minute. Fresh chloroform was used to develop the bands, of which there were three. The free-base porphine formed a reddish-purple band which was washed through the column and collected. The tarry by-products remained near the top of the column as a brown-black band. Any zinc complex which was not decomposed by the acid formed a purple band intermediate between the porphine and the tarry band. The zinc complex could be recovered, by eluting with acetone, and subsequently reprocessed. The free-base porphine obtained from this procedure was about 95% pure.

The chloroform solution of the porphine was concentrated by evaporation and chromatographed on Magnesol. The Magnesol column (a 13 × 15 cm. sintered-glass filter funnel) was packed using suction and the column developed under the same conditions with fresh chloroform. Four bands were obtained on this column, from top to bottom they were: tan-green, light green, brown and dark green. The dark green band was tetraphenylporphine, the tan-green and the light green bands contained considerable tetraphenylchlorin and some tetraphenylporphine. The brown band was not characterized.

The column was permitted to go "dry" under suction. It was then inverted on a glass plate and shaken gently to remove the packing in one piece. The bands were separated mechanically and dried. After drying, the individual bands were packed into appropriately sized columns and eluted. The dark green porphine band was treated first with acetone and then with chloroform. The acetone caused the green Magnesol to turn reddish purple. The chloroform concentrated the porphine and washed it through the column. It was necessary to add alternately acetone and then chloroform until the porphine was completely eluted.

The eluted chloroform solution of the porphine was evaporated to dryness and spectrophotometrically pure tetraphenylporphine was obtained.[3]

Using the above procedure about 80 g. (18% yield on the basis of pyrrole) of pure tetraphenylporphine was prepared. This procedure may also be followed using talc as an adsorbent instead of Magnesol. However, the flow of solvent through talc is considerably slower than through Magnesol. An even greater advantage of Magnesol is that approximately five times more porphine could be chromatographed on it than on talc. About 5 g. of crude porphine could be chromatographed on the 13 × 15 cm. column of Magnesol.

CONTRIBUTION NO. 241 FROM THE
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[3] The absorption spectra were compared with an authentic sample kindly supplied by G. D. Dorough, Washington University, St. Louis, Missouri.

[4] Work was performed at the Ames Laboratory of the Atomic Energy Commission.

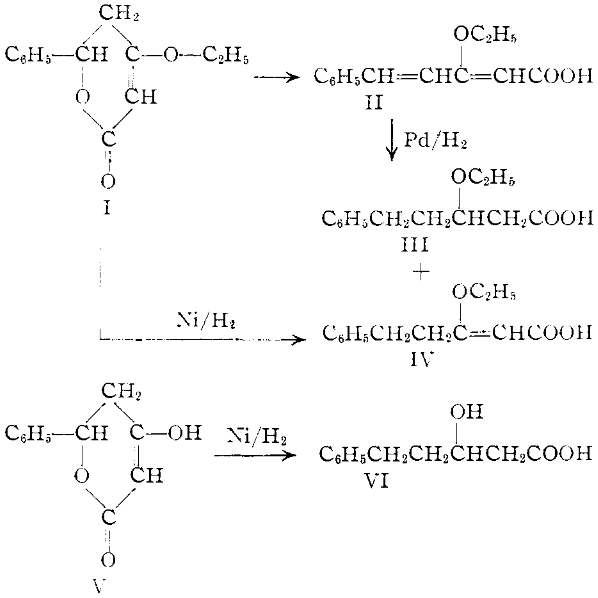
Reduction of δ-Lactones by Catalytic Hydrogen

BY EVANS B. REID AND JOEL R. SIEGEL

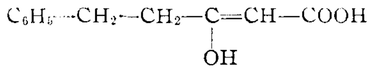
RECEIVED OCTOBER 8, 1953

In a recent study of the chemical properties of 4-ethoxy-6-phenyl-5,6-dihydro-2-pyrone[1] (I) the lactone ring of the latter was opened by treatment with base and the resultant 3-ethoxy-5-phenyl-2,4-pentadienoic acid (II) was subjected to catalytic hydrogenation using 5% palladium black supported on barium sulfate. This led to three products, *viz.*, an unidentified oil, considered possibly to be 2-ethoxy-4-phenylbutane, the expected 3-ethoxy-5-phenylvaleric acid (III) and a different compound, m.p. 109–112°, that gave analytical figures approximating those calculated for 3-hydroxy-5-phenylvaleric acid (VI). Although this product was not obtained in a pure state, it and the ethereal degradation product were considered entirely likely in view of certain hydrogenolyses observed by other workers.[2]

It is the purpose of the present paper to show that this conclusion, in so far as it concerns the impure hydrogenation product, m.p. 109–112°, was in error, and also to place on record our observations regarding the hydrogenolysis of 4-hydroxy-6-phenyl-5,6-dihydro-2-pyrone (V) and of the ethyl enol ether of the latter compound I.



$C_6H_5-CH_2-CH_2-CH=CH-COOH$
VII



$C_6H_5-CH_2-CH_2-\underset{OH}{C}=CH-COOH$
VIII

Upon further purification the impure product was freed of a gummy contaminant, and then had m.p. 114–115.5°. By direct comparison with 3-hydroxy-5-phenylvaleric acid (VI) (*vide infra*), dissimilarity was established.

In separate experiments it was demonstrated that reduction of the ethoxypyrone I by means of hydrogen and Raney nickel, afforded the same material exclusively, identity being established by means of mixed melting point determinations, and by the fact that the infrared absorption spectra of both products, either mulled in mineral oil or taken in chloroform solution, were virtually superposable.

Analysis of the material showed it to be a dihydro derivative of 3-ethoxy-6-phenyl-1,3-pentadienoic acid (II) and the weak acidity of the compound (solubility in carbonate, insolubility in bicarbonate solutions) was confirmed by the presence, in the infrared absorption spectrum, of a strong band at 5.92 μ (carboxyl absorption). Three structures thus became possible for the new acid, two of them being the olefinic isomers of 3-ethoxy-6-phenyl-2-pentenoic acid (IV). That the substance is in fact IV, and that it cannot have the double bond elsewhere than in the 2-position, is shown by the following evidence.

In the infrared the ethylenic absorption band shows strongly at 6.18 μ, which corresponds exactly with the position of the ethylenic absorption of the ethoxy-pyrone I, in which the ethoxylated carbon

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[1] E. B. Reid and W. R. Ruby, THIS JOURNAL, **73**, 1054 (1951).

[2] J. M. Sprague and H. Adkins, *ibid.*, **56**, 2669 (1934).

double bond is known to be conjugated with the lactone grouping. Further, a study of the hydrogenolysis of the hydroxy-pyrone V has revealed that under comparable conditions the lactone ring is opened to form 3-hydroxy-5-phenylvaleric acid,[3] the constitution of which was established *via* analysis and dehydration to form γ-benzylcrotonic acid[3] (VII). The fact that the pyrone ring of I is stable toward Raney nickel in the absence of hydrogen renders it certain that its opening, and also that of the hydroxy-pyrone V, in the presence of hydrogen and nickel is due to reductive cleavage which must saturate the carbons α,β to the benzene ring. It follows from this that the initial product from the hydrogenolysis of the hydroxypyrone V should be given by structure VIII. Further reduction of VIII to yield VII most probably occurs through the keto form, which would equilibrate with VIII, since the enol ether IV is stable to further reduction under these conditions.

It is of interest that the hydroxy-pyrone V showed varying sensitivity toward different catalysts. Thus, although hydrogen with palladium supported with several different bases was without effect, and whereas Adams catalyst gave a mixture of unidentified products that resulted from the uptake of four moles of hydrogen,[4] and the Mozingo, procedure[5] reduced the compound to such an extent that only volatile products were obtained, Raney nickel and hydrogen smoothly reduced the pyrone to the hydroxyacid.

Acknowledgment.—Our thanks are due Dr. Lester P. Kuhn, Ballistic Research Laboratory, Aberdeen Proving Grounds, Md., for infrared absorption spectra. We wish to thank Dr. and Mrs. G. Kleinspehn and Mr. J. Walter for analyses. One of the authors (J.R.S.) acknowledges with thanks receipt of a Grant-in-Aid from the Hynson, Westcott and Dunning Fund.

Experimental

Hydrogenolysis of 4-Hydroxy-6-phenyl-5,6-dihydro-2-pyrone.—Two grams (0.0105 mole) of the pyrone was dissolved in 50 ml. of absolute ethanol and 3 g. of Raney nickel[6] added. After shaking with hydrogen at 43 p.s.i. for five hours the catalyst was separated and the ethanol removed *in vacuo*. The residue solidified, and was taken up in base, leaving a trace of insoluble material. On acidification of the chilled filtrate lustrous white plates of 3-hydroxy-5-phenylvaleric acid separated. After washing, these had the reported m.p.[5] 129–130.5°, yield 1.3 g., or 63.7%. The material, after crystallization from water, was analyzed.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.00; H, 7.2. Found: C, 67.94; H, 7.3.

γ-Benzylcrotonic Acid.—The hydroxyacid V was submitted to distillation at atmospheric pressure, and the distillate dissolved in 15% aqueous sodium hydroxide. Extraction of this solution with ether removed a trace of neutral material. Acidification of the aqueous layer was followed by four extractions with ether. These were dried and evaporated to an oil that slowly solidified and consisted of a mixture of unchanged hydroxy acid and the crotonic acid. Separation by differential solubility in carbon bisulfide furnished pure γ-benzylcrotonic acid,[5] m.p. 102–102.5°.

Hydrogenolysis of 4-Ethoxy-6-phenyl-5,6-dihydro-2-pyrone.—Two grams (0.009 mole) of I[1] was dissolved in absolute ethanol and 3 g. of Raney nickel added. After shaking with hydrogen as described above, the solvent was removed, leaving crystals of 3-ethoxy-6-phenyl-2-pentenoic acid. After recrystallization from aqueous ethanol, white crystals, m.p. 114–115.5°, were obtained.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32; OC_2H_5, 20.46. Found: C, 71.04; H, 7.58; OC_2H_5, 20.50.

The product was soluble in carbonate solution, insoluble in bicarbonate solution, and showed ready oxidation with dilute potassium permanganate. This compound was shown to be identical with the crude acid earlier obtained from the reduction of 3-ethoxy-5-phenyl-2,4-pentadienoic acid,[1] after the impure material had been carefully recrystallized four times using Filter-Cel each time. Identity was established by mixed m.p., infrared absorption spectra, chemical tests and analysis.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.21; H, 7.59.

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[3] T. Hoffmann, *Ann.*, **283**, 308 (1894).

[4] Similar observations have been made with analogous compound by H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3628 (1950).

[5] R. Mozingo, C. Spencer and K. Folkers, THIS JOURNAL, **66**, 1859 (1944).

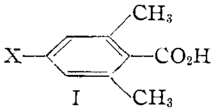
[6] Prepared according to the procedure in *Org. Syntheses*, **21**, 15 (1941), with the modification that the recommended digestion period of 12 hours on the steam-bath was changed to two hours on a hot plate at 100°.

Reactivities of 4-Substituted 2,6-Dimethylbenzoic Acids[1]

BY JOHN D. ROBERTS[1a] AND CLARE M. REGAN

RECEIVED JUNE 15, 1953

In an earlier investigation,[2] it was found that the substituent effects in 4- and 5-substituted 2-methylbenzoic acids paralleled closely those obtained with benzoic acids without the 2-methyl group. One possible interpretation of the results is that in either series of acids, the reactivity of a carboxyl group is not importantly determined by resonance-coupling of the carboxyl group with various 4-substituents. The argument is not strong in view of the certainly limited ability of a single ortho-methyl group to reduce coupling by sterically forcing the carboxyl out of the plane of the aromatic ring. To gain further evidence on this point, we have determined the apparent ionization constants in 50% water–50% ethanol (by volume) at 25.0° and the reactivities toward diphenyldiazomethane in absolute ethanol at 30.0° of a series of 4-substituted 2,6-dimethylbenzoic acids (I).



The procedures have been described earlier in detail.[3] The experimental data along with the physical constants of the compounds are summarized in Table I.

The values of the logarithms of the rate constants k_2 for the diphenyldiazomethane reactions are reasonably linear with the logarithms of the apparent ionization constants (pK_A) and indicate a

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

[1a] Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, Calif.

[2] J. D. Roberts and J. A. Yancey, THIS JOURNAL, **73**, 1011 (1951).

[3] J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).