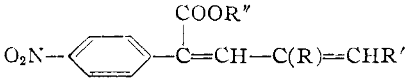
TABLE I

PHYSICAL PROPERTIES OF THE DIENOIC ACIDS AND THEIR ESTERS



| Compound No. | Compound R | Compound R′ | Compound R″ | M.p., °C. | Empirical formula | Analyses, % Neut. equiv. Calcd. | Neut. equiv. Found | Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found | Nitrogen Calcd. | Nitrogen Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | H | $CH_3$ | H | 230–230.5 dec. | $C_{12}H_{11}NO_4$ | 233 | 233 | 61.80 | 61.67 | 4.76 | 4.92 | 6.01 | 5.96 |
| II | $CH_3$ | H | H | 196–197 dec. | $C_{12}H_{11}NO_4$ | 233 | 234 | 61.80 | 61.62 | 4.76 | 4.81 | 6.01 | 6.00 |
| III | $CH_3$ | $CH_3$ | H | 177.5-178 | $C_{13}H_{13}NO_4$ | 247 | 249 | 63.15 | 63.24 | 5.30 | 5.38 | 5.67 | 5.71 |
| IV | H | $CH_3$ | [a] | 174 | $C_{19}H_{16}N_2O_6$ | | | 61.95 | 62.20 | 4.38 | 4.60 | 7.61 | 7.59 |
| V | $CH_3$ | H | [a] | 257.5–258.5 dec. | $C_{19}H_{16}N_2O_6$ | | | 61.95 | 62.24 | 4.38 | 4.54 | 7.61 | 7.53 |
| VI | $CH_3$ | $CH_3$ | [a] | 162.5 | $C_{29}H_{18}N_2O_6$ | | | 62.82 | 63.06 | 4.74 | 4.80 | 7.33 | 7.44 |

[a] R″ = —$CH_2C_6H_4NO_2$(*p*).

ing amounts of neutral, polymeric material which accompanied the *p*-nitrotoluene.

The acids were characterized as their *p*-nitrobenzyl esters (Table I) and by their $pK_A$'s and ultraviolet absorption spectra (Table II). The $pK_A$'s were obtained by measuring the *p*H's of the half-neutralized solutions of the acids.

TABLE II

$pK_A$'S AND ULTRAVIOLET ABSORPTION OF THE DIENOIC ACIDS[a]

| Compound | $pK_A$ | $\lambda_{max.}$, mμ | ε | Shoulder, $\lambda_{infl.}$ | Inflections at ε |
|---|---|---|---|---|---|
| I | 6.88 | 257.5 | 21,950 | 288 | 10,800 |
| | | | | 356 | 2,300 |
| II | 4.40 | 280 | 10,350 | .. | .... |
| III | 6.10 | 260 | 18,250 | 283 | 12,100 |
| *p*-Nitrophenylacetic acid | 3.85[b] | 270 | 10,000 | | |
| 2-(4′-Nitrophenyl)-but-2-enoic acid[c] | 5.00 | 282 | 9,600 | | |

[a] For the general shape of these curves, see footnote 3. [b] J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 162 (1934). [c] Kindly furnished by W. H. Häffcke.

Several preliminary attempts to decarboxylate the acids with copper–quinoline to give the corresponding alkyl-*p*-nitrophenylbutadienes were unsuccessful.

## Experimental[5]

**2-(*p*-Nitrophenyl)-hexa-2,4-dienoic Acid** (I).—The synthesis of this acid can also serve as a model for II.

*p*-Nitrophenylacetic acid (9.05 g., 0.05 mole) and 100 mg. of hydroquinone were dissolved in 25 ml. of warm acetic anhydride. Sodium acetate (4.10 g., 0.05 mole) was then added and followed by 5.0 ml. (4.3 g., 0.06 mole) of crotonaldehyde. Air was displaced by nitrogen and the reaction mixture was held at 63° for 16 hr. with intermittent shaking. At this time a mixture of 100 ml. of water and 25 ml. of hydrochloric acid was added and the contents were heated on a water-bath for 2 hr. After cooling, the contents were taken up in chloroform and washed with several portions of cold water, which were discarded. The organic layer was extracted with three 200-ml. portions of saturated sodium acid carbonate, which were combined and acidified to give an almost white precipitate which was washed with boiling water to leave 6.04 g. of crude acid. Recrystallization from ethanol (charcoal) gave 5.48 g. of pale yellow needles, m.p. 230–230.5° dec.

Evaporation of the chloroform solution gave 1.51 g. of a neutral reddish brown gum. Extraction of the hot water washes of the crude acid with chloroform and evaporation of the organic layer to dryness gave 1.44 g. (8.0 mmoles, 16%) of unreacted *p*-nitrophenylacetic acid, m.p. 143–152°.

**4-Methyl-2-(*p*-nitrophenyl)-penta-2,4-dienoic Acid** (III).—Because of the thermal instability of this compound it was necessary to carry out the condensation at a lower temperature and, therefore, for a longer time than the previously described acids. Otherwise, the reaction was set up as before using 0.05 mole of each of the reactants. At the end of the reaction period (two weeks at 37°) the reaction mixture was taken up in chloroform, transferred to a separatory funnel and washed with water slowly overnight by means of a gas diffuser tube placed at the bottom of the funnel and connected to a water tap and allowing the overflow to run into the drain. The chloroform solution was then extracted with three 250-ml. portions of saturated sodium acid carbonate. Acidification gave a precipitate which was dissolved in chloroform and stirred overnight with charcoal. After filtration hexane was added to incipient crystallization and the solution was cooled to −12° overnight. Filtration gave light yellow needles which, after washing several times with cold, peroxide-free ether, weighed 2.56 g. (0.011 mole, 22%) and melted 196–197° dec.

**Characterization of the Acids.**—The pure acids are unsaturated toward bromine in carbon tetrachloride and potassium permanganate in acetone.

The *p*-nitrobenzyl esters were prepared by the method of Shriner and Fuson[6] in yields of 56% (IV), 37% (V) and 25% (VI).

**Attempted Decarboxylation of the Acids.**—No pure diene was isolated in any of the experiments. A single attempt is described.

A mixture of 5.0 g. of I and 1.0 g. of copper powder was heated to 210° in quinoline with stirring and maintained at that temperature for 15 minutes. Evolution of carbon dioxide began at 185°. The reaction mixture was poured into 150 ml. of 10% hydrochloric acid, filtered, and the filter paper washed free of organic material with acetone. The filtrate was extracted with chloroform, and then the chloroform layer was washed successively with dilute hydrochloric acid, water, and saturated sodium acid carbonate solution, stirred with charcoal, filtered and distilled to dryness. The residue could not be induced to crystallize. Acidification of the sodium acid carbonate extract failed to precipitate any acid.

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(5) All temperatures are corrected. Analyses for carbon and hydrogen were carried out by Dr. K. Ritter, Basel, Switzerland; analyses for nitrogen by Mr. N. J. Alicino, Metuchen, New Jersey.

(6) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

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# Identity of Some 1-(3′,4′-Dimethoxyphenyl)-6,7-dimethoxytetralin Derivatives

BY R. D. HAWORTH AND G. N. WALKER

RECEIVED FEBRUARY 13, 1954

Several compounds recently reported by one of us (G. N. W.)[1,2] have been found to be identical with compounds prepared earlier.[3-5] Thus samples

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(1) G. N. Walker, THIS JOURNAL, **75**, 3387 (1953).

(2) G. N. Walker, *ibid.*, **75**, 3393 (1953).

(3) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 636 (1935).

(4) R. D. Haworth and D. Woodcock, *ibid.*, 813 (1938).

(5) R. D. Haworth and G. Sheldrick, *ibid.*, 291 (1941).

of compounds I through VI were compared (by R.D.H.) with samples of compounds having the same structure prepared previously. Mixed melting points were undepressed and the crystal forms (microscopic examination) were the same when appropriate pairs were examined, and the compounds were identical, structurally as well as stereochemically, in each case.

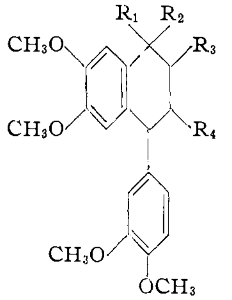
Lactone VII, obtained in the later work by dehydration of acid V in the presence of acetic acid,[2] was identical with the "β-lactone," for which structure VIII was suggested,[3,5] which was prepared earlier by aluminum amalgam reduction of the glyoxylic ester derivative of I followed by thermal dehydration of the resulting hydroxy acid,[3] as well as by another method.[5] In the light of this new evidence, the revised structure VII may be advanced for the "β-lactone."

TABLE I

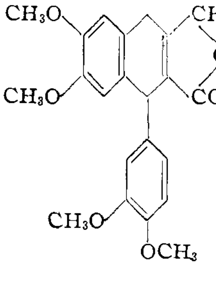
| Compound number | References | Haworth, m.p.,[a] °C. | Walker m.p.,[a] °C. | Mixed m.p.,[a] °C. |
|---|---|---|---|---|
| I | 1,3 | 130–131 | 130–132 | 130–131 |
| II | 1,3 | 202–203 | 205–207 | 204–207 |
| III | 1,3 | 184–185 | 182–184 | 182–185 |
| IV | 2,3 | 164–166 | 172–176 | 165–173 |
| V | 2,3 | 195–201 | 209–210 | 200–208 |
| VI[b] | 2,4,5 | 220–223 | 225–228 | 221–226 |
| VII | 2,3,5 | 209–210<br>(β-lactone) | 206–208 | 207–209 |
| VIII | 2,3 | 186–187<br>(α-lactone) | 187–188 | 186–187 |

[a] Uncorrected. [b] Anhydrous form.

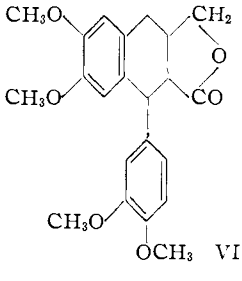
Lactone VIII, prepared by hydrogenation and dehydration of V in the presence of palladium–charcoal in acetic acid,[2] was identical with the "α-lactone," having structure VIII, prepared previously by sodium amalgam reduction of IV followed by thermal dehydration.[3] The nature of the implied reductive lactonization set forth in the earlier paper is still obscure, but the new results provide welcome confirmation of the structure VIII suggested for the "α-lactone."



I, $R_1R_2 = O$; $R_3 = H$; $R_4 = COOEt$
II, $R_1R_2 = O$; $R_3 = H$; $R_4 = COOH$
III, $R_1 = R_2 = R_3 = H$; $R_4 = COOH$
IV, $R_1R_2 = O$; $R_3 = CHO$; $R_4 = COOEt$
V, $R_1 = H$; $R_2 = OH$; $R_3 = CH_2OH$; $R_4 = COOH$
VI, $R_1 = R_2 = H$; $R_3 = CH_3$; $R_4 = COOH$



VII



VIII

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## Active Hydrogen in Aldehydes

BY JOHN A. KING

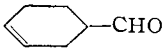
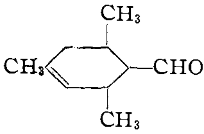
RECEIVED MARCH 9, 1954

In connection with the elucidation of the structure of a natural product it became of interest to verify the prediction that a probably secondary aldehyde group or a β-alkoxy aldehyde would show active hydrogen as it is usually determined.[1] There appears to be no information in the literature on the latter point and the only thing found that is at all pertinent to the former is the report by Young and Roberts[2] of the reduction of isobutyraldehyde by *sec*-butylmagnesium bromide; one can assume that the amount of isobutyraldehyde they recovered (22%) was a measure of enolization of the aldehyde by the reagent.

To test these possibilities, active hydrogen determinations were made on the compounds in Table I, with the indicated results.

TABLE I

ACTIVE HYDROGEN, %

| Compound | Calcd. for one | Found | Ionization[d] of compound, % |
|---|---|---|---|
| $(CH_3)_2CHCHO$[a] | 1.40 | 0.19, 0.23 | 14, 16 |
|  —CHO[b] | 0.92 | 0.06, 0.08 | 7, 9 |
|  —CHO[b] | 0.66 | 0.06, 0.11 | 9, 17 |
| $CH_3OCH_2CH_2CHO$[c] | 1.14 | 0.40, 0.41 | 35, 36 |
| $n\text{-}C_4H_9OCH_2CH_2CHO$[b] | 0.77 | 0.24, 0.26 | 31, 34 |

[a] Eastman Chemical Products, Inc. [b] Carbide and Carbon Chemicals Co. [c] Shell Development Company. [d] "Ionization" is used instead of "enolization" to satisfy the concept that release of α-hydrogen is preliminary to either enolization or β-elimination and that the measured active hydrogen content is the sum of these two processes which are mutually exclusive.

The results make it clear that: (1) secondary aldehydes do enolize with methyl Grignard reagent but the ratio of addition to ionization is about 10:1; (2) when there is an electron-attracting group in the β-position (compounds that undergo β-elimination) the ratio of addition to ionization of primary aldehydes is about 2:1; and (3) active hydrogen determinations on compounds of unknown structure must be treated with caution.

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(1) Aromatic aldehydes show some active hydrogen, presumably because of condensation to benzoins; *cf.* M. Lieff, G. F. Wright and H. Hibbert, THIS JOURNAL, **61**, 865 (1939).

(2) W. G. Young and J. D. Roberts, *ibid.*, **67**, 1040 (1945).