

NOTES.

Action of a Mixture of Acetic Anhydride and Sulphuric Acid on an Acetic Acid Solution of cycloHexene.
By R. SPERLING.

THE products of this reaction, first described by Friese (*Ber.*, 1931, **64**, B, 2103), have now been identified as *cis*-cyclohexanol-2-sulphonic acid and cyclohexene-1-sulphonic acid. Friese, however, isolated *cis*-cyclohexanol-2-sulphonic acid only as its barium salt. If the mother-liquor are concentrated, crystals of barium cyclohexene-1-sulphonate separate and can be purified by extraction with 75% aqueous alcohol, followed by recrystallisation from 50% aqueous alcohol.

This reaction is of interest as cyclohexene-1-sulphonic acid cannot be obtained by the action of a mixture of acetic anhydride, sulphuric acid, and acetic acid on *cis*-cyclohexanol-2-sulphonic acid. It is probable that acetic anhydride reacts with sulphuric acid to form a mixed anhydride (Russell and Cameron, *J. Amer. Chem. Soc.*, 1938, **60**, 1345) which then adds to cyclohexene forming *cis*- and *trans*-isomers of acetoxy-cyclohexanol-2-sulphonic acid, which hydrolyse to give *cis*-cyclohexanol-2-sulphonic acid and cyclohexene-1-sulphonic acid, respectively. There is no experimental evidence in support of this, but, in a similar reaction between sulphuryl chloride and cyclohexene in the presence of acetic anhydride and acetic acid, *cis*- and *trans*-isomers of 2-chlorocyclohexyl acetate are formed (Friese and Djiany, *Ber.*, 1938, **71**, B, 667).

Experimental.—(M. p.s are corrected.) cycloHexene (32 g.) was added to a mixture of acetic acid (130 ml.) and concentrated sulphuric acid (25.5 ml.), cooled to -20° , and acetic anhydride (150 ml.) then added. A slight rise in temperature occurred and the mixture became reddish-brown. After being kept overnight at room temperature, the mixture was poured into 500 ml. of ice water, and the acetic acid removed under reduced pressure. The residue was neutralized with barium hydroxide, and the precipitated barium sulphate filtered off. The filtrate was evaporated to small bulk on the steam-bath, whereupon barium *cis*-cyclohexanol-2-sulphonate (25.8 g.) crystallised; this was recrystallised from water. Barium cyclohexene-1-sulphonate was obtained on concentrating the mother-liquors and was purified by extraction with 75% aqueous alcohol and subsequent recrystallisation from 50% aqueous alcohol (yield, 33.0 g.).

Barium cis-cyclohexanol-2-sulphonate. The above product was identical with that produced by the action of hydrogen sulphites on cyclohexene oxide (Found: Ba, 27.66. Calc. for $C_{12}H_{22}O_8S_2Ba$: Ba, 27.7%). It led to a phenylhydrazine salt, diamond-shaped plates, m. p. $140-141^{\circ}$, alone or mixed with an authentic specimen.

Barium cyclohexene-1-sulphonate. The above product crystallised from water or aqueous alcohol as hexagonal plates (Found: Ba, 28.7. Calc. for $C_{12}H_{18}O_8Ba, H_2O$: Ba, 28.76%), which became anhydrous at 130° . The aqueous solution decolorised potassium permanganate and bromine water, barium sulphate not being precipitated by the latter reagent. Oxidation with nitric acid (d 1.28) at 80° gave adipic acid, m. p. 151° (equiv., 73). It led to a benzylthiuronium salt, needles, m. p. $150-151^{\circ}$ alone or mixed with an authentic specimen, and a phenylhydrazine salt, needles, m. p. $141-143^{\circ}$.

cis-cycloHexanol-2-sulphonic acid was sulphated by sulphuric acid, and the barium salt of the resulting *cis*-2-sulphocyclohexyl hydrogen sulphate converted into the sodium salt by the addition of the calculated amount of sodium sulphate. The sodium salt was heated at 170° for 6 hours, the resulting acidic product dissolved in water, neutralized with sodium hydroxide, evaporated to small bulk, and treated with 3 volumes of alcohol to precipitate sodium sulphate, which was filtered off. When the filtrate was evaporated to small bulk, large rectangular crystals of sodium cyclohexene-1-sulphonate monohydrate crystallised and were purified by recrystallisation from water. Yield, 3 g. The barium salt of *cis*-2-sulphocyclohexyl hydrogen sulphate gave 27.3% of sodium cyclohexene-1-sulphonate (Found: sulphated ash content of anhydrous salt, 38.6. Calc. for $C_6H_9SO_3Na$: ash, 38.55%). The

aqueous solution decolorised potassium permanganate and bromine water, and oxidation with nitric acid gave adipic acid, m. p. 151°. The benzylthiuronium salt formed needles, m. p. 150—151°.

The author thanks the Board and Management of Messrs. Manchester Oil Refinery Ltd. for their permission to publish this work.—CHEMICAL RESEARCH DEPARTMENT, MANCHESTER OIL REFINERY LTD. [Received, February 11th, 1949.]

Preparation of cis-cycloHexane-1 : 2-disulphonic Acid. By R. SPERLING.

THE action of ammonium hydrogen sulphite solution (pH 2.2—5.4) on cyclohexene in the presence of oxygen gives *cis*-cyclohexane-1 : 2-disulphonic acid. If the pH of the mixture is too high, cyclohexanesulphonic acid is produced instead. The acid was found to be identical with that produced by oxidizing 1 : 2-cyclohexylene dithiocyanate with nitric acid. The low solubility of the barium salt in water, and its inability to lead to a benzylthiuronium salt derivative, are indicative of hydrogen bonding (cf. this vol., p. 1925).

Kharasch and his collaborators (*J. Amer. Chem. Soc.*, 1939, **61**, 3092) proposed a radical mechanism for the reaction of hydrogen sulphites with unsaturated compounds, in which a hydrogen sulphite free radical is produced by the removal of an electron from a hydrogen sulphite ion, the free radical then adding to the unsaturated carbon atom forming a free radical complex. In the normal course of the reaction, a hydrogen atom is acquired by the complex, thus giving a saturated sulphonic acid. The reaction between cyclohexene and ammonium hydrogen sulphite solution of pH 2.2—5.4 is unusual in that the free-radical complex appears to acquire a second hydrogen sulphite free radical, forming a disulphonic acid.

Experimental.—(M. p.s are corrected.) *Action of ammonium hydrogen sulphite on cyclohexene.* cycloHexene (12 g.) was shaken with 2*N*-ammonium hydrogen sulphite solution (pH adjusted to 3.9 by addition of SO₂) (200 ml.) for 17 days at room temperature, ammonium persulphate (0.1 g.) being added as catalyst and the space above the liquid filled with oxygen (replenished at intervals since it was absorbed during the reaction). The mixture was then heated to the b. p., barium hydroxide added until no more ammonia was evolved, the excess of barium hydroxide neutralised with sulphuric acid, and the precipitated barium sulphate and sulphite were filtered off. The filtrate was evaporated to small volume, and the resulting crystals recrystallised from water. 8.6 G. of barium of *cis*-cyclohexane-1 : 2-disulphonic acid dihydrate were obtained as colourless needles (Found : Ba, 32.8. C₆H₁₀S₂O₈Ba.2H₂O requires Ba, 33.05%). The solubility of the salt in water is 0.3 g. per 100 ml. at 20°. It does not lead to a benzylthiuronium salt. The phenylhydrazine salt is obtained as colourless elongated rectangular plates, m. p. 264—265°, recrystallised from 75% aqueous alcohol.

Yields of barium *cis*-cyclohexane-1 : 2-disulphonate and cyclohexanesulphonate, respectively, were : at pH 5.4, 0.65 and 4.1 ; at pH 3.9, 8.6 and 0 ; at pH 2.2, 5.5 and 0 g.

Synthesis of cis-cycloHexane-1 : 2-disulphonic acid.—1 : 2-cycloHexylene dithiocyanate was prepared by the action of thiocyanogen on cyclohexene at 0° (Dermer and Dysinger, *J. Amer. Chem. Soc.*, 1939, **61**, 750). Recrystallisation from alcohol gave colourless crystals, m. p. 57.5° (Found : S, 33.2. Calc. for C₈H₁₀N₂S₂ : S, 32.4%). To 2.8 g. of dithiocyanate were added 20 ml. of nitric acid (*d* 1.28) containing 0.1% of ammonium vanadate, and the mixture was heated at 80° for 1 hour. Neutralisation with barium hydroxide precipitated the crude barium disulphonate which crystallised from water as colourless needles (dihydrate) (Found : Ba, 33.37%) ; yield, 5.7 g. (97%). The barium salt becomes anhydrous on heating to 120°. The derived phenylhydrazine salt formed colourless elongated plates, m. p. 264—265° alone or mixed with that described above.

The author thanks the Board and Management of Messrs. Manchester Oil Refinery Ltd. for permission to publish this work.—CHEMICAL RESEARCH DEPARTMENT, MANCHESTER OIL REFINERY LTD. [Received, February 11th, 1949.]

The Benzidine Transformation. By D. LL. HAMMICK and S. F. MASON.

RECENTLY a mechanism for the benzidine transformation was proposed by us (*J.*, 1946, 638), in which an attempt was made to overcome the stereochemical difficulties inherent in any such mechanism.

We suggested that if appreciable *p-p'*-bonding takes place before the fission of the N-N bond, structures of the type (I) must play a large part in the activated transition hybrid, because, with an angle of 120° to the *p*-quinonoid nucleus for the C-NH₂⁺ bond, it becomes possible for the *pp'*-carbon atoms to approach to within 1.50 Å. of each other, *i.e.*, to well within bonding distance (C-C, 1.54 Å.).



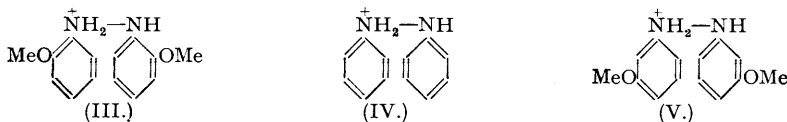
Dewar (*J.*, 1946, 777 ; also "The Electronic Theory of Organic Chemistry," O.U.P., 1949) has entirely misrepresented our views, stating that we propose a boat-shaped quinonoid structure of the type (II). Such a structure was not even mentioned, much less discussed, by us in our paper. Structures of the type (II) would of course bring the *pp'*-carbon atoms into a proximity even closer than 1.50 Å., but, if appreciable resonance with benzenoid structures occurs, the quinonoid ring must be sensibly planar.

Dewar suggests that the observed range of activation energies for the benzidine transformation (11—19 kcal.) definitely rules out our mechanism, since the loss of resonance energy in the benzene ring (39 kcal.) would render the activation energy prohibitively high (we assume in this instance that he

refers to our actual mechanism, and not to his version of it). The advantage of any continuous mechanism proposed for the benzidine transformation is surely that the energy released by the formation of the *pp'*-linkage (58.6 kcal.) effectively lowers the activation energy required for the fission of the N-N bond (23.6 kcal.) and other postulated electron shifts, in this case the transition from a benzenoid to a *p*-quinonoid nucleus (32.2 kcal.). Discontinuous mechanisms, such as that proposed by Dewar (*loc. cit.*), have no such advantage. His proposed initial stage, the fission of the N-N bond, requires an energy higher than any of the observed activation energies.

Dewar (*op. cit.*, p. 236) further criticises the mechanism suggested by us on the grounds that it does not account for other rearrangements of *N*-substituted anilines. Apart from the benzidine transformation, migration to other nuclei has been reported in nearly all other cases of *N*-substituted anilines, so perhaps it is not unreasonable to postulate a special mechanism for the benzidine case.

Finally, Dewar (*loc. cit.*) finds the rates of rearrangement of substituted hydrazobenzenes to be in the order (III) \gg (IV) > (V), and suggests that a reverse order would be expected on the Robinson mechanism, of which our mechanism is a modification.

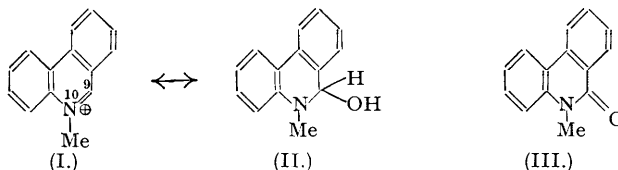


In fact the predominating electromeric effect ($-E$) of the methoxyl group would be expected to promote the formation of a structure of type (I) in the case of (III), and to repress it in the case of (V), thus giving the observed order in the rates of rearrangement.—THE DYSON PERRINS LABORATORY, UNIVERSITY OF OXFORD, and THE MUSEUM OF THE HISTORY OF SCIENCE, UNIVERSITY OF OXFORD. [Received, February 21st, 1949.]

The Ionization of Quaternary Phenanthridine Bases. By D. MAGRATH and J. N. PHILLIPS.

THE ionization constants of phenanthridine and its primary amino-derivatives have recently been published (Albert, Goldacre, and Phillips, *J.*, 1948, 2240). The ionization constants of some simple phenanthridinium compounds are now reported. The results obtained may contribute to an understanding of the mode of action of the trypanocidal phenanthridines, all known examples of which are quaternary (Walls, *J. Soc. Chem. Ind.*, 1947, 66, 182r).

The ionization measured was the pK_a^E , *i.e.*, the ionization constant expressing the equilibrium between (I) and the corresponding non-ionized carbinol (II). This ionization is of the type discussed by Goldacre and Phillips (this vol., p. 1724) for the triphenylmethanes and the quaternary acridine bases. Because carbinols of the type (II), when not substituted in the 9-position, could be biologically oxidized to non-basic ketones of the type (III), 9 : 10-dimethylphenanthridinium chloride was investigated as well as 10-methylphenanthridinium chloride. The results given below show that both these substances are completely ionized at pH 7.



The measurements were made absorptiometrically in a series of aqueous buffers, as described by Goldacre and Phillips (*loc. cit.*) at $25 \pm 1^\circ$ and a concentration of 1.3×10^{-5} M. The pK_a (equilibrium) of 10-methylphenanthridinium chloride was 10.4 ± 0.2 and that of the 9 : 10-dimethyl derivative 10.1 ± 0.2 .

9 : 10-Dimethylphenanthridinium Chloride.—9 : 10-Dimethylphenanthridinium iodide (3 g.; Pictet and Hubert, *Ber.*, 1896, 29, 1185) in water (180 ml.) was heated under reflux and stirred mechanically with 1.5 equivalents of freshly precipitated silver chloride for 2 hours, in subdued artificial light. After filtration, the filtrate was evaporated to give a solid, m. p. 245° , free from iodine. This was recrystallized from aqueous acetone, giving pale yellow crystals of 9 : 10-dimethylphenanthridinium chloride, m. p. 248° (76%) (Found : N, 5.8. $C_{15}H_{14}NCl$ requires N, 5.75%).

10-Methylphenanthridinium Chloride.—10-Methylphenanthridinium iodide, similarly treated, gave 10-methylphenanthridinium chloride (80%) as pale yellow hydrated crystals, m. p. ca. 215° (decomp.) (Found : N, 5.7. $C_{14}H_{12}NCl \cdot H_2O$ requires N, 5.65%).—THE UNIVERSITY, SYDNEY. [Received, February 3rd, 1949.]

The Reaction of "Copper Hydride" with Acid Chlorides. By E. A. BRAUDE.

It has been claimed (Chiozza, *Annalen*, 1853, 85, 232; Wohl and Mylo, *Ber.*, 1912, 45, 328) that benzaldehyde is formed in the reaction between "copper hydride" and benzoyl chloride, and that the reaction with acetyl chloride similarly gives acetaldehyde which under the conditions employed is then reduced to ethanol and converted thence into ethyl acetate. Copper hydride is an endothermic compound (cf. Sieverts and Gotta, *Annalen*, 1927, 453, 289) and the reaction $R \cdot COCl + CuH \longrightarrow R \cdot CHO + CuCl$ is thermodynamically feasible; it therefore appeared worth while to investigate its

possible synthetic applications, especially in view of the successful use of other metal hydrides as reducing agents for organic compounds (cf. Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197; Chaikin and Brown, *ibid.*, 1949, **71**, 122).

The usual procedure for the preparation of copper hydride (cf. Vorländer and Meyer, *Annalen*, 1902, **320**, 122) consists of the reduction of copper sulphate with sodium hypophosphite in dilute sulphuric acid at *ca.* 50°, filtration of the brown precipitate, and washing with alcohol and then ether. When the air-dried product (15 g.) thus obtained was heated under reflux for 2—3 hours with a solution of freshly distilled benzoyl chloride (18 g.) in *n*-hexane or ether, hydrogen was evolved and the products obtained were some unchanged benzoyl chloride, benzoic acid (11 g., 70%), and a small proportion of ethyl benzoate (2 g., 10%), but no trace of benzaldehyde could be detected. The inorganic residue consisted largely of cuprous chloride. The same result is obtained if the reaction is carried out in an atmosphere of nitrogen or in an autoclave, in the absence of solvent. The benzoic acid is therefore *not* produced by the oxidation of benzaldehyde formed as an intermediate.

Copper hydride is known to contain water and to decompose explosively when dried over dehydrating agents (cf. Sieverts and Gotta, *loc. cit.*). The reaction with benzoyl chloride thus appears to be a simple hydrolysis to give benzoic acid, followed by interaction of the hydrogen chloride liberated with the hydride. The production of ethyl benzoate is due to the tenacious retention of some ethanol after the washing; if the moist hydride is washed with acetone, followed by ether, no ethyl benzoate is obtained. The reaction of the acetone-ether washed hydride (15 g.) with freshly distilled acetyl chloride (20 g.) in ether similarly gave only a little unchanged acetyl chloride and acetic acid (12 g., 80%). The acetone-ether washed hydride was found to contain *ca.* 60% of copper, corresponding to the composition $\text{CuH}_2\text{H}_2\text{O}$. Although it has been stated (Müller and Bradley, *J.*, 1926, 1669) that the crystal structure of copper hydride is independent of the water content, it appears that two molecules of water form an essential part of the compound but can be partly replaced by ethanol.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7. [Received, January 26th, 1949.]
