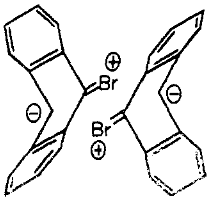
molecules must be essentially non-polar. Although there is a small difference between the observed total polarization (P_2) and the calculated electronic polarization (MR_D) in each case, this difference is scarcely more than experimental error. Any reasonable allowance for atomic polarization would then reduce the orientation polarization, and hence the dipole moment, to zero.

The head-to-head forms (I) of the photodimers of 9-haloanthracenes would be expected to have electric moments of about 3.8 D. (and, therefore, orientation polarizations of about 300 cc.), while the head-to-tail forms (II) should have zero moments. The two dimers studied here must, therefore, have the head-to-tail structures II.

Some modification of the proposed[1] free-radical mechanism of photodimerization appears to be required by the results reported here. It is possible that steric repulsions of the halogens would tend to stabilize the transition states for head-to-tail dimerizations, but it is improbable that this could be the only factor influencing the orientation, since steric repulsions would appear to be at least as great between two hydroxymethyl groups (which go head-to-head[1]) as between two chlorine atoms, from inspection of Fisher–Hirschfelder models. It is interesting that the substituents which give head-to-tail dimers have unshared electron pairs next to the anthracene nucleus, whereas those which do not possess such electron pairs give head-to-head dimers. This suggests that polar structures, such as IV, may contribute to the product-determining transition states. Head-to-tail orientation would certainly be promoted by such contribution. Finally, the possibility exists that head-to-tail orientation results from equilibrium control of products, whereas head-to-head orientation results from purely kinetic control. Further work on the orientation phenomena is expected to reveal the contributions of these and possibly other controlling influences.



IV

Acknowledgment.—We are indebted to Miss Claire Higham for the microanalyses and to Mr. James Brader for the infrared spectra.

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[CONTRIBUTION FROM THE NAVAL STORES STATION, U. S. DEPARTMENT OF AGRICULTURE[1]]

Preparation of 6-Hydroxydehydroabietic Acid from the Photoperoxide of Levopimaric Acid

BY R. N. MOORE AND RAY V. LAWRENCE

RECEIVED JANUARY 21, 1958

A peroxide obtained from levopimaric acid by a photosensitized air oxidation process and tentatively formulated as 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid, was rearranged readily in alkaline medium to a hydroxy-enone. Dehydration of the hydroxy-enone gave 6-hydroxydehydroabietic acid and a dienone presumed to be 6-ketoabietic acid, on the basis of its ultraviolet absorption. The presence of the alcoholic hydroxyl group in the hydroxy-enone was shown by the hydroxyl stretching band at 2.9 μ in the infrared spectrum of its methyl ester, and a tertiary, α,β-unsaturated location was indicated by its ease of dehydration. The hydroxy-enone was therefore formulated as 6-keto-14-hydroxy-$\Delta^{7(8)}$-dihydroabietic acid. The phenolic dehydration product was reduced by $LiAlH_4$ to 6-hydroxydehydroabietinol.

A peroxide, obtained from levopimaric acid by a process of photosensitized air oxidation,[2] has been formulated tentatively as the product of 1,4 addition of oxygen to the homoannular dienic grouping in levopimaric acid, that is, 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (I). This formulation of the peroxide was supported by the absence of selective ultraviolet absorption in the region of 220–320 mμ, the absence of any new Grignard-reactive hydrogen, the neutralization equivalent, elemental analysis, its instability in alkaline medium and by the fact that one mole of oxygen per mole of levopimaric acid was absorbed during its formation.

It is known that the decomposition of certain hydroperoxides and dialkyl peroxides is catalyzed by base, to yield alcohols and ketones. It has been pointed out that only those dialkyl peroxides and alkyl hydroperoxides having a hydrogen on the carbon attached to the peroxide linkage will undergo base-catalyzed decomposition, and a mechanism has been proposed which involves abstraction of this hydrogen as the primary step.[3] Extension of this mechanism to an intramolecular peroxide such as I predicts molecular rearrangement to a hydroxy-enone, rather than decomposition. The predicted product, 6-keto-14-hydroxy-$\Delta^{7(8)}$-dihydroabietic acid (II), having a tertiary, α,β-unsaturated hydroxyl group, should be readily dehydrated to either 6-ketoabietic acid (III) or 6-hydroxy-dehydroabietic acid (IV) or a mixture of the two. The dienone III also should be isomerizable to IV. A similar rearrangement recently has been employed for the preparation of a corticosteroid intermediate.[4] Reinvestigation of the

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(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) R. N. Moore and Ray V. Lawrence, THIS JOURNAL, **80**, 1438 (1958).

(3) N. Kornblum and H. E. De La Mare, *ibid.*, **73**, 880 (1951).

(4) G. D. Laubach, E. C. Schreiber, E. J. Agnello, E. N. Lightfoot and K. J. Brunings, *ibid.*, **75**, 1514 (1953).

several rearrangements of Δ^3-2,5-peroxide-cholestene[5] has shown that a hydroxy-enone is produced by the action of alkali.

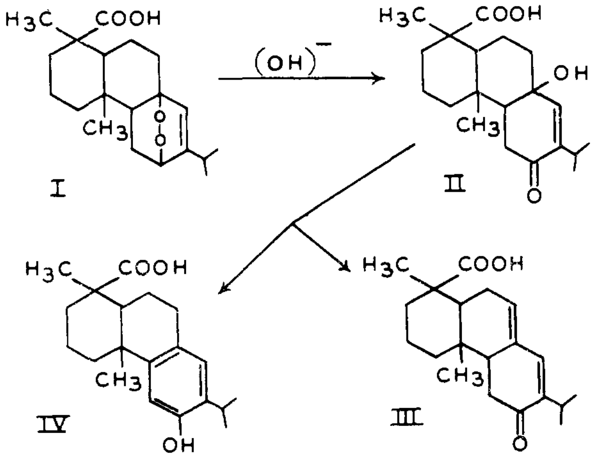
Photo-sensitized oxidation of levopimaric acid in alkaline medium or treatment of the preformed peroxide with alkali yielded a hydroxy-enone (II). The neutralization equivalent (334), ultraviolet spectrum λ^{alc}_{max} 234 mμ, α 20.7, and infrared spectrum were in agreement with predicted values. A crystalline methyl ester, prepared from II, showed similar ultraviolet absorption and retained the alcoholic hydroxyl band at 2.9 μ. Destruction of the characteristic absorption maximum of levopimaric acid at 272 mμ and the related formation of the maximum at 234 mμ characteristic of the hydroxy-enone II, during the oxidation in base, is shown in Table I.

TABLE I

OXIDATION OF LEVOPIMARIC ACID IN ALKALINE MEDIUM AT 25 TO 40°

Reacn. time, minutes	α at 272 mμ	α at 234 mμ
0	18.03	3.45
30	13.34	7.32
60	8.41	11.08
90	4.50	15.16
120	1.32	18.50

Dehydration of II apparently yields a mixture of III and IV, but considerable variation in the ratio of the products is encountered, depending upon the conditions employed. Mild conditions, such as refluxing in glacial acetic acid, favor formation of III, whereas refluxing in alcoholic hydrochloric acid produces a larger proportion of IV. The production of III under mild conditions is indicated by the more intense absorption of ultraviolet light at somewhat longer wave lengths than the absorption maximum of IV at 283 mμ. This absorption maximum in the region of 293 mμ is lowered and shifted back to 283 mμ on prolonged reflux with strong mineral acid, indicating isomerization of III to IV (Fig. 1).



The phenolic acid IV could not be induced to crystallize from most solvents, apparently due to a strong intermolecular hydrogen bonding between the phenol and carboxyl functions. The methyl ester crystallized readily even when prepared from crude samples of IV. The free acid form of IV was obtained crystalline from carbon tetrachloride or glacial acetic acid, in both cases as a complex with the solvent. The product from acetic acid was isolated as an equimolecular compound. Reduction of the molecular compound (or the methyl ester of IV) gave 6-hydroxy-dehydroabietinol (V) in 92% yield. This compound, which was prepared previously from dehydroabietic acid,[6] was reported to show marked estrogenic activity.

Experimental[7]

Apparatus.—The photo-sensitized air oxidations in basic media were conducted in an apparatus which consisted of two concentric tubes mounted vertically, the outer tube being 4.28 cm. in inside diameter and 54 cm. long and fitted at the lower end with a sintered glass gas inlet. The inner tube was sealed at its lower end and was 3.48 cm. in outside diameter, 55 cm. long and contained a 15 watt fluorescent tube. The air employed was presaturated with the solvent employed.

Materials.—Levopimaric acid was prepared from commercial pine gum by a modification[8] of the amine salt technique of Harris.[9] The photoperoxide of levopimaric acid was prepared by photo-sensitized air oxidation of levopimaric acid in neutral or slightly acidic alcoholic solution.[2]

6-Keto-14-hydroxy-$\Delta^{7(8)}$-dihydroabietic Acid (II).—Rearrangement of the prepared 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (I) was effected as follows: 5 g. of I was dissolved in 50 ml. of 1 *M* sodium hydroxide in 95% ethanol, whereupon the solution warmed spontaneously to 46°. The solution was refluxed for 10 minutes, cooled and acidified with 5 ml. of acetic acid. Water was added and the crude hydroxy-enone was filtered and dried under vacuum, wt. 4.78 g., yield 96%. Two recrystallizations from acetonitrile gave 3.20 g. (64%) of the 6-keto-14-hydroxy-$\Delta^{7(8)}$-dihydroabietic acid (II), melting about 148–150° with decomposition, $[\alpha]_D$ +27° (1% in ethanol), λ^{alc}_{max} 234 mμ, α 20.7. Treatment of II with ethereal diazomethane gave the methyl ester, which after recrystallization, once from methanol–water and twice from heptane, melted at 134–135.5°, and had $[\alpha]_D$ +28° (1% in ethanol), λ^{alc}_{max} 234 mμ, α 19.4.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.65; H, 9.21.

Oxidation of levopimaric acid in alkaline medium gave II directly when sufficient time was allowed for catalytic rearrangement of I to II after completion of the oxidation step. Aeration and irradiation of 280 ml. of 0.1 *M* levopimaric acid and 0.24 *M* sodium hydroxide, in 95% ethanol containing 0.028 g. of rose bengal in a 15 watt reactor, resulted in quantitative oxidation of the levopimaric acid in 2.0 hours, as evidenced by the complete destruction of the ultraviolet absorption maximum at 272 mμ (see Table I). Subsequent oxidations were stopped at this point inasmuch as aeration and irradiation of the solution for an additional 5 hours did not significantly alter the ultraviolet absorption spectrum. The product solution, after standing overnight, showed λ^{alc}_{max} 234 mμ, α 18.2 (specific extinction coefficient based on the charged weight of levopimaric acid). The ethanol solution was acidified with dilute acetic acid; the product was watered out of solution with a large volume of water and recovered by filtration to obtain 7.6 g. of crude II, yield 83%.

6-Hydroxydehydroabietic Acid (IV).—The basic alcohol solution of II (λ^{alc}_{max} 234 mμ, α 18.2) resulting from the one-step oxidation and rearrangement of levopimaric acid was used without intermediate isolation to obtain IV. The solution was acidified by addition of 9.5 ml. of concentrated

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(5) R. J. Conca and W. Bergmann, *J. Org. Chem.*, **18**, 1104 (1953).

(6) L. F. Fieser and W. P. Campbell, THIS JOURNAL, **61**, 2528 (1939).

(7) Ultraviolet absorption spectra were determined on ethanol solutions using the Beckman model DU spectrophotometer. Melting points are uncorrected.

(8) Virginia M. Loeblich, Doris E. Baldwin, R. T. O'Connor and R. V. Lawrence, *ibid.*, **77**, 6311 (1955).

(9) G. C. Harris and T. F. Sanderson, *ibid.*, **70**, 334 (1948).

hydrochloric acid in 25 ml. of ethanol and refluxed 3.5 hours. The product solution then showed $\lambda_{\max}^{\text{alc}}$ 288 mμ, α 14.87. The product was watered out of solution and recovered by filtration. The crude IV could not be crystallized from many common solvents, such as ethanol, benzene and acetonitrile. It crystallized readily from carbon tetrachloride as a molecular complex which, after formation, could not be dissolved in carbon tetrachloride: yield 7.80 g. or 61%.

Treatment of 1.0 g. of the carbon tetrachloride complex containing 0.79 g. of IV (on the basis of the neut. equiv. 417) with ethereal diazomethane and subsequent removal of the ether by evaporation, gave the methyl ester which readily crystallized. One recrystallization from methanol-water gave 0.71 g. (90%) of the ester, m.p. 151–154°. Three additional recrystallizations gave 0.42 g. of the pure methyl ester of IV, m.p. 162–162.5, [α]D +71° (1.0% in ethanol), $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 9.72.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.39; H, 9.23.

The carbon tetrachloride complex of IV gave a new molecular compound with acetic acid. Three recrystallizations of the crude carbon tetrachloride complex from glacial acetic acid gave a crystalline equimolecular compound of IV and acetic acid, which decomposed slowly above about 150° and had [α]D +62° (2.0% in ethanol), $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 8.37.

Anal. Calcd. for $C_{23}H_{34}O_5$: neut. equiv., 188; C, 70.74; H, 8.78. Found: neut. equiv., 188; C, 70.76; H, 8.60.

Dehydration of II.—Three grams of the crude hydroxyenone II, [α]D +43° (1% in acetic acid), was dehydrated by refluxing in 30 ml. of glacial acetic acid for 10 min. During this time the rotation decreased to [α]D −12° (1% in acetic acid). No further change occurred on refluxing for an additional 20 minutes. The dehydrated product (III) was precipitated as a white powder from the acetic acid solution by the careful addition of water. The white powder melted over a wide range and little improvement was effected in attempts to crystallize it from several solvents. The crude product showed $\lambda_{\max}^{\text{alc}}$ 293 mμ, α 26.3; calculated(10) for 6-ketoabietic acid $\lambda_{\max}^{\text{alc}}$ 296 mμ.

Rearrangement of III to 6-Hydroxydehydroabietic Acid IV.—One gram of III was refluxed for 15 hours in 20 ml. of glacial acetic acid containing 3 drops of concd. H_2SO_4. During this time the rotation changed from [α]D −12° to [α]D +75° (5% in acetic acid) and the ultraviolet absorption changed from $\lambda_{\max}^{\text{alc}}$ 293 mμ, α 26, to $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 8.7. The crude product was precipitated from the acetic acid by careful addition of water, thoroughly washed with water, suspended in boiling water and dried; yield 0.84 g. of crude IV. On recrystallization from CCl_4 the expected molecular compound was obtained, m.p. 155–160°. This melting point was not lowered by mixing with the CCl_4 molecular compound from pure IV.

6-Hydroxydehydroabietinol (V).—A slurry of 1.31 g. of lithium aluminum hydride powder was prepared in 25 ml. of dry ether in a 100-ml. flask equipped with a stirrer, reflux condenser, heating mantle and addition funnel. A solution containing 2.00 g. of the acetic acid complex of IV described above was added to the stirred slurry over a period of 20 minutes. After the slurry had been heated at reflux for an additional 20 minutes, the excess lithium aluminum hydride was destroyed by addition of wet ether. Following the acidification of the mixture with 40 ml. of 3 *N* aqueous sulfuric acid, the ether layer was separated and washed successively with water, dilute sodium bicarbonate, and water. The ether was evaporated to leave a residue of 1.48 g. (92%) of crude V, m.p. 166–174°. The residue was taken up in methanol–water, treated with a little activated carbon and recrystallized to constant m.p. 181–182°, [α]D +63° (1.0% in ethanol), $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 10.93, yield 0.83 g.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.63; H, 9.79.

Acknowledgment.—We wish to express our appreciation to Mr. L. E. Brown, of the Southern Utilization Research and Development Division, New Orleans, La., for the determination of the elemental analyses.

OLUSTEE, FLA.

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(10) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949 pp. 192–193.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. XIV. The Hydrogen–Deuterium Isotope Effect in the Pinacol Rearrangement of Triarylethylene Glycols[1]

BY CLAIR J. COLLINS, WILLIAM T. RAINEY, WILLIAM B. SMITH AND IRVING A. KAYE

RECEIVED JUNE 19, 1958

The hydrogen–deuterium isotope effects in the acid-catalyzed rearrangement of 1,1,2-triphenylethylene glycol (Iac) and 1,1,2-triphenylethylene-$^2H_1$ glycol (Iefg) have been determined in the presence of several different catalysts to be approximately 3. The first-order rates of rearrangement of the foregoing glycols at 43.3° in aqueous ethanolic 3.13 *N* H_2SO_4 have been determined, as have the rearrangement rates of 1,1-diphenyl-2-*p*-tolylethylene glycol (IVa), 1,1-diphenyl-2-*p*-tolylethylene-$^2H_1$ glycol (IVd), and *threo*- and *erythro*-1,2-diphenyl-1-*p*-tolylethylene glycol (VIII). Each reactant produces an aldehyde and one or two ketones. From (1) a comparison of the rates of appearance of these products, (2) the constancy of the hydrogen–deuterium isotope effect with varying catalyst and (3) the observation that *threo*- and *erythro*-VIII are interconverted in 3.13 *N* aqueous ethanolic H_2SO_4 more rapidly than they rearrange, the mechanism of the rearrangement is believed to consist of a reversible formation of open carbonium ion in which no participation by neighboring substituents is required, followed by irreversible migration of hydrogen or aryl. The previous[2a] observation that the k_ϕ/k_H ratio in the rearrangement of I varies from 7.3 to 0.04, depending on catalyst, is explained on the basis of control of these phenyl/hydrogen migration ratios by the relative populations of particular ionic conformations. The intramolecularity of deuterium migration has been established.

In four earlier papers[2] we discussed the mechanisms of the rearrangements of several triaryl substituted glycols. Although the behavior of these glycols in cold concentrated sulfuric acid is now relatively well understood,[2] it is not clear why the ratio of phenyl to hydrogen migration (k_ϕ/k_H) in the rearrangement of triphenylethylene glycol (I) to II and III is not constant, but varies from 7.3 to 0.04, depending upon the catalyst used.[2a] This phenomenon undoubtedly is related to the

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[1] This paper is based upon work performed at Oak Ridge National Laboratory which is operated by Union Carbide Corporation for the Atomic Energy Commission.

[2] (a) C. J. Collins, THIS JOURNAL, **77**, 5517 (1955); (b) B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4329 (1956); (c) V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958); (d) L. W. Kendrick, Jr., B. M. Benjamin and C. J. Collins, *ibid.*, **80**, 4057 (1958).