Celite (5:1, 24 g.) as previously described[40]. This procedure yielded crystalline α-D-glucose pentaacetate (7 mg.), m.p. and mixed m.p. 108°, $[\alpha]^{26}D$ +105° in chloroform (*c*, 1), after recrystallization from ethanol.

(40) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

Acknowledgment.—The authors thank Dr. James G. Dickson, University of Wisconsin, and Dr. Helen Hart, University of Minnesota, for their interest in this work and for samples of urediospores.

ST. PAUL, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

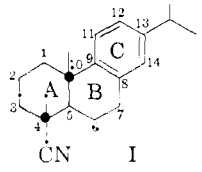
The Stereochemistry of Some Resin Acid Derivatives[1]

BY ERNEST WENKERT AND JAMES W. CHAMBERLIN

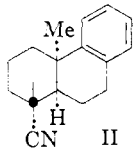
RECEIVED AUGUST 14, 1958

The stereochemistry of the minor product of the aluminum chloride-induced dealkylation of dehydroabietonitrile is presented. The oxidation products of both the major and minor deisopropyl compounds are discussed. The stereoconfiguration of C-13 in pimaric and isopimaric acids is portrayed and its biogenetic significance discussed.

Deisopropyldehydroabietonitrile.—A recent investigation of the aluminum chloride-induced dealkylation of dehydroabietonitrile (I) has shown that the major product of this reaction was 5-isodesoxypodocarponitrile enantiomer (II).[2] It became of interest to isolate and characterize the minor reaction products.

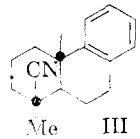


I

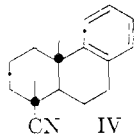


II

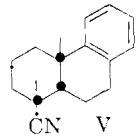
While attempted fractionation of the mother liquor from the crystallization of II failed, the physical behavior of the mixture suggested that it consisted of II and only one other compound. Precipitation from petroleum ether solution finally led to a new product, m.p. 104-105°, whose chemical and spectral analyses proved it to be a stereoisomer of II. Its non-identity with II and desoxypodocarponitrile (III)[2] indicated that it was either deisopropyldehydroabietonitrile (IV) or its 5-iso derivative V. Differentiation between these two possibilities appeared easy in view of the recently described diagnostic test for distinguishing A/B *trans* from A/B *cis* systems of the general structure of II–V.[2] Thus, the new deisopropyl product was exposed to a chromic acid oxidation under controlled conditions. The preponderant formation of a 7-keto product, and the absence of a 6,7-dione, indicated strongly the presence of an A/B *trans* configuration. Hence, the minor dealkylation product was considered to be the long-desired deisopropyldehydroabietonitrile (IV).



III



IV



V

(1) Parts of the first phase of this work were presented at the Ninth Annual Seminar in the Chemistry of Natural Products, University of New Brunswick, Fredericton, Canada, October 23–25, 1957. For a preliminary communication of the second phase *cf.* E. Wenkert and J. W. Chamberlin, THIS JOURNAL, **80**, 2912 (1958).

(2) E. Wenkert and B. G. Jackson, *ibid.*, **80**, 211 (1958).

Soon after starting an oxidative removal of the isopropyl group of dehydroabietonitrile (I)[3] as a means of confirming structure IV, we became aware of the work by Ohta and Ohmori on the deisopropylation of dehydroabietic acid,[4] which showed in most elegant and thorough manner that the reaction mixture consisted of two acids whose stereochemistry corresponded to our nitriles II and IV. A comparison of the physical properties of the hydrolysis product of nitrile IV with those of Ohta's minor acid constituent proved the identity of the dealkylation products.[5]

On the basis of a complete product analysis it now appears that the acid-catalyzed deisopropylation of a dehydroabietic system involves merely the rupture of the C(9)–C(10) bond, besides the cleavage of the isopropyl group, and a subsequent recyclization of the intermediate carbonium ion VI or its equivalent into an A/B *cis* or *trans* system. The amazing similarity in the product ratio of our dealkylation (43% *cis* and 9% *trans*) and that of Ohta (44% *cis* and 6% *trans*)[4] despite an appreciable difference in reaction conditions strongly suggests that the reaction is an equilibrium process and that the product ratio is a reflection of the slightly greater stability of the *cis* configuration in an octahydrophenanthrene of general structure I–V. This is in conformity with previously studied cases of similar structure.[6] Moreover, octahydrophenanthrene (VII) itself led exclusively to a *trans* compound on aluminum chloride-induced equilibration.[7] The presence of an angular methyl group thus strongly diminishes the difference of energy content between a *cis* and *trans* system.[8]

As part of the structural elucidation of II it has been demonstrated that its oxidation by chromic acid yielded a 7-keto compound, a 6,7-dione and an acid of unknown constitution.[2] Investigation of

(3) *Cf.* T. F. Sanderson (assigned to Hercules Powder Company) U. S. Patent 2,750,367 and 2,750,368.

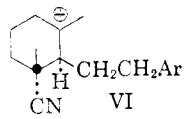
(4) M. Ohta and L. Ohmori, *Pharm. Bull. (Japan)*, **5**, 91, 96 (1957).

(5) The authors are most grateful to Dr. Y. Suzuki of the Kowa Chemical Laboratories, Tokyo, for a mixed melting point determination.

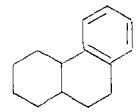
(6) E. Wenkert and T. E. Stevens, THIS JOURNAL, **78**, 2318 (1956), and reference cited therein.

(7) J. W. Cook, N. A. McGinnis and S. Mitchell, *J. Chem. Soc.*, 286 (1944).

(8) *Cf.* R. B. Turner, THIS JOURNAL, **74**, 2118 (1952).

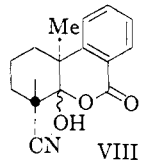


VI



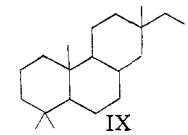
VII

the latter by elemental and spectral analyses showed it to possess structure VIII. It is noteworthy that the lactol moiety, as in VIII, is the common end product of the chromic acid oxidation of ring B of a dehydroabietic system under more drastic conditions.[4,9] Of the two possible modes of the formation of VIII: (a) 6,7-dione → 6,7-dioic acid → 5-hydroxy-6,7-dioic acid → VIII[9a]; (b) 6,7-dione ⇄ 6,7-dione enol → 5-hydroxy-6,7-dione → VIII, path b appears to be more plausible. While the α-oxidation of ketones is well known,[2] that of acids cannot be readily rationalized. Furthermore, a 5-hydroxy-6,7-dione, one of the necessary intermediates in path b, appears to have been isolated.[4,10]

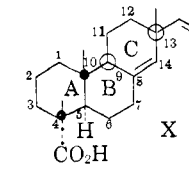


VIII

Pimaric Acids.[11]—Until relatively recently only rimuene, pimarinal[11] (cryptopinone), pimaric[11] and isopimaric acids[11,12] comprised the group of pimarane-type diterpenes (*cf.* IX). With the discovery of two double-bond isomers of the pimaric acids[13,14], the fungal metabolites, rosololactone and rosenonolactone,[15] and darutigenol,[16] with the suggestion of a biogenetic relationship, linking the pimaradienes with the tetracarbocyclic diterpenes and the Garrya and aconite alkaloids,[17] and with the recent flurry of activity in the latter field, attention has been focused again on the family of diterpenes with general structure IX. In order to gain more insight into the steric as well as possible biogenetic interrelationship of various di-, tri- and tetracarbocyclic diterpenes, it became of utmost importance to ascertain the stereochemical features of two of the more representative pimaradienes, pimaric (formerly dextropimaric[11]) and isopimaric (formerly isodextropimaric[11]) acids (X).



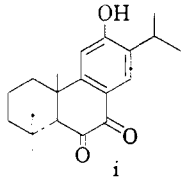
IX



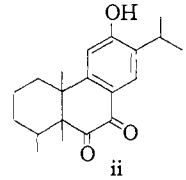
X

Owing to the labors of Ruzicka and co-workers[18] and Harris and Sanderson[19] the stereochemistry of three of the five asymmetric centers of the pimaric acids is known with certainty, *cf.* X, leaving only the configuration of C-9 and 13 in doubt. Whereas the available chemical data were interpreted as showing an epimeric relationship of the two acids at C-13,[19] it was demonstrated later that such inference was based on stereochemically ambiguous grounds.[17] While thus chemical evidence has yet to be brought to bear on the stereochemical points in question, recent surface tension data have suggested strongly a difference between the acids at C-13, pimaric acid possessing a β-vinyl group and isopimaric acid an α-vinyl function, and has hinted at the presence of the natural α-configuration of the hydrogen at C-9 of both acids.[20]

As initial goal it became of interest to compare the steric environments at C-13 of pimaric and isopimaric acids. In view of the identity of configuration of the acids at C-4, 5 and 10, any reaction which would be capable of destroying the asymmetry at C-9 or altering it in both acids in equal fashion, would be expected to lay bare the configuration of C-13. Such reaction appeared to be the well-known acid-catalyzed lactonization of the dihydro derivatives of the resin acids,[21,22a] which in the case of dihydropimaric acid had led to a 5- and 6-membered lactone of suggested structures XI and XII, respectively.[22] Thus, dihydropimaric and dihydroisopimaric acids were exposed to concentrated sulfuric acid under identical experimental conditions—ten minutes at room temperature. Both reactions led to 1.6:1 mixtures of 5- and 6-membered lactones, respectively. However, the two sets of lactones were not identical, as revealed by their melting points, infrared spectra and



i



ii

(9) (a) E. S. Hansen and H. H. Zeiss, THIS JOURNAL, **77**, 1643 (1955); (b) H. H. Zeiss and M. Tsutsui, *ibid.*, **77**, 6707 (1955).

(10) In connection with a previous discussion of 6,7-diones, attention was drawn to their structural similarity to xanthoperol (i).[2] Unfortunately most recently its structure was revised to ii [J. B.-S. Bredenberg, *Acta Chim. Scand.*, **11**, 927 (1957)], mainly on the strength of the facts that it did not enolize spontaneously and that Clemmensen reduction led to a 7-keto compound which proved not to be sugiol. An explanation for the first point has been given already *in toto*,[2] whereas the second fact merely implies that zinc reduction of the 6,7-dione was preceded by enolization and led to the more stable *cis*-5-isosugiol. Thus in the absence of any other data the natural diterpenoid constitution i can be retained for xanthoperol.

(11) It is suggested that for reasons of simplification and unification of the terpene nomenclature the prefix *dextro* be dropped from dextropimaric and isodextropimaric acids, since it has lost all but its historical significance.

(12) *Cf.* Sir John Simonsen and D. H. R. Barton, "The Terpenes," Cambridge University Press, Cambridge, England, Vol. III, 1952, pp. 344, 447 and 457; Sir John Simonsen and W. C. J. Ross, *ibid.*, Vol. V, 1957, p. 610.

(13) T. Ukita, T. Tsumita and N. Utsugi, *Pharm. Bull. (Japan)*, **3**, 441 (1955).

(14) F. Petrů and V. Galík, *Coll. Czech. Chem. Comm.*, **18**, 717 (1953).

(15) A. Harris, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1799, 1807 (1958).

(16) J. Pudles and E. Lederer, Abstracts of the 16th International Congress of Pure and Applied Chemistry, Paris, France, July, 1957, p. 243.

(17) E. Wenkert, *Chemistry & Industry*, 282 (1955).

(18) L. Ruzicka and Sternbach, *Helv. Chim. Acta*, **23**, 124 (1940).

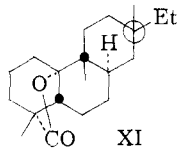
(19) G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 2079, 2081 (1948).

(20) H. H. Bruun, *Acta Acad. Aboensis, Math. et Phys.*, **19** (3), 1 (1954).

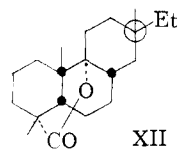
(21) L. A. Subluskey and T. F. Sanderson, THIS JOURNAL, **76**, 3512 (1954), and references contained therein.

(22) (a) Le-van-Thoi and J. Ourgaud, *Bull. soc. chim. France*, 202 (1956); (b) 205 (1956), and preceding papers.

optical rotations.[23] *These data constitute a chemical proof of the dissimilarity of the stereochemistry of pimaric and isopimaric acids at C-13.*[24]

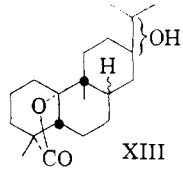


XI

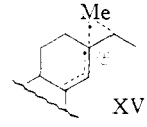


XII

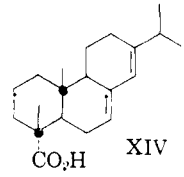
The above results require a slight modification in the theory of diterpene biogenesis.[17] The assumption of all tetracarbocyclic and pimaradienic tricarbocyclic diterpenes being derivable from a pimaradienic precursor, possessing an axial 13-vinyl group, is no longer necessary. Since this supposition had been based on a stereochemical interpretation of the acid-catalyzed pimaradiene–abietadiene conversion,[25] it was of interest to study such a reaction. As a consequence, pimaric and isopimaric acids were treated with concentrated sulfuric acid under identical conditions, at −30° for 15 minutes—a procedure which in the case of pimaric acid had yielded previously a hydroxylactone.[26] A mixture of neutral and acidic substances could be obtained from both starting acids. The neutral fractions consisted of an oily, intimate mixture of 5- and 6-membered lactones as well as the previously reported hydroxylactone.[26] The infrared spectrum of the latter indicated it to be a γ-lactone. On the basis of arguments similar to those put forward for the interpretation of the lactonization of dihydroabietic[21] and dihydropimaric acids[22] it is possible to assign structure XIII to the hydroxylactone. The fact that this lactone resulted from both starting materials suggested that either the intermediate leading to it—an olefin or its conjugate acid—must be identical in both cases, or the lactone represents an equilibrium hydration product. The acidic fractions from both natural products could be shown to be abietic acid (XIV) by its characteristic ultraviolet absorption peak at 241 mμ as well as the identity of the infrared spectrum and optical rotation of its di-*n*-amylamine salt with those of an authentic sample. *These results represent the first conversion of a pimaradiene to an abietadiene, the final step in the generally accepted biogenesis of abietadienic diterpenes.*[25] Furthermore, they suggest that the ease of such transformation is independent of the conformation of the migrating methyl group. Thus, whereas the previous suggestion of an axial methyl group migrating more readily than an equatorial one, because of the former's ability to pass through a low-energy transition state such as XV,[17] undoubtedly is still valid in rigid ring systems, its lack of confirmation in the case of the pimaradienes may be ascribed to the conformational flexibility of ring C and the small ring deformation necessary to attain state XV with a methyl in either quasi-axial or -equatorial orientation.[27,28]



XIII



XV



XIV

With the non-identity of pimaric and isopimaric acids at C-13 assured, it became of interest to ascertain the relative orientation of the C-13 substituents.[29] The acid-catalyzed lactonization of the dihydro acids, if carried to equilibrium, appeared to be a reaction most suitable for stereochemical diagnosis. Irrespective of the structures of the previously obtained lactones, the configuration of the products of an equilibrium-controlled lactonization has to be as represented in formulas XI and XII. These constitute the most stable configurations, as also illustrated by their conformational models XVI and XVII, respectively. Furthermore, as again portrayed by XVI and XVII, a change from the five- to six-membered lactone involves, among other things, a conformational inversion at C-13. As a consequence, it was anticipated that the yield ratios of equilibrated lactones would differ in the cases of two C-13 epimeric compounds. Moreover, it could be predicted that the pimaric acid, which yielded more five-membered lactone at equilibrium than its epimer, would have its bulkier 13-substituent in an axial configuration.[30]

(23) The claim that these data constituted the first proof of the non-racemic nature of isopimaric acid[1] was inadvertently in error, since this fact was already hinted at by T. Ukita and T. Tsumita [*J. Pharm. Soc. Japan*, **72**, 1324 (1952)] and firmly established by D. E. Baldwin, V. M. Loeblich and R. V. Lawrence [*J. Org. Chem.*, **23**, 25 (1958)].

(24) O. E. Edwards and R. Howe [*Chemistry & Industry*, 629 (1958)] and B. Green, A. Harris and W. B. Whalley [*ibid.*, 1084 (1958)] have arrived at the same conclusion independently. We are most grateful to Drs. Edwards and Whalley for sending us their data prior to publication.

(25) *Cf.* L. Ruzicka, *Experientia*, **10**, 357 (1953).

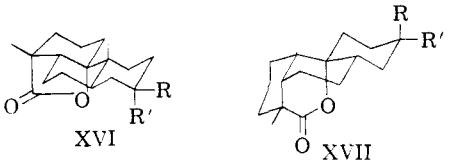
(26) E. E. Fleck and S. Palkin, THIS JOURNAL, **62**, 2044 (1940).

(27) An alternative explanation of the identity of products and product ratios of the acid-catalyzed rearrangement of the pimaric acids may reside in the possibility of there being a conformational dependence of the migratory aptitude of the 13-methyl group after all, but, also, there being a difference in the ease of migration of the Δ^{8-14} linkage toward C-9, the two effects fortuitously being equal in magnitude and opposite in direction. The similarity of the two stoichiometries would suggest further that the resin acids are epimeric not only at C-13 but also at C-9, and that the compound with a quasi-axial 13-methyl group has an unstable C-9 configuration, *i.e.*, a quasi-equatorial 9-hydrogen. While rigorous evidence is still desirable to distinguish between the two possible explanations, the latter interpretation is certainly strengthened by Whalley's data which favor a C-13 as well as C-9 epimeric relationship of the pimaric acids.[24]

(28) While the pimaradiene–abietadiene transformation is the best known biogenetic involvement of the 13-methyl group, it appears not to be the only one. Diterpenes of higher oxidation state display their one-carbon side chain at C-14. Figure 1 portrays the biogenetic relationship of ring C or potential ring C of all di- and tricarbocyclic diterpenes of known configuration. While all transformations are of simple, phytochemically predictable nature, the biosynthesis of the furan nucleus requires comment. On the basis of the apparent biogenetic derivation of menthofuran from pulegone [R. H. Reitsema, *J. Am. Pharm. Assoc., Sci. Ed.*, **47**, 267 (1958)], it appears that bio-oxidation of an α, β-unsaturated carbonyl compound, probably *via* the β,γ-form and the β,γ-epoxide or its equivalent, leads to a furan [*cf.* H. Fritel and M. Fertizon, *J. Org. Chem.*, **23**, 481 (1958)].

(29) One method investigated involved the exhaustive oxidation of the dihydro acids to enantiomeric α-methyl-α-ethylsuccinic acids and the determination of their absolute configuration [*cf.* J. Porath, *Arkiv Kemi*, **3**, 163 (1951)]. However, this scheme was abandoned when the above procedure came to early fruition.

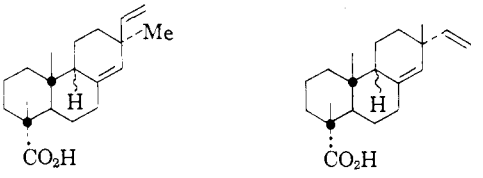
(30) It appeared quite certain that the change of the position of equilibrium of the sets of lactones for the epimeric acids would be very small, since it was dependent merely on the difference in size of a methyl and an ethyl group. Nevertheless, no matter how small the change, as long as it is reproducible, it is an unambiguous stereochemical



XVI XVII

a, R = Et, R′ = Me
b, R = Me, R′ = Et
c, R = H, R′ = i-Pro

After some experimentation it was discovered that equilibrium was attained on exposure of the dihydro acids to concentrated sulfuric acid at room temperature for 19 hours. Under these conditions dihydropimaric acid yielded 5 ± 0.6% 5-lactone and 95 ± 0.6% 6-lactone as determined by infrared spectrophotometric analysis. The attainment of equilibrium was corroborated by the observation that the 6-lactone of dihydropimaric acid led to the same product mixture under identical conditions. Finally, dihydroisopimaric acid produced 3.6 ± 0.8% 5-lactone and 96.4 ± 0.8% 6-lactone. *These results suggest that the dihydropimaric acid lactones are best represented by XVIa and XVIIa and the dihydroisopimaric acid lactones by XVIb and XVIIb and, furthermore, that pimaric acid is XVIII and isopimaric acid XIX.* This is in agreement with the structural assignments of the acids from surface tension data.[20]



XVIII XIX

Characterization of the dihydropimaric 6-lactone (XVIIa) revealed it to be identical with the lactone obtained under kinetic control. Although structure XII had been assigned to it previously,[22] the configuration of the asymmetric centers at only C-4, 5, 9 and 10 rested on a firm basis. The present results are the first to permit an assignment of a β-configuration to the hydrogen at C-8. Unfortunately insufficient amounts of the equilibrium 5-lactone prohibited its comparison with the 5-lactone from kinetically controlled runs. However the structural assignment of the latter (XI) was based on rational reaction mechanisms,[22] so as to make a comparison with the equilibrium product less urgent.

The formation of two lactones in the equilibrium reactions indicates that the products have similar energy contents. The actual product ratio suggests that the 6-lactone is more stable than the 5-lactone by somewhat less than 2 kcal. This value is in agreement with one predicted (*ca.* 1.7 kcal.) from comparison of the two conformations XVI and XVII and the observation that the former has two more 1,3-diaxial non-bonded interactions between its angular methyl group and neighboring hydrogen atoms than the latter. This picture would change drastically in cases where the difference of size of two 13-substituents is greater than in the pimaric acids. In such cases only one lactone might be expected at equilibrium, with its bulkier 13-substituent in an equatorial configuration. The lactones derived from dihydroabietic acid[31] or commercial, partially hydrogenated rosin[21] are interesting test cases. While acid-catalyzed lactonization of the dihydro compounds leads first to a 5-lactone[21,31] further acid treatment results in the formation of a 6-lactone.[32] Since in the latter the 13-isopropyl group would have to be equatorially oriented, the structure of the lactones must be XVIc and XVIIc and the dihydroabietic

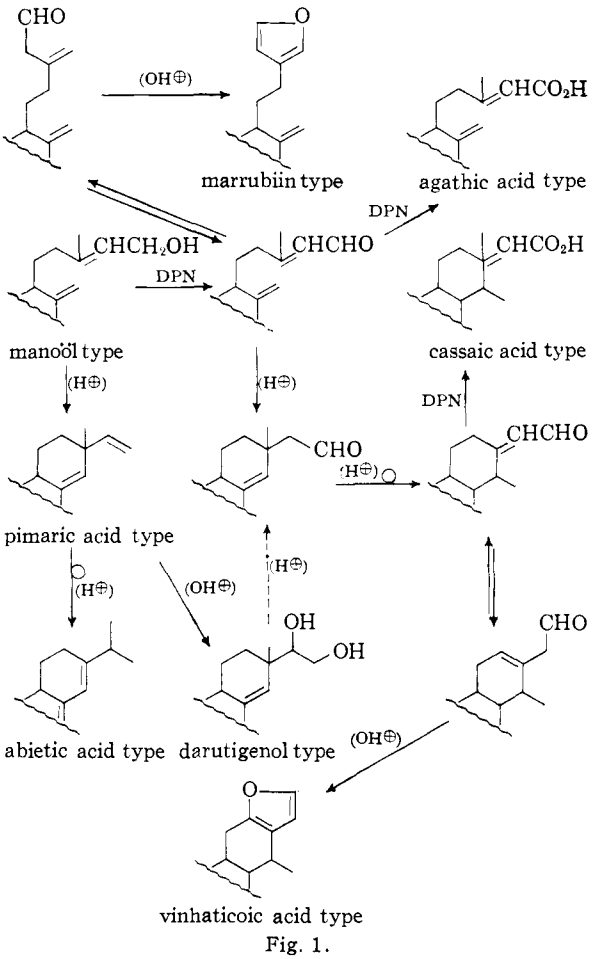
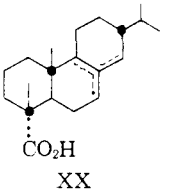


Fig. 1.



XX

criterion. As indicated in the further discussion, the change proved to be indeed little, but the ratio of equilibrium constants was somewhat less than 2, within the order of magnitude expected for a difference in bulk of a methyl and ethyl group.

(31) L. Velluz, G. Muller, A. Petit and J. Mathieu, *Bull. soc. chim. France*, 401 (1954).

(32) Le-van-Thoi, *ibid.*, 761 (1955).

(33) Should Velluz's contention, that the dihydro acids are Δ^{13-14} olefins and that the C-13 asymmetry is introduced during the lactonization and not during the prior hydrogenation of the resin acids, prove to be correct, then the above discussion is relevant only to the stereochemistry of the lactones.

(34) *Cf.* the discussion of catalytic hydrogenation under thermodynamic control [E. Wenkert and D. K. Roychaudhuri, *J. Org. Chem.*, **21**, 1315 (1956); THIS JOURNAL, **80**, 1613 (1958)].

acid mixture XX.[33] The equatorial configuration of the isopropyl group would also be the expected consequence of the partial hydrogenation of the abietic-type resin acids.[34]

Acknowledgments.—The authors are most grateful to Professor O. Jeger and Drs. Le-van-Thoi and Lawrence for gifts of the resin acids, to Ciba Pharmaceutical Products, Inc., Summit, N. J., for financial support and to the Institute for Atomic Research, Ames, Iowa, for the use of a Baird infrared spectrophotometer.[35]

Experimental

Deisopropyldehydroabietonitrile (IV).—Dealkylation of 20.0 g. of dehydroabietonitrile by a previously described procedure[2] led to two crops, 5.4 g. and 1.4 g., of 5-isodesoxypodocarponitrile enantiomer (II). Reduction of the mother liquor, the petroleum ether solution, in volume and cooling gave 2.5 g. of crystalline material, m.p. 70–90°, which on non-equilibrium crystallization from petroleum ether and recrystallization yielded 1.0 g. of deisopropyldehydroabietonitrile (IV), m.p. 104–105°; mixed m.p. with II 70–80°; $[\alpha]_D$ 59.2° (EtOH); spectra: infrared (CCl_4), CN 4.50(m) μ; ultraviolet (95% ethanol), λ_{max} 265 mμ (ϵ 425) and 272m μ (ϵ 385).

Anal. Calcd. for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.86. Found: C, 85.30; H, 8.76; N, 5.64.

The combined filtrates of the petroleum ether crystallizations yielded 1.1 g. of an inseparable crystalline mixture. Its composition could be determined by comparison with prepared mixtures of the two deisopropyl isomers. The best fit between the isolated mixture, m.p. 70–74°, $[\alpha]_D$ 34.9° (EtOH), and a prepared combination was obtained, when the latter consisted of 55% II and 45% IV, m.p. 70–74°, $[\alpha]_D$ 35.2°. Thus the mixture contained 0.6 g. of II and 0.5 g. of IV, resulting in a 43% yield of 5-isodesoxypodocarponitrile enantiomer (II) and 9.4% of deisopropyldehydroabietonitrile (IV).

Alkaline hydrolysis of 100 mg. of deisopropyldehydroabietonitrile (IV) by a previously described procedure[2] led to 75 mg. of a crystalline acid, m.p. 171–173°. Recrystallization from petroleum ether yielded deisopropyldehydroabietic acid, m.p. 172–173°; mixed m.p. with 5-isodesoxypodocarpic acid enantiomer 138–140°; mixed m.p. with Ohta and Ohmori sample[4] 162–170°; $[\alpha]_D$ 63.6° (EtOH) (Ohta and Ohmori sample[4] 69.4°).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.38; H, 8.78.

Oxidations of Nitriles.—The solid acidic product obtained from the previously described chromic acid oxidation of 5-isodesoxypodocarponitrile enantiomer (II)[2] was recrystallized from methanol–water. It (VIII) melted at 230–232°, $[\alpha]_D$ 11.8° (EtOH); spectra: infrared ($CHCl_3$), OH 2.80(m) μ, 3.00(m) μ, 3.10(m) μ, CN 4.48(w) μ, C=O 5.80-(s) μ, C=C 6.24(s) μ; ultraviolet (95% ethanol), λ_{max} 239 mμ (ϵ 17,500) and 284 mμ (ϵ 2660).

Anal. Calcd. for $C_{16}H_{17}O_3N$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.95; H, 6.54; N, 4.96.

Chromic acid oxidation of 100 mg. of deisopropyldehydroabietonitrile (IV) by a previously described procedure[2] yielded 1 mg. of acidic product and 81 mg. of neutral solid, m.p. 157–165°. Three crystallizations from petroleum ether gave 7-ketodeisopropyldehydroabietonitrile, m.p. 170–172°, $[\alpha]_D$ −8.9° (EtOH); spectra: infrared (CCl_4), CN 4.51(w) μ, C=O 5.95(s) μ, C=C 6.30(m) μ; ultraviolet (95% ethanol), λ_{max} 251 mμ (ϵ 13,200) and 291 mμ (ϵ 2260).

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.57; H, 7.56; N, 5.53. Found: C, 80.43; H, 7.65; N, 5.45.

Lactonization of the Dihydropimaric Acids.—A solution of less than 100 mg. of acid in 2 ml. of concentrated sulfuric acid was swirled for 10 minutes at room temperature, then poured on ice, diluted with water and extracted with ether. The combined ether extracts were washed once with water, twice with 5-ml. portions of 1% aqueous sodium hydroxide and once more with water, dried over magnesium sulfate and evaporated to dryness. The non-crystalline neutral residue was chromatographed on 7 g. of alumina. Acidification of the basic washings, extraction with ether, drying of the organic extracts and evaporation of the solvent led to no acidic products.

Exposure of 64 mg. of dihydropimaric acid to the above treatment yielded 50 mg. of a neutral material which on chromatography and petroleum ether elution in 8-ml. portions gave 13 mg. of crystals, m.p. 75–85°, in the first eight fractions. Crystallization from acetone–water led to dihydropimaric 5-lactone (XVIa), m.p. 98–99°; $[\alpha]_D$ −21° (EtOH) [lit. value: m.p.'s 98–99°,[35a] 100°[22a]; $[\alpha]_D$ −17° (EtOH)[22a]]; infrared spectrum ($CHCl_3$), C=O 5.70(s) μ. The succeeding nineteen fractions furnished 25 mg. of a non-crystalline mixture of 5- and 6-lactones, while further fractions afforded 10 mg. of crystals, m.p. 100–117°. Crystallization from acetone–water gave dihydropimaric 6-lactone (XVIIa), m.p. 139–141°, $[\alpha]_D$ −40° (EtOH) [lit. value: m.p.'s 143–144°,[36] 142°[22a]; $[\alpha]_D$ −40° (EtOH),[36] −45° (EtOH)[22a]]; infrared spectrum (CCl_4), C=O 5.82(s) μ. A similar experiment with 65 mg. of dihydropimaric acid gave 19 and 10 mg. of crystalline 5- and 6-lactones, respectively. The average ratio of 5- to 6-lactones based on isolable crystalline products was 1.6:1.0.

Acid treatment of 64 mg. of dihydroisopimaric acid yielded also 50 mg. of neutral material. The first six petroleum ether eluting fractions contained 13 mg. of crystals, m.p. 105–107°. Crystallization from acetone–water yielded dihydroisopimaric 5-lactone (XVIb), m.p. 108–110° (lit.[35a] m.p. 109–110°[35]); $[\alpha]_D$ −15° (EtOH); infrared spectrum ($CHCl_3$), C=O 5.70(s) μ, non-identical with above dihydropimaric 5-lactone in the 8.9–11.5 μ region. Thirteen more fractions gave 10 mg. of a non-crystalline mixture of 5- and 6-lactones, while the remaining fractions yielded 14 mg. of dihydroisopimaric 6-lactone (XVIIb), m.p. 60–65°, $[\alpha]_D$ −40° (EtOH); infrared spectrum (CCl_4), C=O 5.82(s) μ, non-identical with above dihydropimaric 6-lactone in the 8.9–11.0 μ region. A similar experiment with 85 mg. of dihydroisopimaric acid produced 28 and 13 mg. of crystalline 5- and 6-lactones, respectively. The average ratio of 5- to 6-lactones based on isolable crystalline products was 1.6:1.0.

Solutions of 20-mg. samples of dihydropimaric acid in 1 ml. of concentrated sulfuric acid were allowed to stand for 19 hr. After work-up as above, leading only to neutral material, the dry gummy residue was taken up in identical volumes of CCl_4, the infrared spectra of the solutions taken and the intensity of the carbonyl bands in the 5.6–5.9 μ region compared with those of solutions made up of mixtures of pure dihydropimaric 5- and 6-lactones, containing 3–11% of the former. Such comparisons led to an equilibrium value for the dihydropimaric lactones of 5.0 ± 0.6% 5-membered and 95.0 ± 0.6% 6-membered lactone. A similar value was obtained by the identical treatment of dihydropimaric 6-lactone. Similar equilibration of dihydroisopimaric acid yielded 3.6 ± 0.8% 5-lactone and 96.4 ± 0.8% 6-lactone.

Acid Treatment of the Pimaric Acids.—After 100 mg. of pimaric acid was mixed with 1 ml. of concentrated sulfuric acid, frozen solid in a Dry Ice–acetone-bath, the mixture warmed to −25 to −35°, the sulfuric acid having melted, and stirred for 15 minutes. Ice was added at −15 to −20° until the yellow color of the mixture had discharged. Thereupon the mixture was poured into ice-water, extracted with ether, the organic extracts washed twice with water, twice with 5-ml. portions of 1% NaOH solution, once with water, dried over magnesium sulfate and evaporated. The non-crystalline neutral residue, 50 mg., was chromatographed on alumina. The 19:1 petroleum ether–ether eluates afforded 18 mg. of non-crystalline material, whose 5.70 and 5.82 μ peaks and absence of an OH absorption in the infrared showed it to be a mixture of olefinic 5- and 6-lactones. Elution with 1:2 petroleum ether–ether furnished 27 mg. of a solid, m.p. 170–175°, which after crystallization from petroleum ether–acetone could be shown to be a hydroxylactone, m.p. 180–181°

(35) NOTE ADDED AFTER ACCEPTANCE: Mass spectral data have now confirmed Whalley's evidence for an epimeric relationship of pimaric and isopimaric acids at both C-9 and C-13 (*cf.* refs. 24 and 27) [H. H. Bruun, R. Ryhage and E. Stenhagen, *Acta Chem. Scand.*, **12**, 789 (1958)]. Furthermore, these new data are in agreement with our conclusions above regarding the actual orientation of the methyl and vinyl substituents at C-13 in the two acids.

(35a) G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 2081 (1948).

(36) T. Hasselstrom and B. L. Hampton, *ibid.*, **61**, 967 (1939).

(lit.[26] m.p. 181–182°); infrared spectrum (KBr), OH 2.85-(m) μ and C=O 5.75(s) μ.

Acidification of the combined base washings, extraction with ether, drying, and solvent evaporation led to 50 mg. of non-crystalline acidic material, $[\alpha]_D$ −38° (EtOH); ultraviolet spectrum (95% ethanol), λ_{max} 241 mμ. The acidic substance was dissolved in 0.1 ml. of acetone, 2 drops of di-*n*-amylamine (b.p. 190–192°) added[37] and the solution cooled. Filtration of the crystalline precipitate and crystallization from acetone furnished a salt, $[\alpha]_D$ −53° (EtOH), whose infrared spectrum was identical with that of a freshly prepared sample of the di-*n*-amylamine salt of abietic acid, $[\alpha]_D$ −59° (EtOH).

Identical acid treatment and work-up of 100 mg. of isopimaric acid yielded 17 mg. of a non-crystalline mixture of 5- and 6-lactones, 26 mg. of hydroxylactone, m.p. 160–175°, increased to 180–181° after crystallization from petroleum ether–acetone, no depression on admixture with above hydroxylactone, identical infrared spectra, and 45 mg. of acid, $[\alpha]_D$ −45° (EtOH), ultraviolet spectrum (95% ethanol), λ_{max} 241 mμ, whose di-*n*-amylamine salt, $[\alpha]_D$ −58° (EtOH), had an infrared spectrum identical with that of the abietic acid salt.

(37) *Cf.* G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 334 (1948).

AMES, IOWA

[CONTRIBUTION NO. 500 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Aminodihydrofuramides from 3-Amino-1-propynes and Carbon Monoxide

BY J. C. SAUER, B. W. HOWK AND R. T. STIEHL

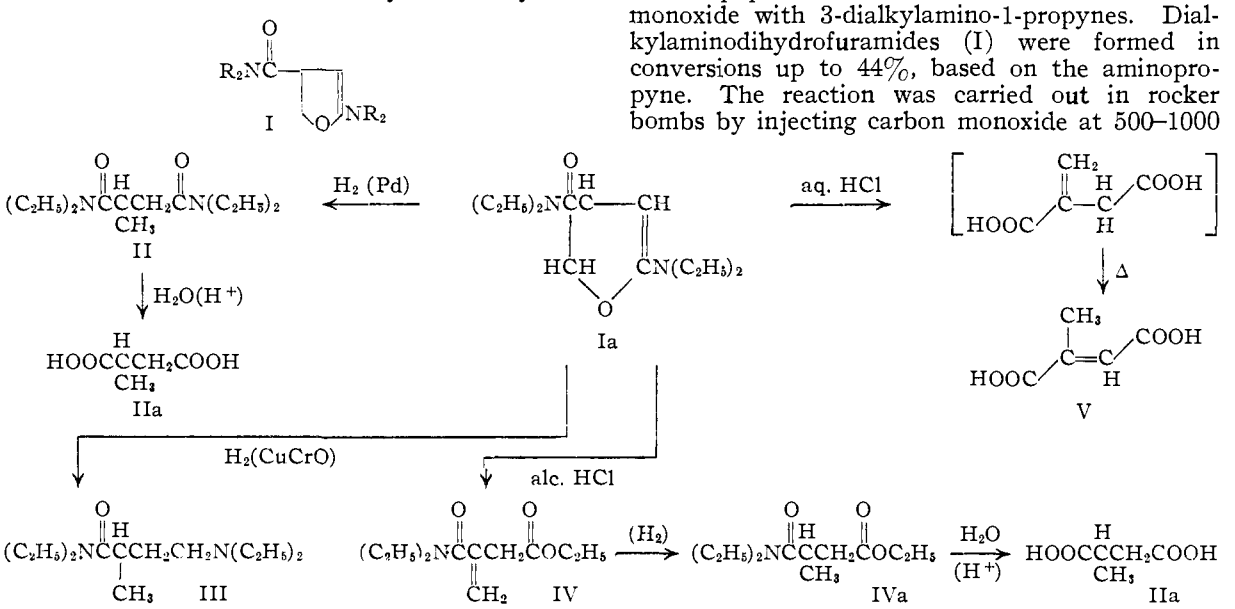
RECEIVED JULY 28, 1958

The reaction of 3-diethylamino-1-propyne with carbon monoxide has given N,N-diethyl-5-diethylamino-2,3-dihydro-3-furamide in 44% yield. The synthesis was carried out by injecting carbon monoxide at 500–1000 atm. into the aminopropyne dissolved in a ketone solvent at a temperature of 125°. Catalytic amounts of dicobalt octacarbonyl were necessary for the synthesis. The reaction has also been extended to several other aminopropynes. The products undergo facile ring cleavage with hydrogen, hydrogen chloride or water to give succinic acid derivatives. The mechanism for this unusual transformation is unknown, in part because other products of the reaction were isolable only as intractable residues.

The literature contains many references to the reactions of acetylene or substituted acetylenes with carbon monoxide. These reactions generally involved various metallic carbonyls as catalysts or reactants, and the products were mainly acrylic compounds or hydroquinones.[1] Although a number of functionally substituted acetylenes have been studied in these reactions, only one reference to the interaction of 3-dialkylamino-1-propynes with carbon monoxide appears to have been reported. With iron carbonyl hydride furnishing the carbon monoxide needed for the synthesis, several 3-dialkylamino-1-propynes were converted into the 2,5-bis-(dialkylaminomethyl)-hydroquinones.[2]

This paper describes a new reaction of carbon monoxide with 3-dialkylamino-1-propynes. Dialkylaminodihydrofuramides (I) were formed in conversions up to 44%, based on the aminopropyne. The reaction was carried out in rocker bombs by injecting carbon monoxide at 500–1000 atm. into a solution of the aminopropyne at 125°. Ketones such as acetone or cyclohexanone were the best solvents tested. Catalytic amounts of dicobalt octacarbonyl were necessary for the synthesis.

The novel products were identified mainly on the basis of the chemical evidence indicated schematically below. N,N-Diethyl-5-diethylamino-2,3-dihydro-3-furamide (Ia) undergoes facile ring cleavage at the bond in the 1,2-position. Open-chain compounds, all of which may be considered to be derivable from methylsuccinic acid, were formed in



(1) (a) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949; (b) J. W. Reppe, *et al.*, *Ann.*, **582**, 1 (1953); (c) E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 230 (1950); 48, 763, 766 (1951); (d) E. R. H. Jones, G. H. Whitham and M. C. Whiting, *ibid.*, 1865 (1954).

(2) Reference 1a, p. 293; J. W. Reppe, *et al.*, *Ann.*, **582**, 142 (1953).