While 2,3,5-tri-*O*-benzoyl-D-ribose shows little if any mutarotation in chloroform or aqueous dioxane, methylation studies and comparisons between its rotation and those of some closely related substances (both to be published in the near future) appear to justify the tentative conclusion that it belongs to the β-D-series.

Acetylation of 2,3,5-tri-*O*-benzoyl-D-ribose in pyridine at a low temperature afforded in 88% yield crystalline 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribose [m.p. 130–131° (cor.); $[\alpha]^{20}\mathrm{D}$ +44.2° ($CHCl_3$)]. Similarly, benzoylation at low temperature gave in 89% yield D-ribofuranose tetrabenzoate [m.p. 121–122° (cor.); $[\alpha]^{20}\mathrm{D}$ +17.0 ($CHCl_3$)]; the same substance was also obtained through the benzoylation of D-ribose in pyridine at 100° although the yield in this case (11%) was low owing to the difficulty of separating the product from β-D-ribopyranose tetrabenzoate which is formed simultaneously.

2,3,5-Tri-*O*-benzoyl-D-ribose has been used for the synthesis of benzyl β-D-ribofuranoside tribenzoate; it is possible that it may prove of general utility for the synthesis of ribofuranosides.

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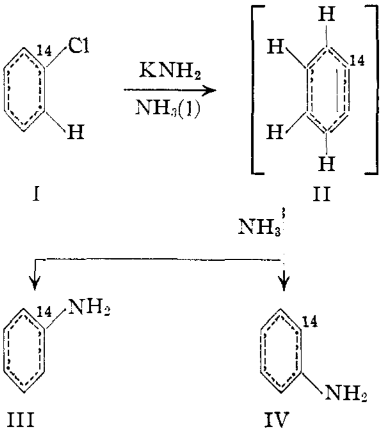
RECEIVED MAY 21, 1953

REARRANGEMENT IN THE REACTION OF CHLOROBENZENE-1-C^{14} WITH POTASSIUM AMIDE[1]

Sir:

No satisfactory explanation has been published for the rearrangements which often occur in the amination of "non-activated" aryl halides with alkali-metal amides.[2] The pattern of the rearrangements shows a considerable disregard for the influences governing the usual aromatic substitutions and is well illustrated by the products obtained from the amination of the methoxy- and trifluoromethylhalobenzenes. Although the methoxy and trifluoromethyl groups orient oppositely in aromatic nitration, *o*- and *m*-methoxy- and trifluoromethylhalobenzenes with alkali-metal amides yield exclusively *m*-substituted anilines, while the *p*-isomers yield mixtures containing roughly equal amounts of *m*- and *p*-substituted anilines.[3]

Besides the seemingly anomalous influence of substituents any mechanism proposed for the reaction must be in accord with the following observations: (1) the reactions are very rapid, even with chlorobenzene, in liquid ammonia at −33°; (2) the entering amino group has never been found farther than one carbon away from the position occupied by the leaving halogen[3,4]; (3) the starting halides and resulting anilines are not isomerized under the reaction conditions[3d,4]; (4) no reaction occurs in the benzene series with halides (*i.e.*, bromomesitylene,[3d] bromodurene[5] and 2-bromo-3-methylanisole[4]), where a hydrogen is not attached to the position adjacent to that occupied by the leaving halogen. These facts as well as the orientation data for various substituents can be accommodated by an elimination-addition mechanism involving at least transitory existence of an electrically neutral "benzyne" intermediate (II).



As is evident from the above reaction sequence, a critical test of the proposed mechanism would be afforded by the reaction of chlorobenzene-1-C^{14} with potassium amide. If a symmetrical intermediate such as II were involved equal amounts of aniline-1-C^{14} (III) and aniline-2-C^{14} would be formed since C-1 and C-2 become equivalent in II.

We have carried out the reaction of I[6] with potassium amide in liquid ammonia and obtained a 43% yield of C^{14}-labeled aniline. The C^{14} in the product was found to be distributed almost exactly as predicted for intermediate formation of II. While this experiment is not considered to "prove" the "benzyne" mechanism, it strongly indicates formation of an intermediate in which the 1- and 2-positions of the ring are, or can become, equivalent.[7] The only alternative is the occurrence of simultaneous rearranging and non-rearranging displacements in a ratio of almost exactly one to one. The utility of intermediates like II in accounting for the pattern of rearrangements with substituted halobenzenes will be demonstrated in a later paper.

An outline of the tracer experiments follows. The last steps were those developed by Loftfield.[8]

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[1] Supported in part by the program of research of the U. S. Atomic Energy Commission.

[2] The scope of this type of reaction has been investigated principally by Gilman and Bergstrom and their co-workers. For a review, see J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

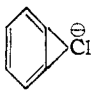
[3] (a) H. Gilman and S. Avakian, THIS JOURNAL, **67**, 349 (1945); (b) H. Gilman and R. H. Kyle, *ibid.*, **70**, 3945 (1948); **74**, 3027 (1952); (c) R. A. Benkeser and R. G. Severson, *ibid.*, **71**, 3838 (1949); (d) C. W. Vaughan, B.S. Thesis, M.I.T., 1951; (e) L. A. Carlsmith, M.S. Thesis, M.I.T., 1953.

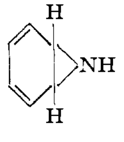
[4] R. A. Benkeser and W. E. Buting, THIS JOURNAL, **74**, 3011 (1952).

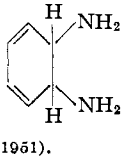
[5] Unpublished experiments by Mr. R. L. Harris.

[6] Obtained from Tracerlab, Inc., on allocation from the U. S. Atomic Energy Commission.

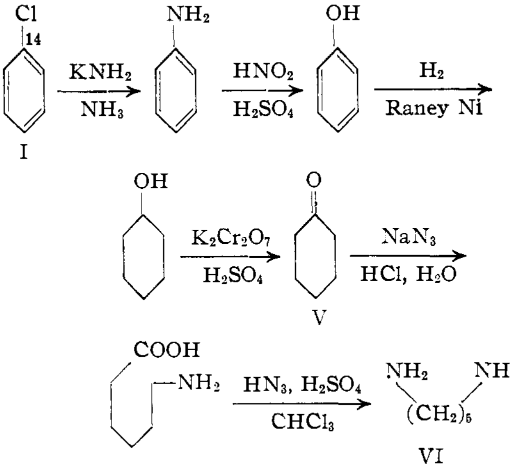
[7] Other possible symmetrical intermediates which would accommodate the C^{14}-tracer experiment and fit the general character of the reaction to a more or less satisfactory degree are:







[8] R. B. Loftfield, THIS JOURNAL, **73**, 4707 (1951).



VI (as the dibenzenesulfonamide) and VII (as barium carbonate) had respectively 51.8 ± 1% and 43.1 ± 1% of the radioactivity of V (as the semicarbazone or 2,4-dinitrophenylhydrazone). In a blank degradation of aniline-1-C^{14} (III),[6,9] the corresponding percentage activity figures for VI and VII were 0.2 ± 1 and 96.7 ± 1%, respectively. Since in the blank degradation the barium carbonate activity was consistently low, we consider the activity of VI to be the most reliable index of the amount of rearrangement in the amination of I.

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[9] Since I was prepared from III by Tracerlab, Inc., using the Sandmeyer reaction, this degradation constitutes a proof of the isotope position assignment for I.

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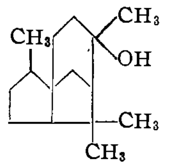
THE STRUCTURE OF CEDRENE

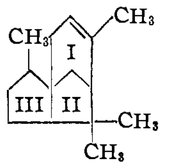
Sir:

The tricyclic sesquiterpenes cedrene, $C_{15}H_{24}$, and cedrol, $C_{15}H_{26}O$, have been the object, since their isolation by Walter in 1841,[1] of a large number of chemical investigations[2] which have led to the proposal of no fewer than thirteen different structures for the tertiary alcohol cedrol and the related anhydro compound, cedrene.[3]

We have elucidated the structures of these two sesquiterpenes which can now be represented by I (cedrol) and II (cedrene).



I



II

The presence of the grouping $—CH—\overset{H}{C}—\overset{CH_3}{C}—$ in the unsaturated ring of cedrene is well established.[2] The size of that unsaturated ring (ring I, fig. II) has incorrectly been deduced to be five-membered by previous investigators[4,4a] on the basis of observations which appeared to us to point clearly to a *six-membered* ring. We have confirmed our deduction by examination of the infrared spectrum of the anhydride of the bicyclic C_{13} diacid, norcedrenedicarboxylic acid (NCDA),[5] which proved to be that of a *glutaric* anhydride, with peaks at 5.57 and 5.67 μ, while a succinic anhydride, derived from a five-membered ring I, would have absorption maxima at 5.40 and 5.63 μ.[6] We have further prepared by the action of phenylmagnesium bromide on dimethyl norcedrenedicarboxylate a *diphenyl lactone*, m.p. 173–173.5°, which had its infrared band at 5.75 μ, in confirmation of the six-membered lactone structure corresponding to a glutaric acid.

The two carboxyls of NCDA are attached to a ring, the size of which we have proved by examination of the infrared spectrum of the anhydride of the monocyclic C_{11} dibasic acid obtained by further degradation of NCDA.[4] Again this proved to be the anhydride of a glutaric acid and ring II is thus established to be five-membered. The position of the *gem* dimethyl group shown in fig. II is considered elsewhere.[7] With respect to ring III two facts pointed strongly to the arrangement indicated in structure II: The isolation in high yield of *p*-cymene from the catalytic dehydrogenation of cedrene,[8] indicating the probable presence of a potential isopropyl group *para* to the methyl group of ring I; and the obvious biogenetic relationship to β-curcumene, of which cedrol is a formal cyclization product. In any event, this surmise is confirmed by the fact that the dehydroacid obtained from the C_{11} dibasic acid[4,5] is oxidized to α,α-dimethylhomotricarballylic acid,[3] an important result, a possible structural implication of which was incorporated, together with previous erroneous structural deductions, into the last published proposals for the structure of cedrene.[3] The full development of the necessarily sketchy outline presented here will be given in a subsequent paper.[9]

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RECEIVED JUNE 10, 1953

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[1] Ph. Walter, *Ann.*, **39**, 247 (1841).

[2] Reviews of the work in this field up to 1947 are found in J. Simonsen and D. H. R. Barton, The Terpenes, Vol. III, Cambridge University Press, London (1952); see also S. H. Harper, *Ann. Repts. Chem. Soc.*, **44**, 143 (1948).

[3] The last published proposals are by Pl. A. Plattner, *Chimia*, **2**, 248 (1948).

[4] Pl. A. Plattner, G. W. Kusserow and H. Kläui, *Helv. Chim. Acta*, **25**, 1345 (1942).

[4a] L. Ruzicka, Pl. A. Plattner and G. W. Kusserow, *ibid.*, **25**, 85 (1942).

[5] Pl. A. Plattner and H. Kläui, *Helv. Chim. Acta*, **26**, 1553 (1943).

[6] We have established that the position of the diagnostically more important lower wave length band is not affected by the degree of substitution.

[7] G. Stork and R. Breslow, THIS JOURNAL, **75**, 3292 (1953).

[8] W. Treibs, *Ber.*, **68**, 1041 (1935).

[9] Structures I and II for cedrol and cedrene were first presented formally in a lecture given by one of us at Harvard on January 27, 1953.