chloride from dimethylhexanol-2 had n^{20}_D 1.4351, n^{25}_D 1.4330, and that from dimethylhexanol-3 had n^{20}_D 1.4353,[15] n^{25}_D 1.4333.

Hydrolysis of the Chloride from *levo*-2,3-Dimethylhexanol-2.—Ten grams of the chloride was shaken with 3 liters of distilled water for six hours, the carbinols were extracted with purified petroleum ether, the combined extracts were washed with 3% sodium bicarbonate, with water, and dried with anhydrous potassium carbonate. After removal of the solvent, the carbinols were found to be free of chlorine and olefins, b. p. 71.5–73° (29 mm.), n^{25}_D 1.4294. The phenylurethan of this material melted at 52–52.5°, and when mixed with a 1:1 mixture of the two pure isomeric phenylurethans (m. p. 56–63°) melted at 53–63°

Summary

1. Treatment of *levo*-2,3-dimethylhexanol-2 with concentrated hydrochloric acid yields a mixture of 2,3-dimethyl-2-chloro- and 2,3-dimethyl-3-chlorohexane, both of which have been completely racemized.
2. Hydrolysis of the above chloride mixture yields a 1:1 mixture of racemic 2,3-dimethylhexanol-2 and 2,3-dimethylhexanol-3.
3. Both isomeric dimethylhexanols yield the same chloride mixture with concentrated hydrochloric acid.
4. The optical activity of the chloride mixture from *dextro*-2,2-dimethylhexanol-3 is due to the formation of the unrearranged secondary chloride, and not to any rearranged tertiary chloride.

NEW HAVEN, CONNECTICUT RECEIVED JULY 27, 1943

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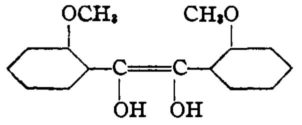
[15] Whitmore and Evers, *loc. cit.*, reported n^{20}_D 1.4350.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

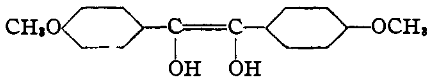
The Preparation and Properties of Mesityl-*p*-methoxybenzylglyoxal

BY R. PERCY BARNES AND HAROLD DELANEY[1]

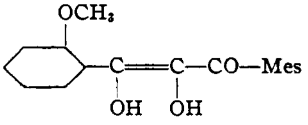
In recent publications[2] we pointed out the effect of methoxyl toward stabilizing enediols. We showed that when the 2,2′- and 4,4′-dimethoxydiphenylacetylene glycol diacetates were completely hydrolyzed, the intermediate 2,2′-dimethoxydiphenylacetylene glycol (I) ketonized to the benzoin, while the 4,4′-intermediate (II) was autoxidized to the corresponding benzil. We also showed that α-*o*-methoxyphenyl-β-mesitoylacetylene glycol (III) was more stable than the unsubstituted α-phenyl-β-mesitoylacetylene glycol (IV).



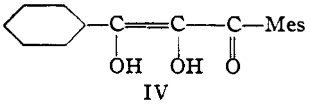
I



II

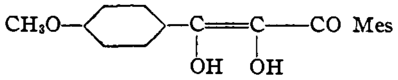


III



IV

Since *p*-methoxyl has a greater stabilizing effect than the *o*-methoxyl in the symmetrical molecules (I) and (II), we set out to make α-*p*-methoxyphenyl-β-mesitoylacetylene glycol (XI) in order to compare the methoxyl effects in (III) and (XI).



XI

We condensed acetylmesitylene with anisaldehyde, producing *p*-methoxybenzalacetomesitylene (V). This substance was oxidized with alkaline hydrogen peroxide to α-*p*-methoxyphenyl-β-mesitoyl ethylene oxide (IV). The oxide was in turn isomerized with alkali to the enolic modification of mesityl-*p*-methoxybenzylglyoxal (VII), which is essentially 100% enolic. It was brominated in chloroform to α-bromo-mesityl-*p*-methoxybenzylglyoxal (VIII), which is a deep orange-colored oil. The bromo compound was acetylated by means of freshly fused potassium acetate in glacial acetic acid to the monoacetate (IX). The acetate is approximately 80% enolic. The acetate (IX) was recovered unchanged after treatment with acetyl chloride. However, when the acetate (IX) was refluxed with freshly fused potassium acetate and acetic anhydride, it was converted into the diacetate (X). Both the monoacetate (IX) and the diacetate (X) upon hydrolysis obviously go by way of autoxidation of the ene-diol (XI) to mesityl-*p*-methoxyphenyltriketone (XII), for when the deep red solution of the monoacetate in cold concd. sulfuric acid is poured over finely crushed ice, a colorless solid is formed immediately. Portions of this solid in alcohol give the characteristic bluish-green color with alcoholic ferric chloride, and also decolorize indophenol. These positive tests indicate the actual formation and existence of the ene-diol.

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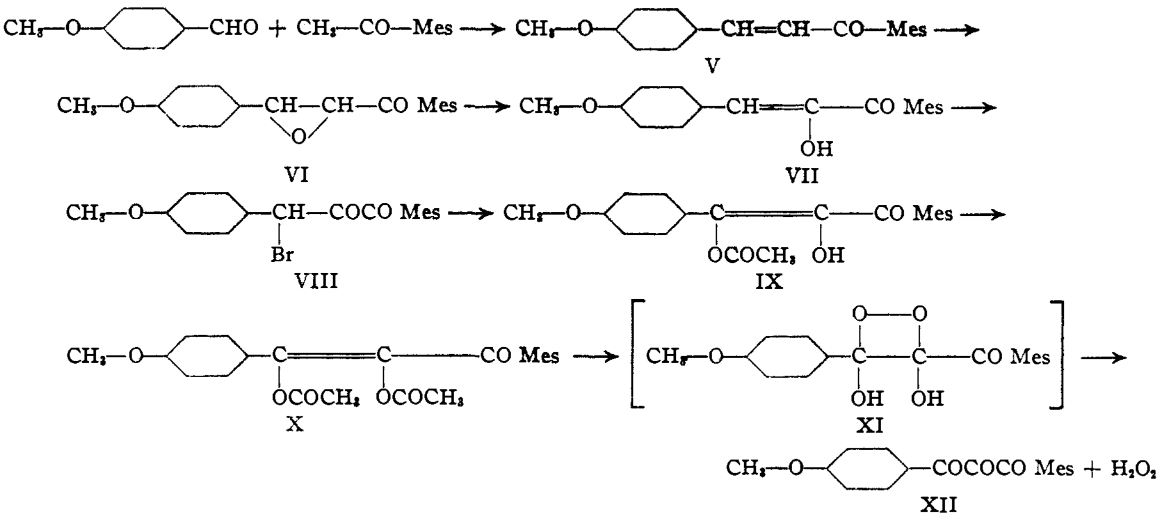
[1] In partial fulfillment of the requirements for the Master's degree.

[2] R. P. Barnes and Wendell M. Lucas, THIS JOURNAL, **64**, 2258, 2260 (1942).



On standing, however, this colorless material undergoes two other rather rapid changes. A very dull but deep orange-colored crystalline solid is formed after twenty to thirty minutes. When this is filtered, it slowly oils out viscous and brown. Finally, a deep yellow crystalline product melting at 106° is formed.

Thus α-*p*-methoxyphenyl-β-mesitoylacetylene glycol (XI) is much more unstable than its isomer, the α-*o*-methoxyphenyl-β-mesitoylacetylene glycol (III).

Experimental

***p*-Methoxybenzalacetomesitylene** (V).—A solution of 15 g. of sodium hydroxide in 50 cc. of water was added to 100 cc. of alcohol. To this solution were added, slowly with cooling and stirring, 23 g. of acetylmesitylene, and 25 g. of anisaldehyde. Stirring was continued for one hour, during which time an orange-colored viscous oil separated, which soon crystallized. It was filtered, washed and dried, yielding 36 g. of crude product. Recrystallized from alcohol, it melted at 103–104°.

Anal. Calcd. for $C_{19}H_{20}O_2$: —OCH_3, 11.07. Found: —OCH_3, 10.91.

α-*p*-Methoxyphenyl-β-mesitoylethylene Oxide (VI).—Fifteen grams of the unsaturated ketone was dissolved in 300 cc. of alcohol. To this solution were added 7 g. of 30% hydrogen peroxide and 8 g. of sodium hydroxide in 30 cc. of water. The temperature of the solution was kept about 35°, and it was stirred for one-half hour. On diluting largely with water and cooling, a colorless oil separated. The oil was taken up in ether, washed with bicarbonate solution, and dried over anhydrous sodium sulfate. On removal of the ether, 11 g. of an almost colorless viscous oil was obtained.

Anal. Calcd. for $C_{19}H_{20}O_3$: —OCH_3, 10.47. Found: —OCH_3, 10.51.

The Enolic Modification of Mesityl-*p*-methoxybenzylglyoxal (VII).—The 11 g. of colorless oxide was dissolved in 75 cc. of methanol, to which was added cautiously and with warming, a solution of 6.5 g. of sodium hydroxide in 20 cc. of water. The solution was boiled for ten minutes. The resulting yellow solution was chilled and acidified with dilute hydrochloric acid. A brown semi-solid mass separated. It was taken up in ether, washed with bicarbonate solution, and dried over anhydrous sodium sulfate. The ether was distilled, and the resulting crystalline mass recrystallized from methanol. The yield was 9.5 g. of a cream-colored solid, melting at 97–98°.

Anal. Calcd. for $C_{19}H_{20}O_3$: —OCH_3, 10.47. Found: —OCH_3, 10.42.

An alcoholic solution of this substance produces a cherry red color. It is 99% enolic as indicated by indirect Kurt Meyer titration.[3] Alkaline hydrogen peroxide cleavage[4] of the enol yields a mixture of mesitoic and anisic acids, which were identified by means of mix-melts with authentic samples.

α-Bromo-*p*-methoxybenzylmesitylglyoxal (VIII).—To 5 g. of the enol in solution in 30 cc. of chloroform was added dropwise 2.7 g. of bromine dissolved in 5 cc. of chloroform. The bromine solution was decolorized instantaneously. The solvent was pumped off. The resulting product was a deep orange-colored viscous oil. The yield was 6.4 g.

Anal. Calcd. for $C_{19}H_{19}O_3Br$: —OCH_3, 8.20. Found: —OCH_3, 8.30.

The Acetate of α-Oxy-*p*-methoxybenzylmesityl-α-diketone (IX).—To the solution of 6.4 g. of the bromodiketone in 50 cc. of glacial acetic acid was added 13 g. of freshly fused potassium acetate, and the mixture was refluxed for one hour. It was then cooled and poured into a large volume of water. A semi-solid brown substance separated. It was filtered and washed thoroughly with water. It was dried and recrystallized from ether. A colorless substance was obtained which melted at 128–129°.

Anal. Calcd. for $C_{21}H_{22}O_5$: —OCH_3, 8.75. Found: —OCH_3, 8.50.

This substance in alcoholic solution produced a cherry red color with alcoholic ferric chloride. It is enolic[3] to the extent of 83%.

The Diacetate of α-*p*-Methoxyphenyl-β-mesitoylacetylene Glycol (X).—One gram of the monoacetate was dissolved in 30 cc. of acetic anhydride, to which solution was added 1 g. of freshly fused potassium acetate, and the mixture was refluxed gently for fifteen minutes. It was then chilled and poured into cold water. On stirring, the oil which separated solidified. It was recrystallized from methanol, melting sharply at 96°.

Anal. Calcd. for $C_{23}H_{24}O_6$: —OCH_3, 7.83. Found: —OCH_3, 7.55.

When the monoacetate was refluxed with acetyl chloride for one hour, it was recovered unchanged.

Hydrolysis of the Mono- and Diacetates.—Two grams each of the mono- and diacetate in separate containers was dissolved in 30 cc. of concd. sulfuric acid. Deep red solutions resulted. Each was poured onto finely crushed ice. A colorless solid separated, which immediately began to

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(3) S. R. Cooper and R. P. Barnes, *Ind. Eng. Chem., Anal. Ed.*, **10**, 379 (1938).

(4) Weitz and Scheffer, *Ber.*, **54**, 2327 (1921).

turn yellow. When dissolved in alcohol and treated with alcoholic ferric chloride, a bluish-green color was produced; an alcoholic solution of the substance also decolorized indophenol. On standing, two other changes were observed: a very dull but deep orange-colored crystalline substance was formed after twenty to thirty minutes; when it was filtered it slowly oiled out viscous and brown and crystallized as a deep yellow substance, which upon recrystallization from methanol, melted at 106°.

Anal. Calcd. for $C_{19}H_{18}O_4$: $—OCH_3$, 10.00. Found: $—OCH_3$, 9.99.

Summary

We have reported the preparation and properties of the enolic modification of mesityl-*p*-methoxybenzylglyoxal (VII), and have shown that the mono- and diacetates (IX) and (X) upon hydrolysis go by way of autoxidation of the acetylene glycol (XI) to *p*-methoxyphenyl mesityl triketone (XII).

WASHINGTON, D. C. RECEIVED AUGUST 7, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

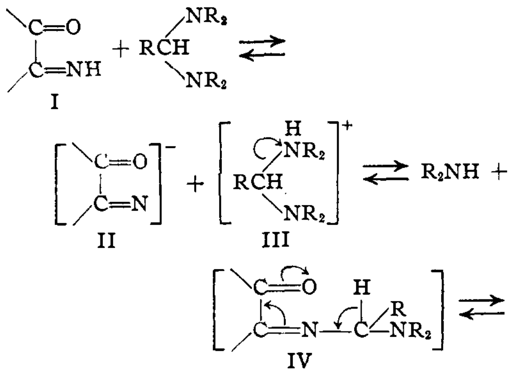
Reaction of Ortho Quinonimines with Alkylidenebisamines and Hydrobenzamide

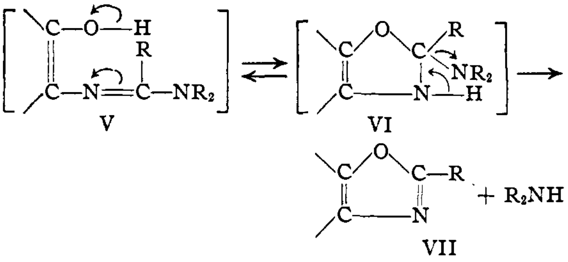
BY GEORGE MCCOY[1] AND ALLAN R. DAY

The validity of the structural analogy between aldehydes, Schiff bases, alkylidenebisamines, and hydrobenzamide was demonstrated by Knoevenagel in 1898.[2] He showed that benzaldehyde, benzalaniline, benzalbispiperidine and hydrobenzamide react with malonic acid to yield cinnamic acid as the final product in each case.

Stein and Day[3] have shown that the hydrogen atom of the imino group in retenequinonimine and phenanthraquinonimine is an active hydrogen. The quinonimines as a result undergo an aldol-type of addition with aldehydes or Schiff bases with the subsequent formation of 2-substituted retenoxazoles and phenanthroxazoles.

It seemed desirable to complete the above noted analogy by studying the reactions of the quinonimines with alkylidenebisamines and to re-examine the reaction of retenequinonimine with hydrobenzamide which is known to produce retenoxazoles.[4] It was found that retenequinonimine reacts readily with benzalbispiperidine and methylenebismorpholine to give almost quantitative yields of 2-phenylretenoxazole and retenoxazole, respectively. The reaction probably proceeds according to the course





In this series of reactions, the bisamine acts as a proton acceptor. The addition of the proton by displacing the electronic system toward the proton creates a tendency to cleave between the nitrogen atom and the *alpha* carbon atom. The electron deficiency on the alpha carbon atom may then be satisfied by union with the anion II. It will be noted that the intermediate IV is similar to that postulated by Stein and Day[3] for the intermediate formed by the interaction of retenequinonimine and a Schiff base.

Hydrobenzamide may be regarded both as a Schiff base and as an alkylidenebisamine. Kreps and Day[4] have shown that retenequinonimine reacts rapidly with hydrobenzamide to form 2-phenylretenoxazole. Their postulated mechanism, which was based on fewer facts than are now available, does not fit in entirely with the known general relationships between the aquo and the ammono systems. For this reason it was decided to re-examine the reaction.

There are only a few published examples involving the reaction of hydrobenzamide with active hydrogen compounds. Busch[5] treated hydrobenzamide, in dry alcohol–benzene solution, with hydrogen chloride and isolated benzaldimine hydrochloride and benzaldehyde diethylacetal. This reaction was repeated, in the present work, in dry ether solution and two moles of benzaldimine hydrochloride were obtained for each mole of hydrobenzamide. The cleavage of the two carbon to nitrogen linkages is undoubtedly initiated by proton addition to nitrogen.

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(1) Present address: *University of Pennsylvania, Philadelphia, Pa.*

(2) Knoevenagel, *Ber.*, **31**, 2596 (1898).

(3) Stein and Day, THIS JOURNAL, **64**, 2567, 2569 (1942).

(4) Kreps and Day, *J. Org. Chem.*, **6**, 140 (1941).

(5) Busch, *Ber.*, **29**, 2143 (1896).