taining 3 ml. of concentrated hydrochloric acid. The solution was then stirred for 1 hr., refluxed for 1 hr., and then left to stir at ambient temperature for 14 hr. Removal of the solvents on a Rinco evaporator using an aspirator gave a gummy, white residue. Digestion with methanol resulted in the crystallization of the residue to yield 1.0566 g. (0.0253 mole, 52.4% yield) of the acid Vb, m.p. 205–208°, m.m.p. 206–208° with authentic acid. The remaining methanol-soluble portion was further refluxed with hydrochloric acid for 5 hr. to yield a yellow oil which did not crystallize.

The attempted acid cleavage of the aminophosphorane XIV was carried out by passing dry hydrogen chloride into a slurry of 2.2 g. (0.005 mole) of the compound in 20 ml. of benzene until no further absorption was observed. The solids became tacky as the addition continued. Excess hydrogen chloride was removed by adding pyridine which caused the precipitation of pyridine hydrochloride. The solids were removed by filtration under dry nitrogen and the benzene–pyridine solution was concentrated to yield a white, tacky residue. That this residue was not the chlorophosphorane was shown by the fact that when it was dissolved in pyridine and then poured into water, the crystalline acidic phosphorane VIb expected from the hydrolysis of the chlorophosphorane XI was not isolated. Only a tacky residue which could not be crystallized was obtained.

Reaction of Phenylphosphonic Diazide (IIa) and 1,4-Bis(diphenylphosphino)benzene (VII).—A 12.9-g. (0.0288-mole) quantity of 1,4-bis(diphenylphosphino)benzene was slurried with 35 ml. of pyridine, and the addition of 40 ml. of the previously prepared pyridine solution of phenylphosphonic diazide was begun at room temperature. The reaction was exothermic and after 30 min. the reaction mixture began to clear up, the solution being complete in 1 hr. At this point the reaction had slowed noticeably, with 625 cc. (corrected) of nitrogen representing 48.35% of the total nitrogen being collected. An infrared examination of the pyridine solution removed at this time showed a strong azide absorption at 2138 cm.$^{-1}$ and a general similarity to the previously isolated azide phosphorane. A 10-ml. (~10.5-g.) aliquot of the reaction solution was removed and 40 ml. of water was added. The resulting pale yellow solid weighed approximately 1.5 g. After drying and standing for several days, the sample was examined by infrared spectroscopy. The expected strong azide absorption at 2138 cm.$^{-1}$ was found to be weak, instead, while the remaining absorptions characteristic of the phosphorane portion of the spectra were present, *i.e.*, absorptions at 1439 (m), 1205 (sb), and 1117 (s) cm.$^{-1}$.

The remaining reaction solution was then brought to reflux to force the formation of polymeric phosphorane. After 4 hr., an additional 630 cc. of nitrogen was collected. The total nitrogen collected was 1255 cc. (calcd. 1292 cc.). A sample of the clear, yellow-brown solution was removed for infrared examination. A weak azide absorption at 2138 cm.$^{-1}$ was observed. Removal of the pyridine at reduced pressure gave approximately 16.0 g. of a tan powder which softened at 94°, foamed from 105 to 130°, and appeared to be completely liquid at 165°. A small sample placed on the high vacuum line and heated to 140° in 1 hr. appeared to soften and melt at 160–170°. Differential thermal analysis showed only a broad indistinct melting range at 136 ± 20° and the first transition or decomposition point at about 477°.

Anal. Calcd. for VIII: N, 4.68; P, 15.50. Found: N, 3.58–4.25; P, 14.2–15.2; mol. wt., 2300.

Attempted Isolation of IXa.—A 20-ml. quantity of a pyridine solution containing about 4.8 g. (0.023 mole) of phenylphosphonic diazide was added to 10.2 g. (0.023 mole) of 1,4-bis(diphenylphosphino)benzene in 20 ml. of pyridine. The exothermic reaction evolved 544 cc. (corrected, 106%) of nitrogen in 45 min. When the reaction mixture was poured into 175 ml. of water, an oil separated. After stirring for 2 hr. and cooling in an ice bath, the oil did not solidify.

The major portion of the oil was skimmed off the water and dried at reduced pressure overnight. The resulting yellow-brown foam weighed 11.7 g. Infrared examination of the foam showed a very weak azide absorption at 2137 cm.$^{-1}$ in addition to typical phosphorane absorptions and perhaps P–O–P absorption at 930 cm.$^{-1}$. In spite of the seemingly weak azide absorption in the infrared, the phosphorus value was in good agreement for IXa. (*Anal.* Calcd. for $C_{36}H_{29}N_4OP_3$: P, 14.83. Found: P, 14.8.) However, when a sample of this material was heated at reflux in pyridine, no further nitrogen was evolved. This implied that the phosphorus value was in error and that polymerization had occurred during the work-up.

The solvent was again removed at reduced pressure to yield an almost white foam which was dried at 0.3 mm. and 100° for 6 hr. (*Anal.* Found: N, 3.58; P, 15.0.) A 3.9-g. quantity of this dried material was extracted for 4 hr. at ambient temperature with 30 ml. of benzene and then on the steam bath for 10 min. After cooling, the clear benzene layer was decanted from the brown insoluble material and the benzene was carefully removed at reduced pressure to give (after drying at 100° and 0.3 mm. for 2 hr.) 1.9 g. of white powder.

Anal. Calcd. for VIII $C_{36}H_{29}N_2OP_3$: C, 72.24; H, 4.88; N, 4.68; P, 15.52. Found: C, 70.71; H, 4.94; N, 3.37; P, 15.0; mol. wt., 1855.

The brown, insoluble fraction (1.4 g.) was similarly dried and analyzed. (*Anal.* Found: C, 71.23; H, 5.08; N, 3.78; P, 15.3.) Differential thermal analysis curves for both of these fractions appeared to indicate a beginning of decomposition at about 455°. Broad endotherms were observed at about 550°.

Acknowledgment.—The author wishes to thank especially Mr. Franklin A. Billig who presented portions of this paper at the 146th National American Chemical Society Meeting and also Mr. Karl Sterner for his assistance with the analyses and infrared determinations.

Ring-Size Effects in the Pinacol Rearrangement

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Received June 2, 1965

One general ring-size effect was observed in the rearrangement of (1-hydroxycyclohexyl)phenylcarbinol (**1**), (1-hydroxycyclopentyl)phenylcarbinol (**2**), (1-hydroxycyclohexyl)methylphenylcarbinol (**3**), and (1-hydroxycyclopentyl)methylphenylcarbinol (**4**) in concentrated sulfuric acid. The five-membered ring compounds gave more ring expansion than the six-membered analogs. An interpretation of this result is offered and its bearing on the mechanism of the rearrangement is discussed.

In a recent paper[2] from this laboratory it was shown that the product distribution from the pinacol rearrangement of cyclopentylcyclohexane-1,1′-diol (**5**) could not be rationalized by the simple application of the I-strain theory.[3] That is the formation of a carbonium ion (or S_N2 intermediate) on the five-membered ring should be favored over the same reaction on the six-membered ring by changes in the strain owing to

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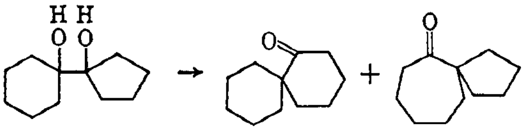
(1) (a) Abstracted from the doctoral dissertation of G. Wood, Syracuse University, 1962. (b) To whom correspondence should be addressed: Department of Chemistry, University of Windsor, Windsor, Ontario, Canada. (c) Bristol Fellow, 1961–1962.

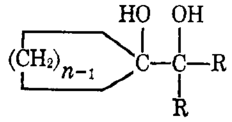
(2) R. D. Sands and D. G. Botteron, *J. Org. Chem.*, **28**, 2690 (1963).

(3) H. C. Brown, J. H. Brewster, and H. Schechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

bond oppositions. However, the pinacol rearrangement of **5** yielded less spiro[4.6]undecan-6-one (**5b**) (from reaction on the five-membered ring) than spiro[5.5]undecan-7-one (**5a**) (from reaction on the six-membered ring).


5 **5a** **5b**

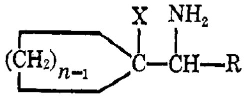
Some precedent for the observed behavior may be found in the literature. Meerwein[4] rearranged a series of glycols of the general formula **6**. The cyclopentyl glycols (**6c** and **6d**) gave more ring expansion than the corresponding cyclohexyl ones (**6a** and **6b**, respectively).



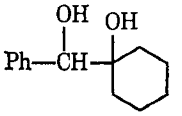
A similar result was obtained in the deamination of some amines and amino alcohols of the general formula

6a, $n = 6$; R = Me
b, $n = 6$; R = Et
c, $n = 5$; R = Me
d, $n = 5$; R = Et

7.[5] For all compounds studied the cyclopentyl analog gave more ring expansion than the cyclohexyl compound.


7, X = H, OH; R = H, Me, Ph; n = 5, 6

In order to further define the nature and magnitude of the ring-size effects and their bearing on the mechanism of the pinacol rearrangement, the glycols **1**–**4** were synthesized and rearranged.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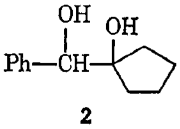
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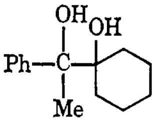
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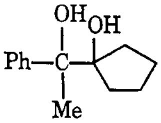

4

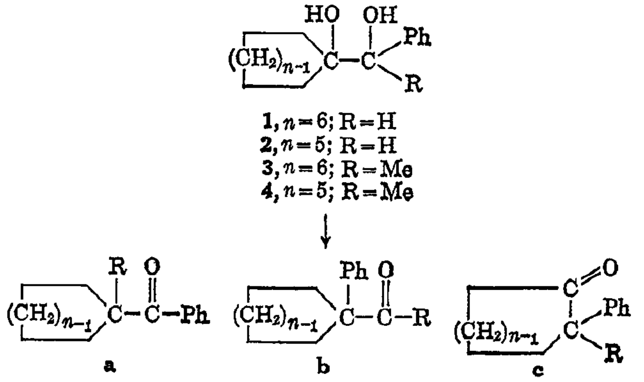
Bimolecular reduction of the appropriate carbonyl compounds was found to be a satisfactory method of synthesis for the glycols, although the yields were low and some difficulty was experienced in separating the product from the symmetrical glycols formed.

The rearrangements were conducted at 0° in concentrated sulfuric acid. Under these conditions no elimination was observed and good yields of rearrangement products were obtained. The crude product mixture was subjected to vapor phase chromatography and identifications were made by comparison with authentic samples.

TABLE I
PRODUCTS OBTAINED FROM THE REARRANGEMENT IN 96% SULFURIC ACID OF SOME GLYCOLS AND RELATED CARBONYL COMPOUNDS

Compd.	Product distribution, % a	b	c
1	25	10	65
2	7	0	93
3	0	28	72
4	0	20	80
1b	68	23	9
2b	0	0	100

For the glycols studied here there are three possible rearrangement products. A general equation for the rearrangement may be written as follows. The results are presented in Table I.


1, $n = 6$; R = H
2, $n = 5$; R = H
3, $n = 6$; R = Me
4, $n = 5$; R = Me
a **b** **c**

Inspection of Table I shows that the per cent of product obtained from reaction on the six-membered ring was greater than that obtained from reaction on the five-membered ring (*i.e.*, **1a** + **1b** > **2a** + **2b** and **3a** + **3b** > **4a** + **4b**) in conformity with the earlier results[2] and in apparent disagreement with the I-strain theory. Since the rate of nucleophilic substitution at a carbon on a five-membered ring has been found to be 10–100 times as fast as the corresponding reaction on a six-membered ring[6] regardless of mechanism, it seems likely that such an effect is also operative here. The fact that this effect does not control product distribution may then be taken as evidence for an opposing and larger ring-size effect. There are at least two possibilities for the latter.

There is general agreement that the first step in the pinacol rearrangement is the reversible protonation of a hydroxyl group. A decrease in the basic strength of one hydroxyl group should shift the equilibrium for the protonation of that group toward pinacol and thus increase the amount of reaction at the other site. There is some evidence that the basicity of cyclopentanol is reduced compared to acyclic secondary alcohols while cyclohexanol has a typical value.[7] This effect would then favor reaction on a six-membered ring site.

For pinacols of the type studied here reaction on the site next to the ring ultimately leads to ring expansion. Thus reaction next to a five-membered ring leads to a six-membered ring product and a decrease in strain

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(4) H. Meerwein, *Ann.*, **419**, 121 (1919), and earlier papers.

(5) I. Elphimoff-Felkin and B. Tchoubar, *Compt. rend.*, **237**, 726 (1953).

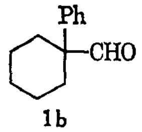
(6) E. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 123.

(7) T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 577 (1957).

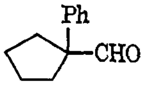
of about 10 kcal.[8] To the extent that the transition state partakes of the nature of products there should also be a decrease in strain in the transition state and an acceleration in the rate of the reaction. Similar arguments would predict a retardation in the rate of ring expansion for the six-membered ring.[9] This effect also favors reaction on a six-membered ring site.

It is difficult to estimate the relative importance of these two effects. However, the work of Stiles[10] on tetraalkyl glycols has indicated that it is the migration step in the reaction which is kinetically measurable and two recent papers have shown that participation of a neighboring five-membered ring in solvolysis may accelerate the rate (compared with that for the six-membered analog) by 5[11] to as much as 60[12] times. It would appear then that strain release by ring expansion is sufficient to explain the observed product distribution without recourse to the basicity effect.[13] The magnitude of the latter cannot be estimated since the necessary basicity data is lacking.

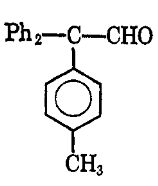
The results of acid rearrangement of the aldehydes **1b** and **2b** which are reported in Table I offer pertinent evidence on the reversibility of the pinacol rearrangement. Collins[14] has shown that loss of hydroxyl from some 1,2,2-triarylethane-1,2-diols is followed by equilibration of the resulting carbonium ions. Thus, **8** and **9** on treatment with concentrated sulfuric acid at 0° gave the same products. This was taken as evidence that each of the starting materials gave rise to the same mixture of interconvertible intermediates. Labeling experiments showed that the related glycol, **10**, gave significant amounts of secondary hydroxyl loss resulting in isotopically different products. An attempt has been made[15] to explain Stiles' results on this basis also. The present results show that the rearrangement of glycols **1** and **2** does not follow the mechanism established by Collins for the 1,2,2-triarylethane-1,2-diols. The product distribution obtained from treatment of the aldehydes **1b** and **2b** is considerably different from that obtained from the glycols **1** and **2**. Further, it may be said that Stiles' interpretation of the rearrangement is in accord with the present results and the dependence of the rate on the rearrangement step is consistent with the observed importance of a ring-size effect in this step.



1b



2b



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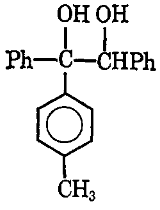

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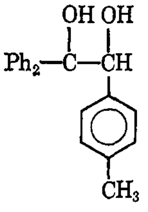

10

Experimental Section[16]

Preparation of the Mixed Glycols.—A typical glycol preparation by the mixed reduction method will be presented in detail followed by an outline of the preparation of other glycols by this method.

(1-Hydroxycyclohexyl)phenylcarbinol (1).—Granular aluminum[17] (27 g., 1 g.-atom) was weighed under nitrogen and placed in a 1-l. three-necked, round-bottomed flask, equipped with a reflux condenser, stirrer, and addition funnel. Sodium-dried, thiophene-free benzene (160 ml.) was added and brought to reflux. A pinch of mercuric chloride and a few drops of mercury were added and a solution of 70 g. of freshly distilled benzaldehyde (0.715 mole), 70 g. of freshly distilled cyclohexanone (0.715 mole), and 12.4 g. of mercuric chloride (0.0455 mole) was added dropwise. The reaction started almost at once and was strongly exothermic. By cooling the flask intermittently in an ice bath the addition was completed in about 1 hr. The mixture was then refluxed 3 hr. and cooled 5 min., and 160 ml. of benzene was added. Hydrolysis was carried out by the careful addition of 100 ml. of water. The mixture was refluxed 3 hr. to complete the hydrolysis, cooled, and filtered, and the cake was washed with 100 ml. of hot benzene. The combined filtrate and washings were distilled to remove benzene, then diluted with 3 vol. of petroleum ether (b.p. 60–90°). The solution was cooled in a freezer and the resulting crystals were filtered and pressed dry. The crude yield was 40 g. One crystallization from petroleum ether and one from benzene–petroleum ether yielded 19.5 g., melting at 101–102°, as well as some less pure material (lit.[18] m.p. 100°).

TABLE II

SUMMARY OF REARRANGEMENT PRODUCTS PREPARED[a]

Compound	M.p. or b.p. (mm.), °C.	Ref.
Phenyl cyclohexyl ketone	52–56	*b*
2-Phenylcycloheptanone	111–114 (4)	*c*
2-Phenylcyclohexylcarboxaldehyde	*d*	*e*
Phenyl cyclopentyl ketone	126–133 (8–9)	*b*
2-Phenylcyclohexanone	57–60	*f*
2-Phenylcyclopentylcarboxaldehyde	83 (1)	*e*
2-Methyl-2-phenylcycloheptanone	130–152 (6)	*g*
1-Methylcyclohexyl phenyl ketone	*h*	*g*
1-Phenylcyclopentyl methyl ketone	100–103 (4)	*i*
2-Methyl-2-phenylcyclohexanone	103–110 (4)	*g*
1-Methylcyclopentyl phenyl ketone	86–88 (2)	*g*

[a] 1-Phenylcyclohexyl methyl ketone had previously been shown[20] to be a product of the rearrangement of **3**. Its preparation was not repeated. [b] C. C. Price and J. O. Karabinos, *J. Am. Chem. Soc.*, **62**, 1160 (1940). [c] C. D. Gutsche and H. E. Johnson, *Org. Syn.*, **35**, 91 (1955). [d] This compound was contaminated with 1-phenylcyclohexyl cyanide. [e] D. Y. Curtin and S. Schmukler, *J. Am. Chem. Soc.*, **77**, 1105 (1955). [f] M. S. Newman and M. D. Farbman, *ibid.*, **66**, 1551 (1944). [g] P. Nedenskov, W. Taub, and D. Ginsburg, *Acta Chem. Scand.*, **12**, 1406 (1958). [h] The best sample contained 65% of this compound. The contaminant was phenyl cyclohexyl ketone. [i] P. A. S. Smith, D. R. Baer, and S. N. Ege, *J. Am. Chem. Soc.*, **76**, 4567 (1954).

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(8) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959). A lower estimate of 6.5 kcal. for the strain in cyclopentane has been made by S. Kaarsemaker and J. Coops [*Rec. trav. chim.*, **71**, 261 (1952)].

(9) The strain in cycloheptane is comparable with that in cyclopentane. See ref. 6.

(10) M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959).

(11) H. Felkin and G. LeNy, *Bull. soc. chim. France*, **24**, 1169 (1957).

(12) A. P. Krapcho and M. Benson, *J. Am. Chem. Soc.*, **84**, 1036 (1962).

(13) A similar discussion of the importance of strain release in the transition state has been presented by A. P. Krapcho, J. E. McCullough, and K. V. Nahabedian, *J. Org. Chem.*, **30**, 139 (1965).

(14) B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4329 (1956).

(15) C. J. Collins, *Quart. Rev.* (London), **14**, 376 (1960).

(16) Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. The infrared spectra were determined with a Perkin-Elmer, Model 137, infrared recording spectrophotometer fitted with a sodium chloride prism. Gas chromatography was done on an Aerograph, Model A-90, gas chromatograph using a 5-ft. silicone grease column for routine work and a 10-ft. silicone grease column for difficult separations. The microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(17) J. T. Baker Co., 8–20 mesh.

(18) I. Elphimoff-Felkin and B. Tchoubar, *Bull. soc. chim. France*, 551 (1952).

(1-Hydroxycyclopentyl)phenylcarbinol (2).—Similar treatment of benzaldehyde and cyclopentanone followed by several recrystallizations from benzene–petroleum ether yielded a material with m.p. 91–92.5° which could not be further purified by this method. Chromatography on alumina was likewise unsuccessful. Gas chromatography of the pinacol rearrangement product of this material indicated that cyclopentylcyclopentane-1,1′-diol was the contaminant. The mixture was separated by treatment with phthalic anhydride in pyridine.[19] The glycol thus purified had a m.p. of 81–82° (lit.[5] m.p. 80°) and its rearrangement product contained only 2% of spiro[4.5]decan-6-one (gas chromatography).

(1-Hydroxycyclohexyl)methylphenylcarbinol (3).—Acetophenone and cyclohexanone yielded 41% of crude material which on recrystallization had a m.p. of 109–110° (lit. m.p. 107.5–108,[20] 101.5,[19] 104°[18]).

(1-Hydroxycyclopentyl)methylphenylcarbinol (4).—Acetophenone and cyclopentanone yielded 37% of crude material which on recrystallization had a m.p. of 108.5–109°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74. Found: C, 75.91; H, 8.78.

Independent Synthesis of Rearrangement Products.—Authentic samples of the rearrangement products of glycols 1–4 were prepared by known methods. This work is summarized in Table II. Purity of all samples was checked by gas chromatography and was over 90% except as noted.

The Rearrangement.—Concentrated sulfuric acid (96%) was cooled to 0° and the glycol (1 g./100 ml. of acid) was added in portions with stirring. When solution was complete, the reaction was poured into a mixture of ice and water (10 vol. of water/1 vol. of acid). When an organic layer separated it was taken off and the aqueous layer was extracted three times with ether. The combined ether layers were dried over magnesium sulfate; the ether was removed on the rotary evaporator. The crude residue was subjected to gas chromatography. Identifications were made by comparison with authentic samples; infrared spectra supplemented the analysis. Gas chromatographic analysis of synthetic mixtures of known composition showed that the method was reliable. Each rearrangement was done in duplicate; the average is reported in Table I. By treating all the measurements together the standard deviation was estimated to be 4%.

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(19) C. A. Russell, L. T. Stroup, and J. English, Jr., *J. Am. Chem. Soc.*, **74**, 3882 (1952).

(20) G. G. Lyle, R. A. Covey, and R. E. Lyle [*ibid.*, **76**, 2713 (1954)] rearranged this compound with the same results obtained in the present work.

Structure of Neo-β-amyrin[1]

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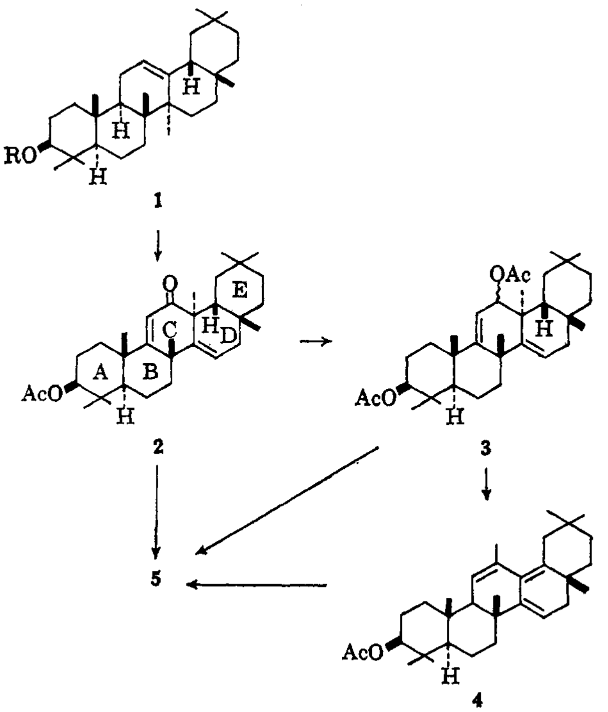
Received June 14, 1965

The reactions leading from β-amyrin acetate to neo-β-amyrin acetate have been re-examined, and structures based on C-nor-D-homooleanane are proposed for neo-β-amyrin and precursors.

There has been obtained from β-amyrin (**1**, R = H) by sequences of reactions involving at least two molecular rearrangements, an isomer which has been named neo-β-amyrin by Spring and co-workers.[2] In any of these sequences, the key intermediate is a dienone (**2**) (Chart I), prepared from β-amyrin acetate in three steps involving consecutive oxidation by (i) hydrogen peroxide in acetic acid to give the saturated 12-ketone[3–5]; (ii) bromine to yield the conjugated 9(11)-en-12-one[5,6]; and (iii) selenium dioxide[7] with methyl group migration from C-14 to C-13. The structure of the dienone **2**, which was first proposed by Jeger and Ruzicka,[8] is now well established.[2,9] In current nomenclature,[10] the dienone **2** is named 3β-acetoxy-D-friedooleana-9(11),14-dien-12-one; it has also been known variously as iso-β-amyradienonyl acetate,[7] oxoiso-β-amyradienyl acetate,[2] 12-oxoisooleana-9(11),-14-dien-3β-yl acetate,[11] and 12-oxotaraxera-9(11),14-dien-3β-yl acetate.[11]

Reduction of the dienone **2** with lithium aluminum hydride[2,6] or with sodium methoxide[2] in methanol at 200° yielded a dienediol, which was characterized as the diacetate and formulated as **3**, with unassigned configuration at C-12. Treatment of this diacetate with hydrochloric acid resulted in deacetoxylation with formation of a cross-conjugated triene (neo-β-amyratrienyl acetate) which Spring and colleagues[2] provisionally formulated as **4**. The production of a

CHART I



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[1] The award of a research grant (AM-3439) from the U. S. Public Health Service (to R. S.) is gratefully acknowledged.

[2] G. G. Allan, J. D. Johnston, and F. S. Spring, *J. Chem. Soc.*, 1546 (1954).

[3] F. S. Spring, *ibid.*, 1345 (1933).

[4] L. Ruzicka, G. Müller, and H. Schellenberg, *Helv. Chim. Acta*, **22**, 758 (1939).

[5] C. W. Picard, K. S. Sharples, and F. S. Spring, *J. Chem. Soc.*, 1045 (1939).

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