.17. Found: N, 12.09.

1-(*p*-Tolyl)-3-carboxy-6-pyridazone (IV, Ar = *p*-Tolyl).—This compound was prepared by the procedure given for the *o*-tolyl analog from 0.5 g. of the *p*-tolylhydrazone. There was obtained 0.37 g., 74%, of 1-(*p*-tolyl)-3-carboxy-6-pyridazone, m.p. 229–230°, recrystallized from ethyl acetate.

Anal. Calcd. for $C_{12}H_{10}O_3N_2$: N, 12.17. Found: N, 12.19.

1-(*o*-Methoxyphenyl)-3-carboxy-6-pyridazone (IV, Ar = *o*-Methoxyphenyl).—This compound was prepared by the procedure given for the *o*-tolyl analog from 0.7 g. of the *o*-methoxyphenylhydrazone. There was obtained 0.49 g., 70%, of 1-(*o*-methoxyphenyl)-3-carboxy-6-pyridazone, m.p. 212–213°, recrystallized from ethyl acetate.

Anal. Calcd. for $C_{12}H_{10}O_4N_2$: C, 58.53; H, 4.07; neut. equiv., 244. Found: C, 58.69; H, 4.37; neut. equiv., 244.

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1,3-*O*-Benzylidene-2,5-di-*O*-*p*-tolylsulfonyl-*DL*-arabitol

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In a preceding communication¹ we described the tosylation of 1,3-*O*-benzylidene-*D*-arabitol. Under forcing conditions (25 molecular equivalents of *p*-toluenesulfonyl chloride in excess pyridine for 5 days at room temperature) the expected tri-*O*-tosyl derivative was obtained, but under milder conditions (6 molecular equivalents of reagent for 3 days at room temperature) the principal product was a di-*O*-tosyl derivative that we presumed, from general rules of substitution, to be 1,3-*O*-benzylidene-4,5-di-*O*-*p*-tolylsulfonyl-*D*-arabitol. Grewe and Pachaly,² in a paper that we had overlooked earlier, effected the unimolecular tosylation of 1,3-*O*-benzylidene-*L*-arabitol; in addition to a 50% yield of the desired 5-*O*-tosyl derivative, they isolated 12% of a di-*O*-tosyl derivative that melted at 136.5° and showed $[\alpha]^{20}_D +11.3^\circ$ in pyridine (*c* 1.1). Our di-*O*-tosyl compound melted at 135–136° and showed $[\alpha]^{20}_D -18.1^\circ$ in chloroform and, we now find, -10.3° in pyridine (*c* 1.1). Thus, Grewe and Pachaly's compound and our compound appeared to be enantiomorphs. Professor Grewe kindly sent us some of his product and we have verified the antipodal nature of the two substances by direct comparison of their infrared spectra and X-ray powder diffraction patterns, and finally through the preparation of a racemic compound whose melting point of 152–154° is nearly 20°

(1) E. Zissis and N. K. Richtmyer, *THIS JOURNAL*, **76**, 5515 (1954)

(2) R. Grewe and H. Pachaly, *Chem. Ber.*, **87**, 46 (1954).

higher than that of its optically active components.

Since Grewe and Pachaly have proved their compound to have a 2,5-di-*O*-tosyl structure rather than the 4,5-di-*O*-tosyl structure that we had guessed for our compound, the latter may now be written with confidence as 1,3-*O*-benzylidene-2,5-di-*O*-*p*-tolylsulfonyl-D-arabitol. The analogous, partially tosylated 1,3-*O*-methylene-D-arabitol (m.p. 161–163°) to which we assigned tentatively a 4,5-di-*O*-tosyl structure, now appears more likely to be 1,3-*O*-methylene-2,5-di-*O*-*p*-tolylsulfonyl-D-arabitol.

Experimental

1,3-*O*-Benzylidene-2,5-di-*O*-*p*-tolylsulfonyl-DL-arabitol.—About 0.15 g. of each enantiomorph was dissolved in 5 ml.

of chloroform, and the mixture diluted with *n*-pentane as the racemate began to crystallize in clusters of needles. After two recrystallizations from chloroform-pentane and one from ethanol, the product melted at 152–154° and showed no detectable rotation in chloroform (c 0.8, l 4).

Anal. Calcd. for $C_{26}H_{28}O_9S_2$: C, 56.92; H, 5.14; S, 11.69. Found: C, 56.77; H, 4.88; S, 11.71.

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COMMUNICATIONS TO THE EDITOR

THE STABILITIES OF 1,3,5-TRINITROBENZENE COMPLEXES OF ORTHO SUBSTITUTED BIPHENYLS

Sir:

X-Ray diffraction studies of crystalline 1:1 complexes of aromatic substances with 1,3,5-trinitrobenzene or benzoquinone, both of which seem to function as electron acceptors in the interactions, show that the acceptor molecule is oriented in the complex with its ring plane parallel to and separated by somewhat over 3 Å. from the plane of the donor ring.¹ Studies are in progress in this Laboratory to test whether or not the attainment of this parallel plane configuration by the complex components is highly critical for the achievement of maximum complex stability.

A clearly positive answer to this question has now been obtained through the evaluation of equilibrium constants for formation of 1:1 complexes of a series of methyl substituted biphenyls with 1,3,5-trinitrobenzene in carbon tetrachloride at 25°. These were determined through colorimetric investigation in the 340–415 $m\mu$ region, in which the complexes show characteristic absorption, of a series of solutions in which the biphenyl concentrations varied from 0.05–0.5 M and the concentration of the nitro compound ranged from 10^{-3} to 10^{-4} M .² The equilibrium constant, K_1 (see equation 1) measured for the complex of

$$K_1 = (\text{complex})/(\text{biphenyl})(\text{TNB}) \quad (1)$$

biphenyl itself was 0.92 mole⁻¹ l. The corresponding constants for the isomeric monomethyl biphenyls were 0.35 (ortho), 1.38 (meta) and 1.70 (para). For symmetrically substituted dimethylbiphenyls values of 0.34 (*o,o'*), 1.65 (*m,m'*) and 2.40 (*p,p'*) were obtained, and for bimesityl K_1 was <0.1.

(1) (a) H. M. Powell and G. Huse, *J. Chem. Soc.*, 435 (1943); (b) J. S. Anderson, *Nature*, **140**, 583 (1937).

(2) The method is essentially that used to measure stabilities of other colored complexes of aromatic substances in solution; cf. L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **75**, 3776 (1953); S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, *ibid.*, **76**, 69 (1954).

The electronically favorable effects of methyl substituents on complex stabilities,³ which are apparent in the K_1 values for the *m*- and *p*-substituted donors, are obviously negated when those substituents are so placed that they offer steric inhibition to the assumption of a coplanar configuration by the two rings of the donor molecule. This steric effect is manifested by even a single ortho substituent and is extreme in the case of bimesityl.⁴

It seems likely that 1,3,5-trinitrobenzene in a 1:1 complex with biphenyl would interact strongly with only one ring of the donor. Apparently, then, in a hindered biphenyl type donor one phenyl group, through interference with the nitro groups which protrude from the perimeter of the acceptor ring, forces the acceptor out of a favorable parallel orientation to the ring with which it is interacting or forces a wider separation between the donor and acceptor rings than is favorable to the interaction. It seems doubtful, in the case of those ortho substituted biphenyl molecules which have actually coordinated with *s*-trinitrobenzene, that the two rings of the donor can have been forced into a coplanar configuration. This would require that the heats of formation of complexes of hindered and unhindered biphenyls would differ by rather large amounts (possibly by as much as the energy of activation reported for the racemization of an optically active biphenyl⁵), and there is

(3) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

(4) It is significant that only those ortho substituted biphenyls in which the substituents are small enough to offer no hindrance to coplanarity of the donor rings form crystalline complexes with 2,4,7-trinitrofluorenone. There is also evidence that the stabilities of complexes of this acceptor with 1-cyclohexenyl- and 1-cyclopentenyl-naphthalenes are reduced by the presence of methyl substituents at ortho positions in the cycloalkenyl rings; cf. C. B. Coleman, Abstracts of Papers Presented at Minneapolis, Minn., Division of Organic Chemistry, American Chemical Society, Sept., 1955; L. H. Klemm, J. W. Sprague and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

(5) R. L. Shriner, R. Adams and C. S. Marvel in "Organic Chemistry," Vol. I, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 357.