solvent was evaporated and the product recrystallized from alcohol–benzene mixture; yield 3.5 g., m. p. 75–76°.

Anal. Calcd. for $C_{48}H_{90}O_2$: C, 82.45; H, 12.97. Found: C, 82.20; H, 13.00.

Ethyl Methyl Cetyl Malonate.—To a solution of 5.2 g. of sodium in 100 cc. of absolute alcohol, 40 g. of ethyl methylmalonate was added. Then, 77 g. of cetyl iodide was added and the mixture refluxed until neutral. The alcohol was distilled *in vacuo* and the residue extracted with ether. The oil obtained after concentration was fractionated at reduced pressure: at 1 mm., b. p. 185–190°; yield 63 g.

Anal. Calcd. for $C_{24}H_{48}O_4$: C, 71.95; H, 12.07. Found: C, 72.47; H, 11.82.

Ethyl α-Methylstearate.—A mixture of 30 g. of the above malonate and 4.6 g. of potassium hydroxide in 52 cc. of alcohol was refluxed for sixteen hours. The solution was diluted with water and alcoholic potassium hydroxide and extracted with ether. The aqueous solution was acidified to congo with concentrated hydrochloric acid and the oil separated. After drying, the oil was heated at 180° until no more carbon dioxide was evolved. After cooling, it was taken up with ether and washed with dilute sodium carbonate and water and distilled, after drying: at 1 mm., b. p. 161–163°; yield 20 g.

Anal. Calcd. for $C_{21}H_{42}O_2$: C, 77.24; H, 12.96. Found: C, 77.56; H, 12.70.

2-Methyl-*n*-octadecyl Alcohol.—An alcoholic solution of 14 g. of the above ester, in the presence of 1 g. of copper chromite, was heated at 250° under 2000 lb. (133 atm.) pressure of hydrogen for eight hours. After cooling and filtering, the product was distilled. At air-bath temperature of 125–130° and 0.05 mm., the alcohol was obtained and upon cooling it solidified; m. p. 32–33°; yield 12 g.

Anal. Calcd. for $C_{19}H_{40}O$: C, 80.21; H, 14.17. Found: C, 80.25; H, 14.00.

2-Methyl-*n*-Octadecyl Iodide.—A mixture of 12 g. of the above alcohol, 6 g. of iodine and 1 g. of red phosphorus was heated at 170–180° for one hour. The product was dissolved in ether and washed with water, thiosulfate, water and then dried. On distilling at 0.05 mm. and air-bath temperature of 185°, a colorless liquid is obtained which soon turns pink; yield 14 g.

Anal. Calcd. for $C_{19}H_{39}I$: C, 57.86; H, 9.96. Found: C, 57.74; H, 10.04.

Ethers of Durohydroquinone and 2-Methyl-*n*-octadecyl Iodide.—In the usual way, 5.5 g. of durohydroquinone, 13 g. of the above iodide in alcohol and 28 cc. of 1.15 *n* alcoholic potassium hydroxide interacted. After several hours of refluxing, water was added and the precipitate dissolved in ether. The extract was washed with Claisen solution, water and then dried. On distillation at 0.05 mm., a fore-run of a hydrocarbon and duroquinone was obtained and then at an air-bath temperature of 210–220°, the monoether distilled. After recrystallization from alcohol, it was obtained pure, m. p. 94–95°; yield 2 g. The reducing power of this ether was rather strong but not like that of α-tocopherol.

Anal. Calcd. for $C_{29}H_{52}O_2$: C, 80.49; H, 12.12. Found: C, 80.44; H, 11.91.

The residue was dissolved in chloroform and filtered through charcoal several times. The solvent was evaporated and the diether recrystallized from alcohol, m. p. 76–78°; yield 1 g.

Anal. Calcd. for $C_{48}H_{90}O_2$: C, 82.45; H, 12.97. Found: C, 82.34; H, 12.99.

We gratefully acknowledge our indebtedness to Messrs. D. F. Hayman and W. Reiss for the microanalyses.

Summary

Several mono- and diethers of durohydroquinone have been prepared.

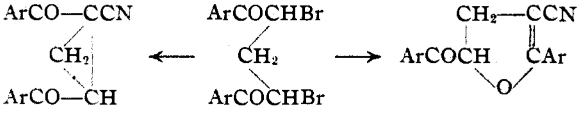
RAHWAY, NEW JERSEY RECEIVED JULY 22, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Action of Sodium Cyanide on 1,3-Dibromo-1,3-dibenzoylpropane

BY REYNOLD C. FUSON, J. R. LITTLE AND GAIL MILLER

The successful closure of the cyclobutane ring by treatment of α,α'-dibromoadipic esters with sodium cyanide[1] could not be extended to 1,4-dibromo-1,4-diaroylbutanes. The latter underwent closure to cyanodihydro-1,4-pyrans, *i. e.*, to six-membered rings.[2] The present work grew out of an attempt to extend the method to the closure of a 1,3-dibromo-1,3-diaroylpropane (I). It was thought that this compound might yield a cyclopropane derivative (II) or a cyanodihydrofuran derivative (III) depending on whether the reaction resembled the cyclobutane or the dihydro-1,4-pyran closure.



II I III

In an effort to determine which of these two courses the reaction would follow, we have treated 1,3-dibromo-1,3-dibenzoylpropane (IV) with sodium cyanide. A rapid reaction took

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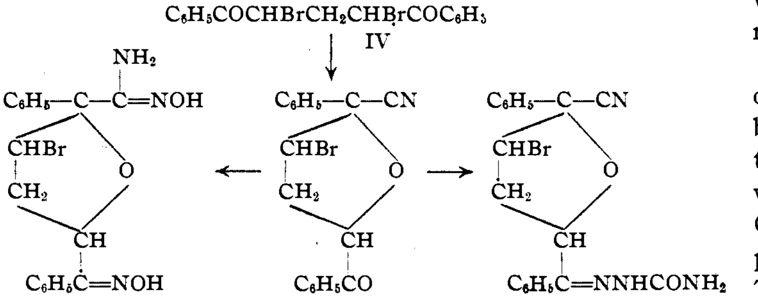
[1] Fuson and Kao, THIS JOURNAL, **51**, 1536 (1929); Fuson, Kreimeier and Nimmo, *ibid.*, **52**, 4074 (1930); Rydon, *J. Chem. Soc.*, 593 (1936).

[2] Fuson, Kuykendall and Wilhelm, THIS JOURNAL, **53**, 4187 (1931).

place, but there were no cyclopropane or dihydrofuran derivatives among the products. A mixture of four isomeric compounds was obtained. The molecular formula was $C_{18}H_{14}O_2NBr$. The net change in the molecule, therefore, consisted in the loss of one bromine atom and the gain of one carbon atom and one nitrogen atom.

The observation that there are four isomers and that they do not give a precipitate with alcoholic silver nitrate greatly restricts the number of possible structures. Of these only that of 2-cyano-2-phenyl-3-bromo-5-benzoyltetrahydrofurans (V) satisfies all of the requirements. In particular, the fact that it is a β-bromo ether would account for the inertness of the bromine atom toward silver nitrate.[3]

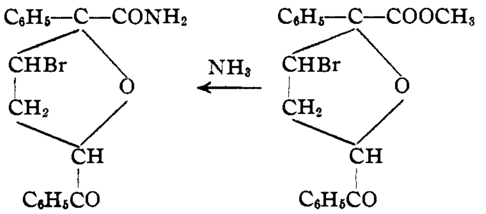
The products correspond to the four pairs of optical isomers theoretically possible on the basis of formula V, and for convenience have been called A, B, C and D. A few reactions have been run on all four compounds to show their similarity, but many of the reactions have been carried out only with A, the most plentiful isomer.



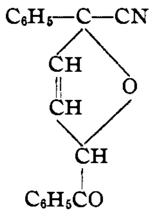
VI V VII

Treatment with hydroxylamine converted the four compounds into similar derivatives having the formula $C_{18}H_{18}O_3N_3Br$. These have been assigned formula VI—that of 2-phenyl-3-bromo-5-oximinobenzoyltetrahydrofuramidoxime. The change in composition indicates that the ketone group has been converted to an oximino group and the cyano group to an amidoxime group as reported by Tiemann.[4]

Isomers A, B and D yielded different monosemicarbazones (VII) which confirm the presence of one carbonyl group. Treatment of A and B with acids gave amides (VIII) which resisted attempts to bring about hydrolysis to the corresponding acids. Isomer A was transformed into a mixture of the amide (VIII) and the methyl ester (IX) by treatment with a solution of hydrogen chloride in methanol. Ammonia converted the ester to the amide.



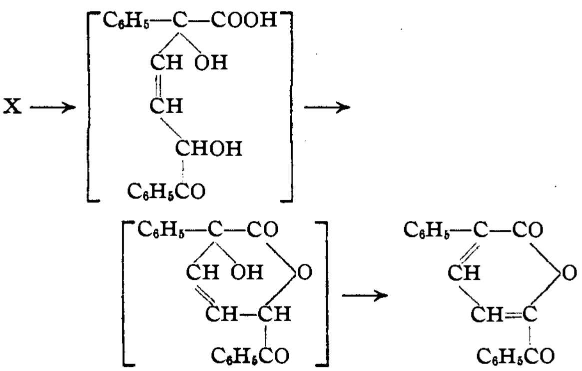
VIII IX



X

The most interesting reaction of A, B, C and D occurred when they were treated with aqueous alkali. All lost a molecule of hydrogen bromide and gave the same product. This result may be explained by reference to formula X which has two asymmetric carbon atoms one of which—that attached to the benzoyl group—might be expected to undergo inversion due to enolization. The latter process would be favored by the alkalinity of the reaction medium. In this connection it is interesting to note that isomer C was found to change spontaneously into isomer B—a result which can be explained in a similar manner.

Further evidence for the structure of the dihydrofuran (X) was obtained by treating it with strong acid. By this process a nitrogen-free product was obtained which had the formula $C_{18}H_{12}O_3$, and was shown to be 3-phenyl-6-benzoyl-1,2-pyrone (XI). The following sequence of reactions appears probable



XI

In an attempt to benzoylate the 1,2-pyrone (XI) it was dissolved in hot alkali and treated with benzoyl chloride. From the alkaline solution it was possible to isolate an acid whose com-

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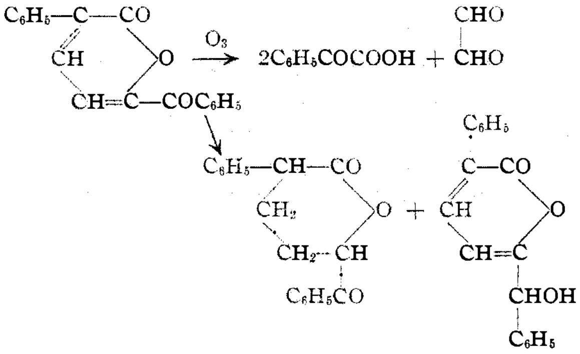
(3) See Kirner, THIS JOURNAL, **48**, 2745 (1926).

(4) Tiemann, *Ber.*, **17**, 126 (1884).

position corresponded to that of the monohydrate of the diketo acid, $C_6H_5COCOCH_2CH{=}C(C_6H_5)\text{-}COOH$. The presence of a ketone group in the 1,2-pyrone (XI) was established by oximation; two forms of the oxime were isolated. Degradation of the 1,2-pyrone into known compounds was accomplished by ozonization followed by catalytic reduction of the ozonide. Phenylglyoxylic acid and glyoxal were isolated in the form of their phenylhydrazine derivatives

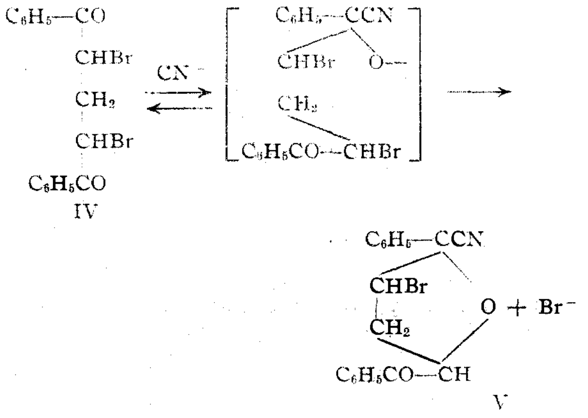


XII XIII

When the pyrone was reduced catalytically α-phenyl-δ-benzoyl-δ-valerolactone (XII) was isolated. It was accompanied by a dihydro derivative of the pyrone which formed an acetate, and may be the carbinol (XIII) resulting from reduction of the carbonyl group.

Discussion of Results

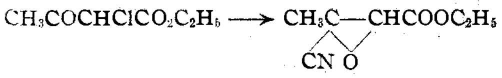
The transformation of 1,3-dibromo-1,3-dibenzoylpropane (IV) into the 2-cyano-2-phenyl-3-bromo-5-benzoyltetrahydrofurans (V) is complete in a minute or two and no appreciable amount of heat is liberated. It does not take place at all unless water is present. Apparently the first step in the reaction is the addition of cyanide ion to one of the carbonyl groups.[5] Ring closure is then effected by the elimination of a bromide ion.



IV V

This suggests that the addition of the cyanide ion is a rapid reversible reaction which goes to completion because the ring closure is irreversible.

The process is similar to that involved in the formation of α-epoxy nitriles from α-halo ketones. Favrel and Provost,[6] for example, showed that potassium cyanide converted ethyl α-chloroacetoacetate into the corresponding epoxy nitrile



$$CH_3COCHClCO_2C_2H_5 \longrightarrow \underset{CN\ O}{CH_3C\text{—}CHCOOC_2H_5}$$

Similar results were obtained by Kohler and Brown[7] and by Richard[8] with desyl chloride. Richard[9] also converted α-chloro-α-phenylacetone into α-epoxy-α-methyl-β-phenylpropionitrile by this method.

These examples might lead one to think that this type of reaction would be general for ketones which have a halogen atom in the α-, γ- or perhaps δ-position. Yet Wohlgemuth[10] reported that it could not be carried out with γ-chloropropyl ethyl ketone. Allen and Boyer[11] found that γ-chlorobutyrophenone when treated with potassium cyanide in absolute alcohol gave cyclopropyl phenyl ketone and none of the cyanotetrahydrofuran which might have been expected. Since the closure under consideration occurs only in the presence of water, we repeated the experiment of Allen and Boyer using, however, aqueous alcohol as the solvent; there was no reaction after two hours at room temperature.

Another and perhaps more striking example of this sort is afforded by the work on 1,4-dibromo-1,4-diaroylbutanes which, as has been indicated earlier, react in a manner entirely different from that observed with the next lower homolog.

In conclusion it may, therefore, be said that the action of sodium cyanide on 1,3-dibromo-1,3-dibenzoylbutane to give 2-cyano-2-phenyl-3-bromo-5-benzoyltetrahydrofurans is an extension of a new type of reaction hitherto limited to the formation of epoxy nitriles. The conditions which have obtained in all of the examples cited are the following:

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(5) See Jones, *J. Chem. Soc.*, **105**, 1561 (1914); Lapworth, *ibid.*, **83**, 995 (1903).

(6) Favrel and Provost, *Bull. soc. chim.*, [4] **49**, 243 (1931).

(7) Kohler and Brown, THIS JOURNAL, **55**, 4299 (1933).

(8) Richard, *Compt. rend.*, **198**, 943 (1934).

(9) Richard, *ibid.*, **199**, 71 (1934).

(10) Wohlgemuth, *Ann. chim.*, **3**, 141 (1915).

(11) Allen and Boyer, *Can. J. Research*, **9**, 159 (1933).

1. Water is present in the solvent. 2. The halogen atom directly involved is in the α-position relative to an activating group such as a carbonyl or phenyl group. 3. The carbonyl group which enters into the reaction has a halogen atom in the α-position with respect to it. 4. The reactive groups involved are conveniently spaced for ring formation.

That the foregoing conditions are necessary remains to be shown. That they are not always sufficient is indicated by the results with 1,4-dibromo-1,4-dibenzoylbutane. This and other types of halo ketones are being examined in an effort to determine more precisely the generality of the reaction.

Experimental Part

The Preparation of **the Isomeric 1,3-Dibromo-1,3-dibenzoylpropanes.**—1,3-Dibenzoylpropane made by the method of Auger[12] was brominated according to the procedure of Conant and Lutz.[13] The latter authors reported two isomeric dibromides melting at 115–115.5 and 89°. In the present work the crude bromination product was fractionally crystallized from carbon tetrachloride. From 74 g. of crude product there was obtained 40 g. of a dibromide melting at 117–118° and 21 g. of a mixture which melted at 90–94°.

In an effort to separate the mixture absolute alcohol was used as a solvent. A chance seeding gave crystals which melted at 112–113°. A mixture of these with those melting at 117–118° melted at 92–95°. It appears probable that the low-melting isomer reported by Conant and Lutz is really a mixture of the two forms.

Anal. Calcd. for $C_{17}H_{14}O_2Br_2$: C, 49.8; H, 3.4. Found for the compound melting at 117–118°: C, 49.8; H, 3.7. Found for the compound melting at 112–113°: C, 50.2; H, 4.2.

Conversion of **1,3-Dibromo-1,3-dibenzoylpropane into the Isomeric 2-Cyano-2-phenyl-3-bromo-5-benzoyltetrahydrofurans.**—Sixty grams of 1,3-dibromo-1,3-dibenzoylpropane was suspended in 800 cc. of 95% ethyl alcohol in a flask equipped with a mechanical stirrer. A solution of 10 g. of sodium cyanide in 40 cc. of water was added gradually, with stirring, over a period of about three minutes. A slight coloration occurred and the dibromide went partially—sometimes wholly—into solution. A few minutes after the addition of the cyanide was complete a heavy precipitate formed suddenly. The stirring was discontinued after about fifteen minutes, the solid collected on a filter, dried and crystallized from carbon tetrachloride. In this way isomer A was obtained in white cotton-like needles melting at 166–167°.

The alcoholic mother liquors from the reaction were poured into water and the semi-solid material which separated was extracted with benzene. Acidification of the water–alcohol solution with hydrochloric acid seemed to hasten the extraction. The benzene layer was dried over sodium sulfate and concentrated under diminished pressure. Absolute alcohol was added to the viscous concentrate; cooling and triturating induced the formation of a finely divided crystalline precipitate. Alternate concentration of alcohol solutions and trituration with absolute alcohol gave several more crops of a mixture which proved to consist of A and its isomers.

No successful method was found for separating the isomers by fractional crystallization. This was finally accomplished by dissolving the mixture in hot methyl alcohol (about 200 cc. for each 10 g. of crystals), allowing the solution to cool so that the crystals formed slowly. The crystallization was carried out by pouring the hot methyl alcohol solution into a large crystallizing dish such that the depth of the solution was from 1 to 2 cm. The dish was then covered with a watch glass and allowed to stand for several days without disturbance.

When the crystals had grown to a sufficient size for handling, the mother liquor was carefully decanted and the different types of crystals were separated by picking them out mechanically. Compound A was found in clusters of very fine needles. Long oblong crystals occurring singly or in rosettes melted at 101–102° and were designated Compound B. Compact clusters of opaque needles usually having a slight color melted at 120–123° and were called Compound D. Thick square plates softening at 101–102° and melting at 120° were found to contain both B and a third isomer, D. These square crystals formed only occasionally with methyl alcohol as the solvent, more frequently with a mixture of benzene and petroleum ether as solvent. The crystals of isomer D were tough and hard to grind whereas those of the other isomers were brittle. Isomer D was also found to exist in long slender needles melting at 108–109°. By rapid cooling and stirring the lower-melting form usually could be isolated; slower crystallization gave the higher-melting form.

Diamond-shaped crystals melting at 86–88°—obtained in only two of the several runs—were called isomer C. On being allowed to stand for long periods of time this isomer underwent isomerization to Compound B. The fact that C was not found in all preparations was probably due to its tendency to rearrange to B during the process of recrystallization.

The yields of the isomers were: A, 52–68%; B, 12–16%; C, 0–2%; D, about 6%. Approximately the same ratio of isomers was obtained from either the high-melting or the low-melting dibromide. Similarly, sodium cyanide and potassium cyanide gave about the same results.

Anal. Calcd. for $C_{18}H_{14}O_2NBr$: C, 60.7; H, 4.0; Br, 22.5; mol. wt., 356. Found for A (m. p. 166–167°): C, 60.4, 60.3; H, 4.0, 4.1; Br, 22.3; mol. wt., 346. Found for B (m. p. 101–102°): C, 60.3, 60.3; H, 4.1, 4.1. Found for C (m. p. 86–88°): C, 60.4, 60.4; H, 4.0, 4.1. Found for D (m. p. 120–123°): C, 60.5; H, 4.2.

Each of the four isomers was shown to contain bromine and nitrogen. None, however, gave even a turbidity when treated with boiling alcoholic solutions of silver nitrate.

Treatment of 1,3-Dibromo-1,3-dibenzoylpropane with Potassium Cyanide in Absolute Alcohol.—To a suspension of 1 g. of the dibromide (m. p. 116–118°) in 300 cc. of carefully prepared absolute ethyl alcohol was added 0.4 g. of

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[12] Auger, *Ann. chim.*, [6] **22**, 358 (1891).

[13] Conant and Lutz, THIS JOURNAL, **49**, 1083 (1927).

potassium cyanide. After three days the mixture was found to contain none of isomers A, B, C and D but a new compound melting at 127–128.5°. It contained halogen, but was not further investigated.

The Isomeric 2-Phenyl-3-bromo-5-oximinobenzoyltetrahydrofuramidoximes.—The usual procedure for oxime formation was employed. The following table shows solvents used for recrystallization, the melting points and the analytical data. Mixed melting point determinations showed the four derivatives to be different.

Furamidoxime from	M. p., °C.	Recrystallization solvent	Analyses, % C	H	N	Br
A	171–173	Methyl alcohol	53.4	4.2	10.5	19.6
			53.5	4.5		
			53.7	4.5		
B	179–181	Methyl alcohol	53.6	4.7		
C	182–183	Ethyl alcohol			10.5	
D	180–182	Chloroform	53.4	4.5		
Calcd. for $C_{18}H_{18}O_3N_3Br$			53.5	4.5	10.4	19.8

The Semicarbazones of Isomers A, B and D.—These derivatives were prepared in the customary manner. Their melting points and analytical data are listed in the table.

Semicarbazone from	M. p., °C.	Analyses, % C	H	N	Br
A	202	55.2	4.3	13.4	19.4[a]
B	178–179	55.4	4.0	13.9	
D	202	55.5	4.1	13.2	
Calcd. for $C_{19}H_{17}O_2N_4Br$		55.2	4.1	13.5	19.4

[a] This compound was prepared and analyzed by Sister M. Faith Hand.

2-Phenyl-3-bromo-5-benzoyltetrahydrofuramide.—Three grams of isomer A was dissolved in a solution of 50 cc. of concentrated hydrochloric acid and 50 cc. of glacial acetic acid and the mixture was heated on a steam-bath for three hours. The resulting dark green solution was poured into water and the mixture neutralized with sodium bicarbonate and extracted with benzene. In addition to some unchanged A there was obtained colorless crystals of the amide which after recrystallization twice from ethyl alcohol and then once from methyl alcohol melted at 200–201°. The compound was insoluble in alkali. It contained nitrogen and halogen but gave no precipitate with hot alcoholic silver nitrate.

Anal. Calcd. for $C_{18}H_{16}O_3NBr$: C, 57.8; H, 4.3; N, 3.8. Found: C, 57.5; H, 4.4; N, 3.8.

Methyl 2-Phenyl-3-bromo-5-benzoyltetrahydrofuroate.—An ice-cold suspension of 6 g. of isomer A in 400 cc. of absolute methyl alcohol was saturated with dry hydrogen chloride gas. After the mixture had stood at room temperature for fifteen hours it was poured into 2 liters of water. The ester was extracted with benzene, the benzene evaporated and the residue crystallized from methyl alcohol. The compound formed compact crystals melting at 101–102°. It contained nitrogen and halogen but was not soluble in alkali and gave no precipitate with hot alcoholic silver nitrate.

Anal. Calcd. for $C_{19}H_{17}O_3Br$: C, 58.6; H, 4.4. Found: C, 58.4, 58.6; H, 4.6, 4.4.

A small amount of the corresponding amide (m. p. 200–201°) was also obtained.

A similar treatment of isomer B (later found to contain some of isomer D) gave no ester but an amide probably derived from isomer B but possibly from isomer D. It melted (from alcohol) at 207°, with decomposition.

Anal. Calcd. for $C_{18}H_{16}O_3NBr$: C, 57.8; H, 4.3; N, 3.8. Found: C, 58.0; H, 3.4; N, 3.9.

2-Cyano-2-phenyl-5-benzoyl-2,5-dihydrofuran (X).—To a solution of 50 g. of isomer A in 400 cc. of hot methyl alcohol was added a solution of 9 g. of sodium hydroxide in 250 cc. of water. After being refluxed for one hour on the steam-bath the hot solution was poured into 2 liters of water. Acidification with dilute hydrochloric acid changed the dark red color of the solution to a bright yellow. By extraction of this acidified solution with benzene the dihydrofuran was obtained which crystallized from benzene in bright yellow, cotton-like needles, melting at 136–137°, with darkening at 130°. These crystals turn brown in the light. The yield was 28 g.

Anal. Calcd. for $C_{18}H_{13}O_2N$: C, 78.6; H, 4.7; N, 5.1. Found: C, 78.5; H, 4.5; N, 5.2.

The same product was obtained from isomers B, C and D by similar treatment with sodium hydroxide. Potassium cyanide or sodium acetate could be used in place of sodium hydroxide but with those reagents conversion was incomplete.

3-Phenyl-6-benzoyl-1,2-pyrone (XI).—A mixture of 20.5 g. of dihydrofuran, 400 cc. of glacial acetic acid and 180 cc. of concentrated hydrochloric acid was heated on a steam-bath for fifteen hours and poured into 2500 cc. of water. The brown crystals which formed were treated with decolorizing charcoal and recrystallized from alcohol. In this way 16.5 g. of the pyrone was obtained as slightly colored crystals melting at 126–127°. The compound was insoluble in alkali, contained neither halogen nor nitrogen and readily decolorized an acetone solution of potassium permanganate.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.3; H, 4.4. Found: C, 78.2; H, 4.4.

The oxime crystallized from alcohol in large needles melting at 193–194°.

Anal. Calcd. for $C_{18}H_{13}O_3N$: N, 4.8. Found: N, 4.8.

From the mother liquors was obtained **an isomeric oxime** which crystallized from alcohol in large squares melting at 159–161°.

Anal. Calcd. for $C_{18}H_{13}O_3N$: N, 4.8. Found: N, 4.9.

The Ozonolysis of the 1,2-Pyrone.—In a large test-tube were placed 1.0 g. of the pyrone and 30 cc. of glacial acetic acid. The mixture was cooled in an ice-bath and ozonized oxygen was bubbled through it for five hours at 0° and then continued overnight, during which time the bath came to room temperature. About 0.1 g. of palladium catalyst on charcoal was added to the mixture and the test-tube was placed in the shaker of a catalytic reduction machine equipped with an open mercury manometer. The apparatus was evacuated until bubbles formed in the solution, and then hydrogen was admitted up to 800 mm. pressure. After the mixture had been shaken for four hours the pressure was 680 mm. The catalyst was removed by filtration and 5 cc. of water and 2 cc. of phenylhydrazine were added to the filtrate. The precipitate which formed almost immediately was collected on a filter and recrystallized several times from alcohol and from benzene. The **phenylosazone** of **glyoxal** was obtained in almost colorless crystals melting at 162–166°. The melting point of a mixture of this sample with an authentic one (m. p. 166–169°) was 163–167°.

The filtrate was poured into water and the solution extracted with benzene. The benzene was extracted with sodium carbonate solution. The resulting solution when acidified gave **the phenylhydrazone** of **phenylglyoxylic acid** which crystallized from benzene in bright yellow crystals melting at 159–160°. A mixture of this compound with an authentic specimen (m. p. 159–160°) melted at 159–160°.

α-Phenyl-δ-benzoyl-δ-valerolactone.—The 1,2-pyrone in methyl cellosolve was reduced catalytically in the presence of a platinum oxide catalyst. In addition to a small amount of unchanged 1,2-pyrone there were formed two hydrogenation products. These were separated by crystallization from carbon tetrachloride. The less soluble was purified by crystallization from benzene or aqueous alcohol. It melted at 137–138°. It was very soluble in alcohol, did not decolorize bromine in chloroform solution and was not attacked by chromic acid in acetic acid solution.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1. Found: C, 77.8; H, 5.1.

The acetate was formed by treatment with acetic anhydride and sodium acetate. It melted at 102–103°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 75.1; H, 5.0. Found: C, 75.7; H, 5.0.

The oily residue left after the carbon tetrachloride mother liquor had evaporated was solidified when triturated with ethyl alcohol. Recrystallization from ethyl alcohol gave the valerolactone in diamond-shaped crystals mixed with crystals of the original 1,2-pyrone. The two types of crystals were separated mechanically. The new compound when pure melted at 142–143°. It was very soluble in carbon tetrachloride and did not decolorize a solution of bromine in carbon tetrachloride.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.8. Found: C, 77.3; H, 5.8.

In a second run in which fresh catalyst was introduced twice during the course of the hydrogenation the lactone was the only product which could be isolated.

Summary

1,3-Dibromo-1,3-dibenzoylpropane (IV) reacts with sodium cyanide to give a mixture of the four theoretically possible 2-cyano-2-phenyl-3-bromo-5-benzoyltetrahydrofurans (V).

Treatment with alkali converts the four isomeric tetrahydrofurans into 2-cyano-2-phenyl-5-benzoyl-2,5-dihydrofuran (X).

The dihydrofuran is transformed into 3-phenyl-6-benzoyl-1,2-pyrone (XI).

Ozonolysis of the 1,2-pyrone gave glyoxal and phenylglyoxylic acid. Reduction converted the 1,2-pyrone into α-phenyl-δ-benzoyl-δ-valerolactone (XII).

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XVIII. Synthesis of Acyl Compounds Derived from 1- and 4-Phenanthrol

BY HARRY M. DUVALL[1] AND ERICH MOSETTIG

In the search for substances with oestrogenic activity, the plan has been developed to synthesize more or less simple phenanthrene derivatives containing a phenolic hydroxyl group and a carbonyl group, the latter being located either in a side chain attached to, or in a five- or six-membered hydroaromatic ring condensed with, the phenanthrene nucleus.

This communication describes the preparation by means of the Fries rearrangement and the Friedel–Crafts reaction of methyl and ethyl ketones derived from 1- and 4-phenanthrol. It was found that in the "1-series" the Fries rearrangement was much superior to the Friedel–Crafts reaction. 1-Hydroxy-2-acetylphenanthrene (I) and 1-hydroxy-2-propionylphenanthrene (II) were obtained in yields of 60 and 72%, respectively, in the Fries rearrangement, and in yields of only 30 and 26% by the Friedel–Crafts reaction.

In the "4-series," 4-hydroxy-*y*-acetylphenanthrene was formed in a poor yield only (30%) in the rearrangement of 4-acetoxyphenanthrene together with a small amount (6%) of another compound that is probably 4-hydroxydiacetylphenanthrene. In the Friedel–Crafts reaction, employing acetyl and propionyl chloride, diketones could be isolated in satisfactory yield (60–70%), but no monoketones were found.

While 4-methoxyphenanthrene reacted smoothly with acetyl and propionyl chlorides in the pres-

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