only traces of nickel sulfide, an isomerization takes place and the product contains isoöleates (elaidates). In the absence of sulfur elaidinization does not take place.[10]

In conformity with the above hypothesis it was found that pyridine, which is a base, did not inhibit the reductive dehydroxymethylation of 3-cyclohexylpropanol using nickel–kieselguhr as a catalyst (expt. 16). If, however, thiophene and pyridine or thiophene and aniline are added together to 3-cyclohexylpropanol the nickel–kieselguhr catalyst becomes deactivated and the alcohol is recovered unchanged (expt. 17). This is not surprising since it was shown that thiophene deactivates the contact sites of the hydrogenation catalyst, and pyridine or aniline, being a strong base, deactivates the acid part of the catalyst. The combination of the two types of additives, therefore, deactivates the catalyst both for reductive dehydroxylation and dehydroxymethylation.

The effect of chloroform upon the hydrogenolysis of 3-cyclohexylpropanol can be interpreted also in the same manner as the effect of sulfur compounds. It had been reported that carbon tetrachloride or chloroform causes a partial deactivation of the hydrogenation properties of a nickel catalyst.[11,12]

(10) For the survey of the literature see W. J. Kirkpatrick, "Nickel Sulfide Catalysts" in "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, pp. 329–339.

Experimental

Materials. **2-Cyclohexylethanol** and **3-cyclohexylpropanol** were prepared from the respective aromatic alcohols by catalytic hydrogenation in the presence of a nickel–kieselguhr catalyst at 150° and under 120 atmospheres of initial hydrogen pressure.

3,3-Dimethylbutanol and **1-methyl-1-hydroxymethylcyclohexane** were prepared according to the methods described previously.[1a,d]

Catalysts.—The preparations of precipitated nickel, Raney nickel and the source of nickel–kieselguhr were reported previously.[4]

Analytical Procedure.—The liquid product obtained from the reaction was distilled in a Piros–Glover spinning band column,[13] and the various fractions were analyzed by means of infrared spectroscopy.

The infrared spectrogram of methylcycloheptane was furnished us by Dr. H. L. Dryden, Jr., the other spectra of the hydrocarbons are reported by the American Petroleum Institute Project 44.

The gaseous products from the reactions were analyzed in a few instances by means of mass spectroscopy by Dr. D. Mason, of the Chemical Engineering Department. Whenever reductive dehydroxylation occurred, the gas consisted of hydrogen only. When dehydroxymethylation took place both hydrogen and methane were found in the gaseous product.

EVANSTON, ILLINOIS

(11) R. Cornubert and J. Phélisse, *Bull. soc. chim.*, **19**, 403 (1952).
(12) R. Cornubert and M. Réal, *ibid.*, **19**, 407 (1952).
(13) Manufactured by H. S. Martin and Co., Evanston, Ill.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

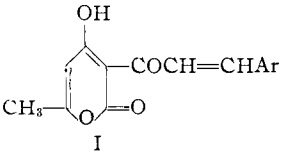
2-Pyrones. XV. Substituted 3-Cinnamoyl-4-hydroxy-6-methyl-2-pyrones from Dehydroacetic Acid

BY RICHARD H. WILEY, C. H. JARBOE AND H. G. ELLERT

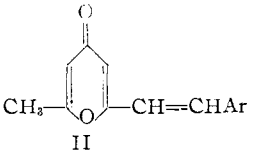
RECEIVED APRIL 13, 1955

The base-catalyzed condensation of dehydroacetic acid with fifteen aromatic aldehydes has been shown to give substituted 3-cinnamoyl-4-hydroxy-6-methyl-2-pyrones (I). The ultraviolet absorption characteristics of all of these products, some of which are unusually fluorescent, and the rearrangement of four of them to substituted 2-styryl-6-methyl-4-pyrones (II) are described. The available data are consistent with the 4-hydroxy-2-pyrone structure previously assigned to another product.

2-Pyrone structures resembling the chalcones have so far been unavailable for characterization and further study. One such chalcone-like structure is presented in the 3-cinnamoyl-4-hydroxy-2-pyrones (I) which are theoretically available by aldol condensations of aromatic aldehydes with the methyl ketone group of dehydroacetic acid. The possibility that such a reaction product could be obtained apparently was first recognized by Hale[1] who attempted the aqueous sodium hydroxide catalyzed condensation of benzaldehyde with dehydroacetic acid. He obtained a compound, m.p. 105°, to which he assigned the structure 3-cinnamoyl-4-hydroxy-2-pyrone (I, Ar = phenyl) on the basis of a satisfactory ultimate analysis. The product was said to decompose on heating to give dehydroacetic acid. This fact is difficult, if not impossible, to reconcile with the assigned structure. We wish to present data in this paper describing a different type of product, obtained from this reaction, whose structure has been established more adequately as that given in formula I.



I



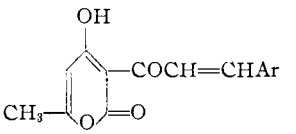
II

The use of aqueous sodium hydroxide as a catalyst for the condensation of aromatic aldehydes with dehydroacetic acid does not appear to be promising. It is known that strong bases decompose dehydroacetic acid to acetone and carbon dioxide.[2] However, on the basis of Hale's prior reported successful condensation of benzaldehyde, several aldehydes—veratraldehyde, 3,4-diethoxybenzaldehyde, *p*-dimethylaminobenzaldehyde and 3,4-dichlorobenzaldehyde—were used in aqueous alkali-catalyzed condensations. The products obtained from

(1) N. J. Hale, THIS JOURNAL, **33**, 1119 (1911).
(2) W. H. Perkin and C. Bernhart, *Ber.*, **17**, 1522 (1884).

TABLE I

SUBSTITUTED 3-CINNAMOYL-4-HYDROXY-6-METHYL-2-PYRONES FROM DEHYDROACETIC ACID



Ar	M.p., °C.	Yield, %	Recrys. from[a]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Phenyl	130–132	55	M	70.30	70.29	4.72	4.83
o-Nitrophenyl	161–163	65	A/W	59.80	59.60	3.68	3.77
m-Nitrophenyl	192	60	C	59.80	59.79	3.68	3.72
p-Nitrophenyl	245	56	C,E	59.80	59.76	3.68	3.70
p-Dimethylaminophenyl	217	63	C,E,B	68.21	68.26	5.73	5.73
p-Diethylaminophenyl	150	58	C,E	69.70	69.56	6.47	6.38
2,3-Dimethoxyphenyl	147	47	E	64.55	64.47	5.10	5.22
3,4-Dimethoxyphenyl	185	46	E,B	64.55	64.61	5.10	5.29
3,4-Diethoxyphenyl	163	43	E	66.27	66.09	5.85	5.81
3,4-Dichlorophenyl	185	46	E,C/B	55.40	55.36	3.09	3.23
p-Isopropylphenyl	139–141	65	M	72.46	72.22	6.08	6.04
1-Naphthyl	190	62	E	74.45	74.56	4.60	4.80
β-Styryl	185	57	C,E	72.33	72.18	5.00	5.88
2-Furyl	144	85	B,E	63.41	63.34	4.09	4.34
2-Thenyl	157		E	59.54	59.60	3.84	3.87

[a] C, chloroform; E, ethyl acetate; B, benzene; M, methanol; A, acetic acid; W, water.

these reactions were difficult to purify and only from 3,4-diethoxybenzaldehyde was a product obtained for which the analytical data agreed with a structure of type I. Even in this instance, however, some doubt attaches to the structure of this product since its melting point, 183°, does not agree with that, 163°, observed with the product prepared from this aldehyde by the technique described in the next paragraph.

An alternative procedure for the condensation using a piperidine catalyst in chloroform solution gave uniformly excellent results. After removal of the water formed in the reaction as the chloroform azeotrope, the products precipitated from the chloroform solution in 46–63% yields. The data describing these preparations and characterizing the products obtained from fifteen aldehydes are given in Table I. The product obtained from *p*-acetamidobenzaldehyde did not analyze in agreement with structure I. The benzaldehyde product obtained using this procedure melts at 130–132° and cannot, therefore, be the same product obtained by Hale. Hale's product had a melting point (105°) which is very close to that of dehydroacetic acid (109°) which may be the product he had in hand. We have noted that it is possible to recover unreacted dehydroacetic acid from these reactions. It is believed that the chloroform–piperidine process is much more likely to give a pure product than the aqueous alkali procedure and that our product has the assigned structure on the basis of the additional data we now have confirming this structure.

The β-cinnamoyl structure for the aldehyde condensation products obtained from dehydroacetic acid is confirmed by the rearrangement, accompanied by decarboxylation, of four of the compounds to 4-pyrones. The conversion of dehydroacetic acid itself to 2,6-dimethyl-4-pyrone is well known.[3] If the structural assignment given in formula I is correct, these products also should rearrange and decarboxylate to give substituted 2-(β-styryl)-6-methyl-4-pyrones (II). Such transformations have been demonstrated with the *p*-dimethylaminophenyl, *p*-diethylaminophenyl, *o*-nitrophenyl and *p*-isopropylphenyl derivatives. The rearrangement is completed readily with the aqueous acid-soluble aminophenyl derivatives but is rather difficult with other derivatives apparently because the reactant is insoluble in the acid solutions we have used. Acetic acid was used successfully as a solvent for the rearrangement of the isopropylphenyl derivative. Only products of undetermined structure were obtained from the *p*-acetaminophenyl, 3,4-dichlorophenyl, β-styryl and phenyl derivatives. The 3,4-dimethoxyphenyl and β-naphthyl derivatives were recovered unchanged from attempted rearrangements.

The ultraviolet absorption characteristics of the cinnamoyl derivatives I are summarized and presented in Fig. 1 and Table II along with data for chalcone[4] and for dehydroacetic acid.[5] Absorption in the 220–230 mμ range, observed with all of these cinnamoyl 2-pyrones, chalcone and dehydroacetic acid, is generally attributed to the carbonyl group. Some of the compounds containing amino or alkoxy groups show an additional maximum in the 235–255 mμ range which also may be attributed to the carbonyl function shifted under influence of the auxochromic group. An absorption maximum in the 299–330 mμ region is present in all but three of these compounds and in chalcone and dehydroacetic acid. This is probably associated with the ring-conjugated carbonyl function. The differentiating characteristic of the cinnamoyl compounds is the absorption maxima in the 342–450 mμ region. Absorption at this wave length is not observed with dehydroacetic acid or with chalcone and is probably, therefore, associated with the additional carbonyl conjugation introduced in the cinnamoyl deriva-

(3) F. Arndt and P. Nachtwey, *Ber.*, **57**, 1491 (1924).

(4) N. H. Cromwell and H. Hoeksema, THIS JOURNAL, **71**, 708 (1949).

(5) The authors are indebted to Miss LaVerne Duckwall for determination of the ultraviolet absorption data of dehydroacetic acid.

TABLE II

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF SUBSTITUTED 3-CINNAMOYL-4-HYDROXY-6-METHYL-2-PYRONES[a]

Compound	220–230	235–255	299–330	342–357	365–450
Chalcone	226, 4.08	.....	299, 4.38	.....	.....
Dehydroacetic acid	225, 4.06	.....	310, 4.08	.....	.....
Phenyl	230, 4.31	.....	305, 4.21	342, 3.96	.....
p-Isopropylphenyl	220, 4.44	.....	325, 4.33[b]	357, 4.46	.....
1-Naphthyl	220, 4.70	255, 4.08[b]	.....	.....	365, 4.22
β-Styryl	220, 4.46	.....	.....	.....	370, 4.52
o-Nitrophenyl	220, 5.09	.....	320, 4.61	.....	368, 4.71
p-Nitrophenyl	220, 4.56	.....	320, 4.37	355, 4.37	.....
2,3-Dimethoxyphenyl	220, 4.47	.....	.....	355, 4.42	.....
3,4-Dichlorophenyl	220, 4.30	235, 4.14[b]	310, 4.21[b]	350, 4.31	.....
3,4-Dimethoxyphenyl	220, 4.25	250, 4.03	330, 4.03[b]	.....	390, 4.49
3,4-Diethoxyphenyl	220, 4.30	250, 4.08	330, 4.04	.....	375, 4.37
p-Dimethylaminophenyl	220, 4.13	255, 4.15	320, 4.01	.....	440, 4.52
p-Diethylaminophenyl	220, 4.38	255, 4.15	323, 3.99	.....	450, 4.59

[a] Figures state the wave length in mμ and log ε of the maxima. [b] Shoulder.

tives. In the compounds carrying the auxochromic 3,4-dialkoxy, *p*-dialkylamino and *o*-nitro groups and the more unsaturated naphthyl and styryl groups this absorption is shifted to even longer wave lengths. It appears at 440 mμ with the dimethylaminophenyl derivative which also is characterized, as a magenta solid, by an unusual absorption in the visible range. Several of the compounds in this series, notably the dialkylaminophenyl and dialkoxyphenyl derivatives, show pronounced fluorescence on exposure to ultraviolet light.

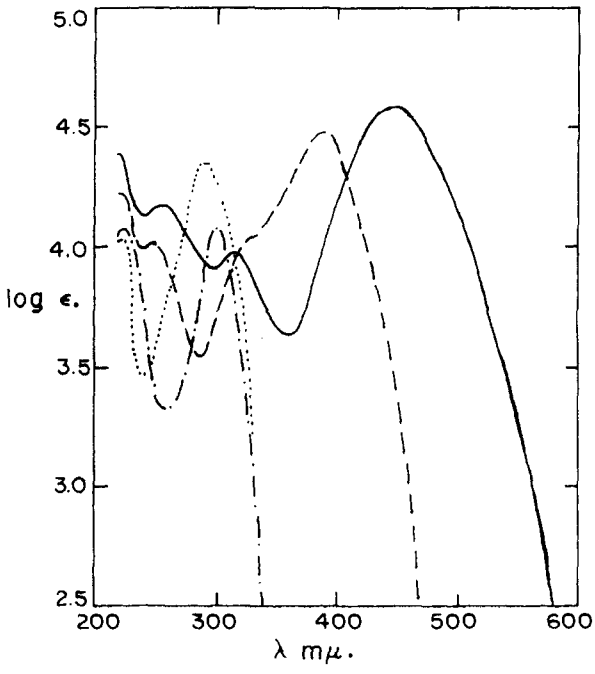


Fig. 1.—Ultraviolet absorption data: ....., chalcone (in hexane); -·-·-·-· dehydroacetic acid; ·····, 3-(3',4'-dimethoxycinnamoyl)-4-hydroxy-6-methyl-2-pyrone; ——, 3-(*p*-dimethylaminophenyl)-4-hydroxy-6-methyl-2-pyrone.

The 4-hydroxy structure I has been assigned to these products on the basis of their enolic character, as evidenced by positive ferric chloride tests, and by analogy with the data from the Diels–Alder reaction[6] which has established the 4-hydroxy structure for the related 4-hydroxy-6-methyl-2-pyrone (triacetic lactone). The presence of an intramolecularly hydrogen bonded hydroxyl group is indicated in the infrared absorption data for compounds of this series which show an absorption at 3.4–3.6 μ characteristic of the conjugate chelation associated with enolic β-diketones.[7]

2-[β-(*p*-Diethylaminostyryl)]-6-methyl-4-pyrone shows ultraviolet absorption maxima at 230 mμ (log ε 4.07), at 265 mμ (log ε 4.16), and at 415 mμ (log ε, 4.47). 2[β-(*o*-Nitrostyryl)]-6-methyl-4-pyrone shows absorption maxima at 220 mμ (log ε 4.48), at 240 mμ (log ε 4.18), and at 280 mμ (log ε 4.36). The principal absorption band in each of these probably results from a bathochromic shift of the absorption band at 248 mμ (log ε 4.13) shown in 2,6-dimethyl-4-pyrone[8] and is paralleled by a similar absorption at 408 mμ apparent in the absorption data for 2,6-di-(β-styryl)-4-pyrone.[9]

Acknowledgment.—The authors wish to acknowledge support of this research through a grant (NSF-G55) from the National Science Foundation.

Experimental[10]

The aldehydes used in the following experiments were obtained from commercial sources and recrystallized before use. The dehydroacetic acid was generously supplied by the Carbide and Carbon Chemicals Co.

Substituted 3-Cinnamoyl-4-hydroxy-6-methyl-2-pyrones.—The products listed in Table I were prepared as follows. A solution of 3.4 g. (0.02 mole) of dehydroacetic acid, 10 drops of piperidine and 0.02 mole of the aldehyde in 25 ml. of chloroform was refluxed for 8–10 hours. Ten ml. of the chloroform–water azeotrope was separated in a Barrett-type distilling receiver. Crystals of the product which separated on slow evaporation of the remaining chloroform were collected and recrystallized.

2-[β-(*p*-Dimethylaminostyryl)]-6-methyl-4-pyrone.—One gram of 3-(*p*-dimethylaminocinnamoyl)-4-hydroxy-6-methyl-2-pyrone was refluxed for 4 hours in 50 ml. of 12 *N* hydrochloric acid. The solution was cooled and neutralized

(6) K. Alder and H. F. Rickert, *Ber.*, **70**, 1354 (1937).

(7) The authors are indebted to Mrs. E. V. Mochel for determination of the infrared spectra.

(8) R. C. Gibbs, J. R. Johnson and E. C. Hughes, THIS JOURNAL, **52**, 4895 (1930).

(9) A. A. Boon, F. J. Wilson and I. M. Heilbron, *J. Chem. Soc.*, **105**, 2176 (1914).

(10) All m.p.'s are corrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.

to precipitate the crude product. Recrystallization from ethyl acetate–petroleum ether gave 1.0 g., 82%, of the pure product, m.p. 156°.

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.71. Found: C, 75.07; H, 6.61.

2-[β-(*p*-Diethylaminostyryl)]-6-methyl-4-pyrone.—This compound was prepared from the diethylamino analog by the process described in the preceding experiment; yield 68%, m.p. 128–130°. Recrystallized from methanol–water.

Anal. Calcd. for $C_{18}H_{21}O_2N$: C, 76.29; H, 7.47. Found: C, 76.32; H, 7.29.

2-(*o*-Nitrophenyl)-6-methyl-4-pyrone.—One gram of 3-(*o*-nitrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone was refluxed for 10 hours in 100 ml. of concd. hydrochloric acid. The solution was cooled and neutralized to precipitate the crude product. Recrystallization from methanol–water gave 52.5% of product, m.p. 187–189°.

Anal. Calcd. for $C_{14}H_{11}O_4N$: C, 65.36; H, 4.31. Found: C, 65.19; H, 4.30.

The 2-(*p*-Isopropylphenyl)-6-methyl-4-pyrone.—One-half gram of 3-(*p*-isopropylcinnamoyl)-4-hydroxy-6-methyl-2-pyrone was refluxed in 100 ml. of glacial acetic and 50 ml. of concd. hydrochloric acid for 6 hours. The solution was cooled and neutralized to precipitate the crude product. Recrystallization from ethanol and water gave 0.19 g. (44.5%) of product, m.p. 110–112°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.47; H, 7.13.

Ultraviolet Absorption Data.—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer using 1.00-cm. silica cells and hydrogen and tungsten discharge lamps as light sources. Methanol solutions of the compounds were used.

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Preparation, Structure and Properties of 4,5,6,7-Tetrachlorobenzotriazole and its 1- and 2-Substitution Products

BY RICHARD H. WILEY, K. H. HUSSUNG[1] AND JAMES MOFFAT[2]

RECEIVED MAY 6, 1955

4,5,6,7-Tetrachlorobenzotriazole has been prepared in 87% yield by the chlorination of benzotriazole with aqua regia. 1-Methyl- and 2-methyl-4,5,6,7-tetrachlorobenzotriazole have been obtained by alkylation and the latter by chlorination of 2-methylbenzotriazole. Ultraviolet absorption spectra establish the structural assignments and show that in 1,4-additions to unsaturated systems, a reaction giving 1-substituted derivatives from benzotriazole, the 2-substituted isomers are formed apparently for steric reasons. Tetrachlorobenzotriazole is a weak acid, pK_a 3 × 10^{-5}, and forms interconvertible salts in mole ratios of 2/1 and 3/1 with benzyltrimethylammonium hydroxide.

The problem of the structural isomerism of the 1- and 2-substituted-1,2,3-triazoles has been clearly resolved with only one parent triazole—benzotriazole. With benzotriazole—but not with uncondensed triazoles—ultraviolet absorption data distinguish the two isomers and chemical data establish the positions of the substituents. Because it has been necessary to extend these data to situations and structures not closely related to benzotriazole, it is highly desirable that additional data about the distinguishing characteristics of such isomers be available. One attractive source of such information lies in the possibility of separating and identifying the 1- and 2-isomers of substituted benzotriazoles. The difficulty presented by this approach is that practically nothing is known about the substitution reactions of benzotriazole and its derivatives. Fries and co-workers have reported[3] that nitration gives the 4-nitro derivative and Zincke and Arzberger that chlorination[4] converts 5-methyl- or 5-bromobenzotriazole to 4,6,7-trichloro derivatives. Some additional work has been reported on the substitution reactions of 4- and 5-hydroxy- and 4- and 5-aminobenzotriazoles.[3,5] Indeed, the few substituted benzotriazoles known—5-nitro, 5-chloro, 5-bromo, 5-methyl and 5,6-dimethyl—are the 5-substituted type which are available from *p*-substituted anilines by cyclization of the derived *o*-phenylenediamine. Since all of these substituted benzotriazoles (except the unaccessible dimethyl compound) are unsymmetrical themselves, additional structural isomeric possibilities arise. Thus, although there are only two N-methylbenzotriazoles (1-methyl and 2-methyl), there are three N-methyl-4-chlorobenzotriazoles. This complication is not present in symmetrically substituted benzotriazoles and in order to have such material readily available for study, our attention was directed to the possibility of preparing 4,5,6,7-tetrachlorobenzotriazole by the chlorination of benzotriazole. We wish to report the results of studies which make this compound, 4,5,6,7-tetrachlorobenzotriazole, readily available and studies of its reactions which considerably extend the presently available knowledge of the structural problems encountered in the 1- or 2-isomerism of triazoles.

Since Zincke had reported,[4] without complete experimental details, the chlorination by means of aqua regia of 5-bromobenzotriazole and of 5-methylbenzotriazole to the corresponding trichloro derivatives it seemed possible that 5-chlorobenzotriazole could be chlorinated in this way to 4,5,6,7-tetrachlorobenzotriazole. This chlorination now has been achieved, and, in addition, benzotriazole itself has been found to chlorinate to the same tetrachlorobenzotriazole. Yields of 87–89% of tetrachlorobenzotriazole are obtained by refluxing benzotriazole with aqua regia for 3 hours. The reaction is easy and quick so that the tetrachloro compound can be considered the most accessible symmetrically substituted benzo-

(1) Eli Lilly and Co. Graduate Research Assistant.
(2) Office of Ordnance Research, Research Assistant Professor.
(3) K. Fries, H. Güterbock and H. Kühn, *Ann.*, **511**, 213 (1934).
(4) Th. Zincke and H. Arzberger, *ibid.*, **249**, 370 (1888).
(5) K. Fries, *et al.*, *ibid.*, **389**, 318, 358, 367 (1912).