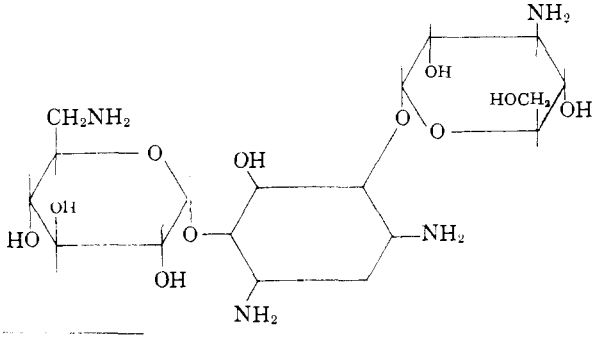
The strongly dextrorotatory properties of kanamycin, tetra-N-acetylkanamycin and especially kanamycin decaacetate[4], $[\alpha]^{24}D$ +117° (*c* 1, $CHCl_3$), support this configurational assignment. As expected, the rotation of acetylated derivatives of 3-D-glucosamine and 6-D-glucosamine[1] agree closely with the rotations of the corresponding glucose derivatives. The contribution of each of the two anomeric centers to the molar rotation (106,000) of kanamycin decaacetate must be in the order of +25,000 ± 5,000.[7] The remaining portions of each of the acetylated sugar residues may be assigned a contribution of about +20,000. Thus the total contribution of the two sugar residues, assuming the *alpha*-D configuration, must be in the order of 90,000 ± 10,000. The magnitudes of the molar rotations generally found for acetylated carbohydrates clearly favor a contribution of 16,000 ± 10,000 by the 2-deoxystreptamine moiety, compared to 66,000 or 116,000 which would be required if one or both of the glycosidic unions were of the *beta*-D-configuration.

These data allow one to write a structure for kanamycin, in which the only remaining problem is that of determining the order of attachment to the 4(6) and 6(4) positions on the all-*trans* 2-deoxystreptamine.



(7) C. S. Hudson, THIS JOURNAL, **31**, 66 (1909).

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NEW PRODUCTS FROM THE REACTION OF BENZOYL PEROXIDE WITH BENZENE[1]

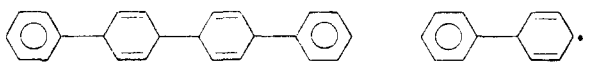
Sir:

We have been reinvestigating the reactions of aroyl peroxides with benzene at relatively high dilution in a study of the detailed reaction mechanisms. Previous product studies[2] have utilized quite concentrated solutions leading to results complicated by induced decomposition of the peroxide and by the attack of radicals on the initial products.

(1) This research was supported by the United States Air Force under Contract No. AF 49(638)-88 monitored by the AF Office of Scientific Research of the Air Research and Development Command.

(2) (a) *Cf. e.g.* the summary by C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 482; (b) B. M. Lynch and K. H. Pausacker, *Austral. J. Chem.*, **10**, 40 (1957).

We have discovered two significant new products of the thermal decomposition of benzoyl peroxide (20 g.) in benzene (4 l.) at reflux under nitrogen. In addition to the expected carbon dioxide (1.7 mole per mole of peroxide), benzoic acid (0.1 mole) and biphenyl (0.6 mole), we obtained a solid, m.p. 145–146°, identified as 1′,4′,1″,4″-tetrahydro-*p*-quaterphenyl (I) (0.03 mole) and a liquid (isolated by chromatography of the biphenyl fraction on alkaline Grade I alumina using hexane) identified as 1,4-dihydrobiphenyl (0.4 mole). We also have some evidence of 1,2-dihydrobiphenyl.



I II

The tetrahydroquaterphenyl (I) had C, 92.9; H, 7.18; mol. wt. (Signer), 303. Calcd. for $C_{24}H_{22}$: C, 92.86; H, 7.14; mol. wt. 310. It absorbed four moles of hydrogen to give the dodecahydroquaterphenyl, m.p. 202°; C, 90.0; H, 9.44. Calcd. for $C_{24}H_{30}$: C, 90.5; H, 9.50. On dehydrogenation at 300° over palladium on carbon *p*-quaterphenyl was formed, but some cleavage to biphenyl also occurred. The ultraviolet spectrum of the tetrahydroquaterphenyl is similar to that of toluene, indicating that the double bonds are not conjugated with each other nor with a benzene ring. The relatively high m.p. suggests that the compound is the nearly planar all-*cis* isomer.

1,4-Dihydrobiphenyl prepared by the Birch reduction of biphenyl[3] also has an ultraviolet curve similar to that of toluene. The infrared spectra of the initial oily fraction isolated by chromatography and the synthetic dihydrobiphenyl correspond exactly. However the ultraviolet spectra of the total dihydrobiphenyl fraction isolated by gas chromatography had an absorption maximum of 256 mμ with an apparent ε of 2000–3000, suggesting strongly the presence of some 15–30% of 1,2-dihydrobiphenyl.

Although the phenylcyclohexadienyl radical (II, and other contributing structures) is the most plausible of the previously suggested intermediates in biphenyl formation,[2] the present isolation of its combination and disproportionation products is the first direct experimental evidence for this key intermediate. We feel that this evidence taken with other data regarding radical reactivities effectively eliminates a different mechanism of biaryl formation suggested several years ago.[4]

The biaryl products obtained in a solvent such as nitrobenzene are now seen to depend on at least two distinguishable processes (a) the relative rates of formation of the isomeric substituted phenylcyclohexadienyl radicals and (b) the subsequent possibly differing rates of these radicals. It is therefore to be expected that precise values of the reactivity ratios will vary somewhat with the experimental conditions used although large variations are unlikely.[2a] Detailed interpretations of such ratios clearly require further careful studies of these systems.

(3) W. Hückel and E. Schwen, *Ber.*, **89**, 50 (1956).

(4) D. F. DeTar and S. V. Saginanli, THIS JOURNAL, **72**, 965 (1950).

Recently Davies, Hey and Williams[5] have investigated the very interesting formation of binaphthyls (among other products) from the reaction of benzoyl peroxide with naphthalene. A possible alternative to their mechanism is the formation of the dibenzoate of a dihydroxytetrahydrobinaphthyl (III), a close analog of the tetrahydroquaterphenyl (I). Such a compound could easily give a

$$C_6H_5COOC_{10}H_8\cdot \longrightarrow \underset{\text{III}}{C_6H_5COOC_{10}H_8C_{10}H_8OCOC_6H_5}$$

binaphthyl by various routes, *e.g.*, by attack of radicals or during the alkaline hydrolysis step used in the isolation procedure.

(5) D. I. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1878 (1958).

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OXYGEN FUNCTION REARRANGEMENT IN BENZOPINACOLONE[1]

Sir:

Acid catalyzed ketone rearrangements,[2] aldehyde–ketone interconversions[2,3] and closely related pinacol rearrangements[3,4] have received much attention recently. The reversibility of the ketone forming step in the pinacol rearrangement has been considered frequently and there is excellent experimental evidence that it is not reversible under many conditions.[3,5–7] However, under conditions of high acidity the reversibility of certain aliphatic ketone–ketone interconversions is well established, and Rothrock and Fry[2] have pointed out that the carbonium ion intermediates involved in the sulfuric acid catalyzed rearrangement of 3,3-dimethyl-2-butanone-1-C^{14} are identical, except for the label, with those usually proposed in the rearrangement of pinacol to pinacolone.

A further step in this reversibility of ketone rearrangements, with the concurrent pinacol rearrangement implications, has now been demonstrated. Upon treatment with strong acids under certain conditions, 1,2,2,2-tetraphenyl-1-oxoethane-1-C^{14} (benzopinacolone), is converted into a mixture of the 1- and 2-labelled ketones. Thus the oxygen function in benzopinacolone has rearranged[8] from one of the central carbon atoms to the other.

The labelled ketone was prepared by treating benzoyl-α-C^{14} chloride with triphenylmethylsodium. After rearrangement, the recovered ketone was cleaved to benzoic acid and triphenylmethane with alcoholic sodium hydroxide, and the activities of the reactants and degradation products were determined by standard methods.[2] The reaction conditions and experimental results are summarized in Table I.

The demonstration by Barton and Porter[9] that the main path for the acid catalyzed rearrangement of 2,2,4,4-tetramethyl-3-pentanone-3-C^{14} did not involve oxygen function rearrangement perhaps may be explained by the facile cleavage of the product 3,3,4,4-tetramethyl-2-pentanone.

Three of the mechanisms[2] which have been considered for ketone rearrangements would account for the oxygen function rearrangement. (1) The conjugate acid of the ketone, by a concerted or stepwise process, may form the conjugate acid of the symmetrical oxide, which upon reversal, would give equal quantities of the 1- and 2-labelled compounds. (2) In the intermediate carbonium ion, the conjugate acid hydroxyl group may migrate to the adjacent position. (3) The intermediate carbonium ion may react reversibly with water or solvent to give a pinacol or pinacol ester.[2,3,5]

These results point up the necessity for keeping the possibility of oxygen function migration clearly in mind in interpreting results of studies of the

TABLE I

OXYGEN FUNCTION REARRANGEMENT IN BENZOPINACOLONE

Reaction medium	Temp., °C.	Time, hr.	Relative molar activities[a] Benzoic acid	Triphenylmethane	Benzoic acid + triphenylmethane	Isomerization[b] %
Aluminum chloride–water (1:1) in benzene	25	12	99.3	0.8	100.1	1.6
Iodine in acetic acid	Reflux	1/4	99.0	0.06	99.1	0.1
Zinc chloride in acetic anhydride	Reflux	5	99.5	4.2	103.7	8.4
Dilute sulfuric acid in acetic acid	Reflux	26	98.1	0.0	98.1	0.0
Concd. sulfuric acid	10	1/2	97.4	1.7	99.1	3.4
92.8% sulfuric acid	50	3	90.9	9.2	100.1	18.4
Concd. sulfuric acid in acetic acid	Reflux	1	75.6	23.4	99.0	46.8
Perchloric acid in acetic acid	50	24	84.8	16.8	101.6	33.6

[a] Relative to an initial activity of benzopinacolone of 100.0; actual benzopinacolone activity = 0.04111 mc./mole. [b] Calculated from triphenylmethane activities; 100% isomerization corresponds to complete randomization of the activity between the two central carbon atoms.

(1) This work was supported by the Atomic Energy Commission.

(2) For a recent review, see T. S. Rothrock and A. Fry, THIS JOURNAL, **80**, 4349 (1958).

(3) V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958), and previous work cited there.

(4) H. J. Gebhart, Jr., and K. H. Adams, *ibid.*, **76**, 3925 (1954).

(5) C. A. Bunton, T. Hadwick, D. R. Llewellyn and Y. Pocker, *J. Chem. Soc.*, 403 (1958).

(6) D. N. Kursanov and Z. N. Parnes, *Zhur. Obshchei Khim.*, **27**, 668 (1957).

(7) J. F. Duncan and K. R. Lynn, *J. Chem. Soc.*, 3512 (1956).

(8) Oxygen function rearrangement does not necessarily imply oxygen migration (see mechanism 3 below).

(9) S. Barton and C. R. Porter, *J. Chem. Soc.*, 2483 (1956).