temperature for 2 hr. The solvent mixture of acid and anhydride was removed by distillation at aspirator pressure and the residue was collected at 60° (2 mm.) to yield 6.43 g. (36%) of nitro-*tert*-butyl trifluoroacetate. The infrared spectrum of this material was virtually identical with that of authentic nitro-*tert*-butyl trifluoroacetate.

Hydrolysis of nitro-tert-butyl trifluoroacetate. To 2.0 g. (0.0168 mole) of nitro-*tert*-butyl trifluoroacetate were added 10 ml. of water and 3 drops of concd. sulfuric acid. The mixture was refluxed for *ca.* 5 min., and then solid sodium bicarbonate was added in sufficient quantity to neutralize the sulfuric and trifluoroacetic acids. The product was extracted with ether and the dried ether extract evaporated; 1.5 ml. of phenyl isocyanate was added to the residue and the mixture was heated overnight on the steam bath. The mixture was worked up as in the preparation of the phenyl urethane of nitro-*tert*-butyl alcohol to yield 2.39 g. of crude product, m.p. 80–85° after one recrystallization.

Characterization of the tert-butyl nitrate trifluoroacetolysis product. Two grams of the trifluoroacetolysis product was worked up as in the hydrolysis of nitro-*tert*-butyl trifluoroacetate to yield 2.17 g. of urethane, m.p. 80–81°, after one recrystallization. The mixture melting point with nitro-*tert*-butyl phenyl urethane was 81–82°. The infrared spectra of the two samples were identical.

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Studies of the Cyclization of *o*-Benzoylbenzoic-Carboxyl-C^{14} Acid

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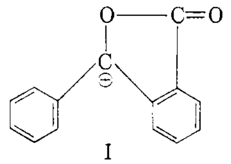
Newman and co-workers[1,2] have presented strong arguments that when *o*-benzoylbenzoic acid is dissolved in concentrated sulfuric acid, the organic acid is almost entirely converted to a cyclic positive ion, I. According to their views the cyclization of



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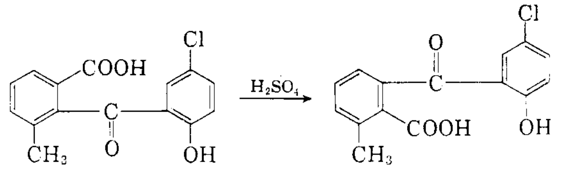
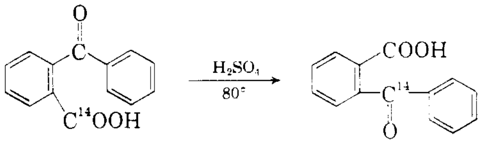
the dissolved *o*-benzoylbenzoic acid upon heating this sulfuric acid solution involves a rate-determining conversion of the cyclic positive ion to anthraquinone with the ejection of a proton.

Studies of the cyclization of *o*-benzoylbenzoic-carboxyl-C^{14} acid have provided additional information bearing on the mechanism of the cyclization in concentrated sulfuric acid.

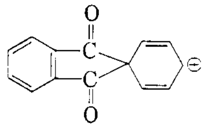
Hayashi rearrangement[3,4] accompanies cyclization of certain substituted *o*-benzoylbenzoic acids. This rearrangement is exemplified by the reaction[3]: It is apparent that any Hayashi rear-



rangement accompanying the cyclization of *o*-benzoylbenzoic acid could be detected only by the use of isotopic labeling. A sample of *o*-benzoylbenzoic-*carboxyl*-C^{14} acid was cyclized to the extent of 16% at 80° in concentrated sulfuric acid. The 84% unchanged acid was recovered, purified, and degraded by decarboxylation at 275° to benzophenone. As the pure 2,4-dinitrophenylhydrazone prepared from this benzophenone contained little more than background activity, no measurable degree of Hayashi rearrangement could be detected. Hayashi rearrangement of *o*-benzoylbenzoic-*carboxyl*-C^{14} acid would lead to carbon-14 in the keto group:



This result also eliminates any intermediate in the cyclization reaction in which the two nonaromatic carbon atoms are equilibrated with each other and with the unchanged acid at a rate which is rapid in comparison with the overall reaction rate. The symmetrical ion, for example, is not a



significant part of the reaction path. The present result is in accord with the Newman[1] mechanism, inasmuch as the latter does not provide a path for Hayashi rearrangement during cyclization of *o*-benzoylbenzoic acid to anthraquinone.

It now appears that the 3.5% carbon-14 isotope effect[5] in the cyclization of *o*-benzoylbenzoic-carboxyl-C^{14} acid is *not* an effect of carbon-14 substitution on the pre-rate equilibrium between *o*-benzoylbenzoic acid and the oxocarbonium ion, $C_6H_5COC_6H_4CO^+$ (II), as was suggested earlier.[5] Rather, this carbon-14 isotope effect, being of *intermediate magnitude*, appears to be either (a) an isotope effect on a pre-rate equilibrium between I and II or (b) a kinetic isotope effect on a concerted process which converts I directly to anthraquinone with ejection of a proton.

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(1) M. S. Newman, *J. Am. Chem. Soc.*, **64**, 2324 (1942).

(2) M. S. Newman, H. G. Kuivala, and A. B. Garrett, *J. Am. Chem. Soc.*, **67**, 704 (1945).

(3) M. Hayashi, *J. Chem. Soc.*, 2516 (1927).

(4) R. B. Sandin, R. M. Melby, R. Crawford, and D. McGreer, *J. Am. Chem. Soc.*, **78**, 3817 (1956).

(5) Gus A. Ropp, *J. Chem. Phys.*, **23**, 2196 (1956).

EXPERIMENTAL

Partial conversion of o-benzoylbenzoic-carboxyl-C^{14} acid to labeled anthraquinone. In 25 ml. of C.P. sulfuric acid, 850 mg. of *o*-benzoylbenzoic-carboxyl-C^{14} acid was dissolved at room temperature to form a clear, red solution. This was heated in an oil bath 20 min. at 80°. The solution was poured onto ice, warmed to room temperature, and digested for 15 min. on a steam bath. The mixture was cooled in ice and the precipitated solid was collected on a filter and washed with water. The solid was extracted with $4N$ sodium hydroxide. The alkali-insoluble residue was washed with water and dried to give 130 mg. (16.5%) of labeled anthraquinone which was identified by its melting point after a recrystallization from ethanol. The alkaline solution was acidified and the recovered *o*-benzoylbenzoic-carboxyl-C^{14} acid was collected on a filter, washed with water, dried, and recrystallized from a hexane-benzene solution. Degradation of the purified, recovered acid was performed by the method of Dougherty.[6] Radioassays were performed by a modification of the method described by Neville.[7]

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(6) G. Dougherty, *J. Am. Chem. Soc.*, **50**, 571 (1928).

(7) O. K. Neville, *J. Am. Chem. Soc.*, **70**, 3501 (1948).

2,4′-Biquinolyl

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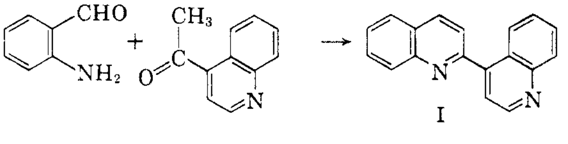
2,4′-Biquinolyl (I) is not among the series of known biquinolyls. The possibility that derivatives of this diquinolyl system might be formed in certain reductive coupling reactions that are currently under investigation prompted us to prepare the parent heteroaromatic compound for reference and for comparison with other known biquinolyls.

The intermediates for the synthesis of I were all known compounds. Starting from isatin, the sequence included 1-acetylisatin, 4-carboxycarbostyril, 2-chlorocinchoninic acid, cinchoninic acid, ethyl cinchoninate, and methyl 4-quinolyl ketone.[1] The last stage involved a Friedländer condensation of the ketone with *o*-aminobenzaldehyde to give 2,4′-biquinolyl.



I

The structure I for the final base is shown by the method of synthesis, its absorption spectra, and the preparation of salts. Spectroscopically, the base shows absorption in the ultraviolet like quinoline and other biquinolyls.[2] 2,4′-Biquinolyl forms a monopicrate salt in accord with the pattern observed by Abramovitch in the pyridylquinoline series.[3] Even with perchloric acid, the stable salt obtained was the monoprotonated derivative. Although a high-melting salt (m.p. 274°) was obtained from 2,4′-biquinolyl and concentrated perchloric acid, recrystallization from acidic methanol repeatedly afforded only a lower-melting monoperchlorate (m.p. 239–240°).[4]

Further evidence for the 2,4′-biquinolyl structure (I) is obtained from the infrared spectrum. There is no band in the region of 3.0 μ(N–H) nor in the range 5.8–6.0 μ (ketone or aldehyde carbonyl). There is a series of bands (6.20, 6.28, 6.35, 6.40, and 6.43 μ) of weak to medium intensity that show a general similarity to the spectra of other quinoline derivatives. However, the strongest bands appear in the region 11–14 μ where the C—H out-of-plane deformation vibrations arise. This portion of the spectrum has been widely used to study substitution in aromatic compounds, and it has been proposed that the correlations of the band positions with the number of adjacent hydrogens can be extended to pyridine and quinoline if the nitrogen is regarded as a substituted ring atom and, in the case of a bicyclic aromatic compound, if the two rings are considered separately.[5] For 2,4′-biquinolyl, however, there were only three strong bands observed within the usually accepted region. These were found at 11.96, 13.27, and 13.53 μ. The first of these is like the band in *p*-disubstituted benzenes and may, as a single band, be ascribed to vibrations involving two adjacent hydrogens on both pyridine rings. The other two bands are like those found in the spectra of *o*-disubstituted benzenes and may arise from the C–H deformation frequencies associated with the two benzenoid rings. Moreover, the spectrum of 2,4′-biquinolyl is generally similar in the 11–14 μ region to a composite spectrum of quinaldine and lepidine.[6]

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(1) (a) T. L. Jacobs, *et al.*, *Org. Syntheses*, **Coll. Vol. III**, 456 (1955); (b) K. N. Campbell and J. F. Kerwin, *J. Am. Chem. Soc.*, **68**, 1837 (1946); (c) C. F. Koelsch, *J. Am. Chem. Soc.*, **65**, 2460 (1943).

(2) M. Crawford and I. F. B. Smyth, *J. Chem. Soc.*, 1433 (1952).

(3) R. A. Abramovitch, *J. Chem. Soc.*, 3839 (1954).

(4) P. Krumholz, *J. Am. Chem. Soc.*, **73**, 3487 (1951) observed that the second dissociation constant for those dipyridyls in which one ring was linked at the 2-position was high compared to other isomers and that no biacid salt was formed for 2,2′-bipyridyl.

(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, 1958, p. 281. The principal limitation of this technique is that frequently the number of bands present exceeds that expected on the basis of the formulated rules, even in the carbocyclic series; *cf.* L. Cencelj and D. Hudzi, *Spectrochim. Acta*, **7**, 274 (1955); R. F. Curtis and G. Viswanath, *J. Chem. Soc.*, 1670 (1959); C. G. Cannon and G. B. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951).

(6) Although the biquinolyl spectrum was recorded from a mulled sample and the two methylquinoline spectra were taken with liquid films, our examination of other closely related compounds does not indicate that there are appreciable variations from the two sampling techniques.