relationship holds for benzimidazole.[9] It is not unreasonable to assume that this relationship is also applicable to imidazole any error arising from this assumption being smaller than the uncertainty in the K_h of imidazole at ionic strength 0.5. Using the average value of 3.89 obtained at ionic strength 0.5 we obtain a pK_h° of -0.52. Using a pK_w° of 14 for water we obtain a thermodynamic acidity constant, pK_a°, of 14.52. This value is greater than the value previously estimated[3] by 0.3 pK units which difference shows that a 2-phenyl group is more effective in increasing the acid strength of imidazole than of benzimidazole or 4 (or 5)-phenylimidazole. The experimentally based value though differing from the estimated one is nevertheless in harmony with the qualitative theoretical arguments presented previously[3] relative to the acid strengths of imidazole and its derivatives.

The observed acid strength of imidazole readily explains the aforementioned instability of alkali salts of imidazole in water. However, our experiments show no justification for referring to imidazole as pseudoacidic.

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(9) Details of this determination will be reported as part of a separate communication.

Bromination of β-Phenylglutaric Acid

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β-Phenylglutaric acid might be expected to undergo bromination in either the *alpha* position of the glutaric acid or in the phenyl ring, depending on the conditions of the bromination. We have found that even under conditions which should favor bromination in the *alpha* position (*e.g.*, in the presence of phosphorus trichloride) the only product isolated is β-(*p*-bromophenyl)glutaric acid. The bromination of the aromatic portion of the molecule even in the absence of the usual catalysts is surprising. The yield is only 18% when the bromination is carried out in the presence of phosphorus trichloride but a 60–65% yield can be obtained by simply mixing β-phenylglutaric acid with bromine and allowing the mixture to stand until no more hydrogen bromide is given off. Efforts to effect side chain halogenation by exposing the reaction mixture to ultraviolet light did not affect the yield of *para*-substituted product.

The low yields under some conditions may be the result of attack at the benzylic or *beta* position as well as at the *alpha* and *para* positions to give a mixture from which no definite product could be isolated. The failure to form any appreciable amount of *alpha* substituted product may possibly be due to failure of phosphorus trichloride to convert the acid to its acid chloride. This point has not been investigated.

The great ease with which bromine enters the ring of β-phenylglutaric acid prompted us to look for other examples of facile ring substitution by bromine. Both side chain and nuclear bromination of cumene is reported to take place in sunlight.[2] Qvist[3] reports the preparation of *p*-bromocumene by the action of bromine alone on cumene.

The nuclear bromination described here can perhaps be explained by an ionic mechanism in which the aromatic system exhibits basic characteristics and complexes with the bromine to form intermediates of the type A Br^+ Br^-. Such an explanation has been suggested by Buckles. Hausman, and Wheeler[4] for the formation of *p,p'*-dibromobiphenyl from biphenyl and bromine vapor.

EXPERIMENTAL

β-(p-Bromophenyl) glutaric acid. To 5 g. (0.024 mole) of β-phenylglutaric acid[5] in an open beaker was added 5.7 g. (1.8 ml., 0.036 mole) of bromine. The mixture was stirred with a glass rod so that all of the acid came in contact with the bromine. Evolution of hydrogen bromide started immediately and ceased after 7 to 8 hours. The mixture was washed repeatedly with cold water, dried, and recrystallized from acetone to give 4.1 to 4.5 g. (60–65%) of β-(*p*-bromophenyl) glutaric acid, m.p. 177–178°.

Anal. Calc'd for $C_{11}H_{11}BrO_4$: C, 46.0; H, 3.86. Found: C, 46.2; H, 3.81. Neut. equiv., Calc'd: 143.5. Found: 142.5.

When a sample of the product was heated with alkali, the resulting solution upon acidification gave a negative test with silver nitrate. Oxidation with permanganate gave *p*-bromobenzoic acid, m.p. 245–246°. Neut. equiv., Calc'd: 201. Found: 203.

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[1] Guest Scholar, 1954–1955.

(2) Varma and Arinivasan, *J. Indian Chem. Soc.*, **13**, 187–188 (1936).

(3) Qvist, *Acta Acad. Aboensis, Math. et Phys.*, **10**, No. 5 (1937).

(4) Buckles, Hausman, and Wheeler, *J. Am. Chem. Soc.*, **72**, 2494 (1950).

(5) Smith and Kort, *J. Am. Chem. Soc.*, **72**, 1877 (1950).