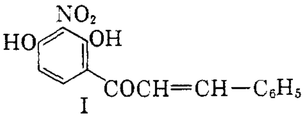
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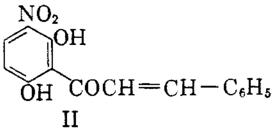
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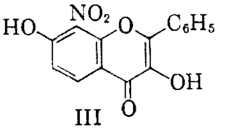
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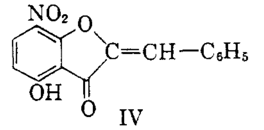
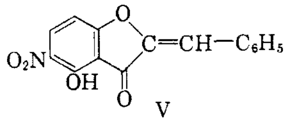

IV


V

The products of oxidation of the type II chalcones, on the other hand, gave deep red colors with concentrated sulfuric acid, the colors being comparable to those given by the original chalcone itself. Because of the 4-hydroxy group they also gave a reddish-brown color with alcoholic ferric chloride. The alternative structure, 2-benzylidene-4-hydroxy-5-nitro-3(2H)-benzofuranone (V), was eliminated from a study of the reactivity of the hydroxyl group. Products could be acetylated even at room temperature by acetic anhydride and pyridine. Structure V contains a hindered hydroxyl group which will not undergo such ready acetylation. The reactivity of 5-hydroxy-8-nitroflavone and the nonreactivity of 5-hydroxy-6-nitroflavone towards acetylation of the hydroxyl group[4] may be cited as an analogous case.

The formation of 3-hydroxyflavones from chalcones of type I was expected as it has been shown that the nitro group does not affect the normal reaction to give 3-hydroxyflavones.[5]

The type II chalcones, however, possess a 6′-hydroxyl group which is chelated. A survey of the literature showed that oxidation of 6′-hydroxyl chalcones had not been carried out so far. On the basis of the mechanism of the abnormal reaction, postulated by Geissman,[6] the 6′-hydroxyl group should be expected to have the same influence as a 6′-methoxy or methyl group. Chalcones with a 6′-hydroxyl group should therefore be expected to give rise to 2-benzylidene-3(2H)-benzofuranones. The formation of the benzylidene benzofuranones shows that the nitro group does not alter the course of the abnormal reaction either.

EXPERIMENTAL

General procedure for oxidation of the chalcines. Sodium hydroxide solution (10 ml.; 10%) was added to the chalcone (0.5 g.). If an insoluble sodium salt formed (as in the case of type I chalcones), sufficient pyridine was added to dissolve it. Hydrogen peroxide solution (15 ml.; 20 vols.) was gradually added to this solution of the chalcone which was kept in ice. After addition, the reaction mixture was left in the refrigerator for 4 days and then for a day at room temperature (about 30°). The reaction mixture was then acidified by dilute hydrochloric acid and the precipitate obtained crystallized from a suitable solvent. Yields: 80 to 100 mg.

In the case of 2′,6′-dihydroxy-3′-nitrochalcone, the reaction mixture on acidifying gave a very small amount of yellowish white material which was very soluble in the usual solvents and could not be crystallized.

The benzylidene benzofuranones obtained from the type II chalcones were acetylated as follows: A 50-mg. sample of the compound was dissolved by heating in acetic anhydride (5 ml.) and a few drops of pyridine. The reaction mixture was then left at room temperature overnight. The solid obtained from the usual work-up was crystallized from a suitable solvent.

The physical and chemical properties of the compounds obtained and their analyses are given in Table I.

Acknowledgments. We are grateful to Dr. G. V. Jadhav for his keen interest in the work.

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Some Reactions of *N*-Hydroxymethyldodecanamide

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Several years ago we had occasion to prepare the then unknown *N*-hydroxymethyldodecanamide (Ia) for use as an analytical standard. Its straightforward preparation, elemental analysis, positive Eegriwe test for combined formaldehyde and infrared spectrum left little room for doubt as to its structure. However hydroxyl determinations by the usual method,[2,3] which involve acetylation at steam bath temperature, gave such reproducibly low results that further characterization of (Ia) seemed desirable.

The acetate was prepared and found to decompose at 100°, which makes the low OH values less surprising.

A puzzling phenomenon occurred when (Ia) was heated with 1-naphthyl isocyanate. Instead of the desired urethane derivative a good yield of a dehydration product, $C_{26}H_{52}N_2O_3$, was obtained in the first trial, and nothing but intractable mixtures in later trials. There are two possible simple dehydration products involving the loss of the elements of water between two molecules of Ia;

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[4] R. M. Naik and V. M. Thakor, *Proc. Indian Acad. Sci.*, **37A**, 774 (1953).

[5] F. A. Atchabba, P. L. Trivedi, and G. V. Jadhav, *J. Univ. Bombay,* **26(5)**, 1 (1958).

[6] T. A. Geissman and D. K. Fukushima, *J. Am. Chem. Soc.*, **70**, 1686 (1948).

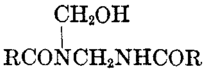
[1] Present addresses: (a) Department of Chemistry, Imperial College of Science and Technology, London S.W. 7. (b) Pittsburgh Plate Glass Co., Torrance, Calif.

[2] S. Siggia, *Quantitative Organic Analyses via Functional Groups*, J. Wiley and Sons, Inc., New York, 1949, p. 4.

[3] Long-chain *N*-2-hydroxyethylamides have been analyzed successfully by this method. *Cf.* E. T. Roe, J. T. Scanlan, and D. Swern, *J. Am. Chem. Soc.*, **71**, 2215 (1949).

the hydroxymethylmethylenebisamide IIa and the ether IIIa.

$RCONHCH_2OH$
I
a. $R = C_{11}H_{23}$
b. $R = C_6H_5$



$RCON(CH_2OH)CH_2NHCOR$
II
a. $R = C_{11}H_{23}$
b. $R = C_6H_5$

$(RCONHCH_2)_2O$
III
a. $R = C_{11}H_{23}$
b. $R = C_6H_5$

$(RCONH)_2CH_2$
IV
a. $R = C_{11}H_{23}$
b. $R = C_6H_5$

No report of any substance being formulated as III has been found and only four compounds seem to have been assigned structure II (with $R = C_2H_5$,[4] C_6H_5-, C_2H_5NH-, and C_2H_5O-[5]), all by Einhorn. Little is known about these compounds except that the phenyl compound liberates formaldehyde on pyrolysis and is easily converted to *N*,*N'*-methylenebisbenzamide(IVb). These slender facts can also be explained with structure IIIb, which would be much less stable than an ordinary ether.[6]

Our dehydration product is evidently of the same type as those of Einhorn as it could also be prepared from Ia by one of the unusual reactions by which IIb (or IIIb) was produced from Ib,[4] *viz.* by an attempted benzoylation under alkaline conditions.

A decision in favor of the hydroxymethylmethylenebisamide structure IIa was made after comparing the infrared spectrum of the dehydration product with the spectra of Ia and of IVa, which was prepared for this purpose (see Fig. 1). If the structure were IIIa there would probably be a stronger, broader absorption band in the 1060–1150 cm.$^{-1}$ region where CH_2OCH_2 absorbs[7] than is actually found, although this is not certain. The hydrogen-bonded OH stretching frequency in Ia is found at 3190 cm.$^{-1}$, and also appears as a poorly resolved but reproducible shoulder near 3200 cm.$^{-1}$ in the spectrum of the dehydration product. One or both of the 1052 and 1023 cm.$^{-1}$ bands is probably also caused by the primary alcohol group as somewhat similar bands are observed in the curve of Ia but not in that of IVa. The 3305, 3055, 1654, and 1545 cm.$^{-1}$ absorptions are normal for a secondary amide[7] and are at nearly the same frequencies in the other two curves.

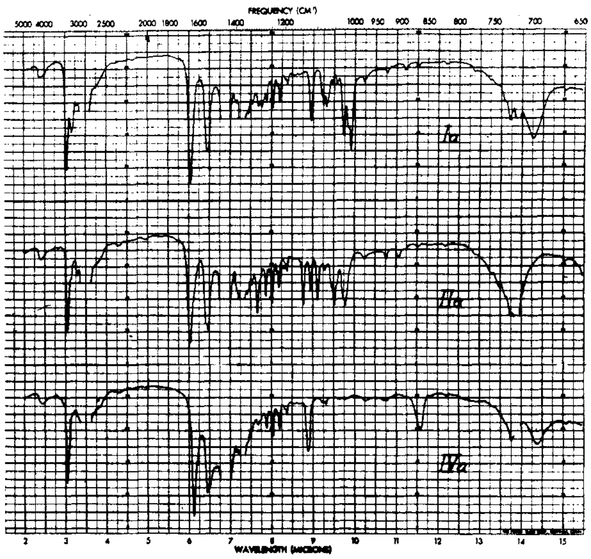


Fig. 1. Infrared absorption spectra of *N*-hydroxymethyldodecanamide (Ia), *N*-hydroxymethyl-*N*,*N'*-methylenebisdodecanamide(IIa), and *N*,*N'*-methylenebisdodecanamide (IVa) in Nujol mulls

EXPERIMENTAL[8]

N-Hydroxymethyldodecanamide (Ia). A brief report of the preparation of this compound in 70–80% yield appeared in Japanese[9] after we had developed our method. As our preparation gives a somewhat better yield details will be given. A solution of lauramide (10 g.), 36% aqueous formaldehyde (14 g.) 30% sodium hydroxide (1.15 ml.), and methanol (90 ml.) was heated to reflux for 2 hr. and allowed to cool.[10] The product separated as shiny colorless blades, m.p. 105–106°, yield, 10.1 g. (88%). Recrystallization from 95% ethanol raised the melting point to 110–111° (lit.[9] m.p. 109–110°). It gives a positive Eegriwe test,[11] and liberates formaldehyde at 170°. The infrared spectrum (Nujol) showed bands at 3285, 3190, 3060, 1654, 1545, 1118, 1082, 1073, 1028, 1016, and 1009 cm.$^{-1}$ (see Fig. 1).

Anal. Calcd. for $C_{13}H_{27}O_2N$: N, 6.11; OH, 7.43. Found: N, 5.99; OH[2], 3.25, 3.33.

A mixture of *N*-hydroxymethyldodecanamide (Ia) (0.5 g.), acetic anhydride (14 ml.), and acetic acid (19 ml.) was warmed to 40°, allowed to stand 2 days at room temperature, then poured onto ice. The crude product was taken up in benzene, washed with sodium carbonate (5%), then freed of benzene and water and leached with ether (15 ml.). The ether-soluble solid was crystallized from acetone-isopentane and from ethanol to give the pure *acetate*, m.p. 74°, which exhibited infrared absorption at 1750 cm.$^{-1}$ (ester C=O) and at 3290, 1715, and 1555 cm.$^{-1}$ (secondary amide).

Anal. Calcd. for $C_{15}H_{29}NO_3$: N, 5.16. Found: N, 4.85.

When heated at 100° an odor of acetic acid appeared, and when cooled after 0.5 hr., an unidentified solid, m.p. 80°, was obtained.

Reaction of Ia *with 1-naphthyl isocyanate.* When *N*-hydroxymethyldodecanamide (1.15 g.) was heated on a water bath with 1-naphthyl isocyanate (Eastman 1816) (0.9 g.) for 0.5 hr. an orange solid was produced. Spontaneous

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[4] A. Einhorn, *Ann.*, **343**, 207 (1905).

[5] A. Einhorn, *Ann.*, **361**, 113 (1908).

[6] *Cf.* J. W. Weaver, H. A. Schuyten, J. G. Frick, Jr., and J. D. Reed, *J. Org. Chem.*, **16**, 1111 (1951), for the properties of ethers of the type $RCONHCH_2OR'$.

[7] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., J. Wiley and Sons, Inc., New York, 1958.

[8] Elemental analyses are by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif. Melting points are uncorrected. Infrared spectra were run as Nujol mulls on a Perkin-Elmer Model 21 spectrometer (sodium chloride prism) by Mr. Everett P. Honorof.

[9] S. Sakakibara, K. Nambu, and S. Komori, *J. Oil Chemists' Soc.* (*Japan*), **3**, 118 (1954).

[10] *Cf.* J. A. Shipp, U. S. Patent **2,232,485** (1941). Our method was evolved from one given by Shipp for *N*-hydroxymethyloctadecanamide, which gave only a 33% yield when applied to the synthesis of Ia.

[11] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

evaporation of the ligroin (b.p. 90–120°) leachings yielded about 1 g. of *N-hydroxymethyl-N,N′-methylenebisdodecanamide* (IIa) as a colorless wax which melted at 106–106.5° after two crystallizations from alcohol and drying *in vacuo* at 55°.

Anal. Calcd. for $C_{26}H_{52}N_2O_3$: C, 70.86; H, 11.89. Found: C, 71.08; H, 11.82.

IIa gave a positive Eegriwe test, liberated formaldehyde at 220° and depressed the melting point of Ia by 23°. Three attempts to repeat this reaction, two using 1-naphthyl isocyanate from a different source (Matheson Coleman & Bell), and one employing purified isocyanate, b.p. 153.0–153.5°/20 mm., gave only colorless, low-melting mixtures in which no IIa could be detected; infrared evidence indicated that a good deal of unchanged Ia was present.

N-Hydroxymethyl-N,N′-methylenebisdodecanamide (IIa) was also obtained from Ia under Schotten-Bauman conditions.[4] When 10% aqueous potassium hydroxide (10 ml.) and benzoyl chloride (1 ml.) were added with shaking to *N*-hydroxymethyldodecanamide (1.0 g.) a vigorous reaction occurred. After cooling the colorless slurry was shaken mechanically for 1 hr. at room temperature. The solid was filtered and crystallized twice from 95% alcohol and once from chloroform. Evaporation of the chloroform mother liquors gave a solid, which was recrystallized from 100% alcohol to yield 80 mg. of colorless IIa, m.p. 104–105°, which proved to be identical with IIa from the aforedescribed reaction by mixed melting point and infrared spectrum (16 peaks checked).

N,N′-Methylenebisdodecanamide (III) has been prepared from lauroyl chloride in 20% yield[12] and, it has been claimed in the patent literature, from lauronitrile in "excellent" yield.[13] Using a variation of a convenient method of Einhorn,[4] a mixture of lauramide (1 g.), 36% aqueous formaldehyde (2 ml.), 5% sulfuric acid (1 ml.), and ethylene dichloride (10 ml.) was heated to reflux for 1.5 hr., cooled, filtered, and washed with water. The crude product, m.p. 145–148° (0.6 g., 57%), recrystallized from ethanol as colorless crystals, m.p. 155–156° (lit. 156–157°,[12] 154–155°[13]), infrared absorption (see Fig. 1) at 3310, 3055, 1633, 1553, 1535, 1128, and 863 cm.$^{-1}$, in apparent agreement with the literature.[12]

Anal. Calcd. for $C_{25}H_{50}O_2N_2$: N, 6.82. Found: N (Kjeldahl), 6.78.

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[12] A. Cannepin and A. Parisot, *Compt. rend.*, **239**, 180 (1954).

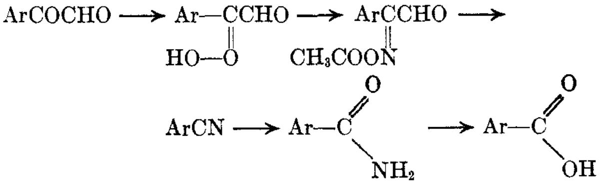
[13] D. T. Mowry, U. S. Patent **2,534,204** (1950).

Bromination Products of Mesitylglyoxal and Configuration of the Corresponding Monoximes

R. PERCY BARNES AND COLEMAN R. SEWARD[1]

Received November 16, 1959

In the light of the behavior of benzene, toluene, the xylenes, and mesitylene toward bromine in polar solvents,[2,3] we decided to investigate phenylglyoxal and mesitylglyoxal under similar conditions. In both aqueous methanol and aqueous acetic acid, mesitylglyoxal underwent both mono- and dibromination, and the products proved to be identical with those obtained by Fuson *et al.*,[4,5] whereas phenylglyoxal did not undergo bromination. In aqueous acetic acid, both more rapid bromination and higher yields resulted than in aqueous methanol. Gray and Fuson[6] characterize the monoxime of mesitylglyoxal in terms of molecular formula and physical properties. We decided to investigate the configurations of the mono- and dibromoglyoxal monoximes. Thus we prepared the monoximes, acetylated them, and subjected the acetates to treatment with dilute aqueous sodium hydroxide.[7] These oximino esters underwent cleavage and not hydrolysis, thus indicating that they were of the α-configuration, and in terms of the products, that the oximino groups had replaced the ketocarbonyl oxygens.



Ar = 3-bromomesityl or 3,5-dibromomesityl

EXPERIMENTAL

Mesitylglyoxal and phenylgalyoxal were prepared according to the method of Gray and Fuson.[6]

Phenylglyoxal did not undergo bromination in aqueous methanol or aqueous acetic acid.

3-Bromomesitylglyoxal. To a 200-cc. 2-necked round bottom flask equipped with a mechanical stirrer, was added 5.3 g. (0.03 mole) of mesitylglyoxal dissolved in the minimum volume of cold methanol or glacial acetic acid. To this solution water was added to incipient cloudiness, followed by a few drops of the chosen solvent to give a clear solution. To the prepared solution 4.8 g. (0.03 mole) of bromine was added dropwise with vigorous stirring. The color of the bromine disappeared very rapidly. After the addition of the bromine, stirring was continued for some time. Finally enough water was added to produce slight turbidity, and the contents of the flask were chilled overnight. A pale yellow crystalline substance was obtained which when recrystallized from methanol exhibited the same physical and chemical properties as the compound obtained by Fuson and Soper.[4] A boiling aqueous solution of the glyoxal to which a few drops of methanol were added, on cooling, deposited the colorless hydrate. Both the glyoxal and its hydrate upon oxidation with alkaline hydrogen peroxide gave 3-bromomesitoic acid,[8] melting and mixed melting point with an authentic sample at 168°.

3,5-Dibromomesitylglyoxal was prepared by the same method as 3-bromomesitylglyoxal by using 2 moles of

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[1] In partial fulfillment of the requirements for the M.S. degree.

[2] P. B. D. de la Mare and P. N. Robertson, *J. Chem. Soc.*, 279 (1943).

[3] R. Oda and K. Tumura, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **33**, No. 728, 129 (1937).

[4] R. C. Fuson and Q. F. Soper, *J. Org. Chem.*, **9**, 193 (1944).

[5] R. C. Fuson, C. H. McBurney, and W. E. Holland, *J. Am. Chem. Soc.*, **61**, 3246 (1939).

[6] A. R. Gray and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 739 (1934).

[7] R. P. Barnes and A. H. Blatt, *J. Am. Chem. Soc.*, **57**, 1330 (1935).

[8] P. R. Shildneck and R. Adams, *J. Am. Chem. Soc.*, **53**, 347 (1931).