scribed.[2] The absorption spectra were measured with a Beckman Quartz Spectrophotometer.

The Reduction of 4',5,7-Trimethoxyflavone.—A solution of 1.5 g. of 4',5,7-trimethoxyflavone in 100 ml. of 50% alcohol was stirred with 50 g. of 3% sodium amalgam for one-half hour at 40–45°. and allowed to stand for six hours at room temperature with an additional 50 g. of sodium amalgam. The solution was filtered, heated to boiling, diluted with water until turbid, and allowed to cool. The precipitate which formed was crystallized from dilute alcohol, affording 148 mg. of colorless crystals of β-4-hydroxy-4',5,7-trimethoxyflavane[2]; monoacetate, m. p. 127–128°.

The alkaline mother liquor from which the flavane separated was acidified with dilute acetic acid, and the yellow precipitate crystallized from carbon bisulfide. There was obtained 62 mg. of 2'-hydroxy-4,4',6'-trimethoxychalcone, m. p. and mixed m. p. with an authentic specimen, 114–115° (lit.[4] 113–114°).

Summary

The sodium amalgam reduction of polyhydroxy- and polymethoxyflavones leads to the same colored reduction products as the reduction of the corresponding flavanones. There is some evidence that some of the flavylium salt is formed in the former case, but this is not the predominant product.

[4] Bargellini, *Gazz. chim. ital.*, **44**, II, 421 (1914) (*Chem. Abstr.*, **9**, 1042 (1915)); Shinoda and Sato, *J. Pharm. Soc. Japan*, **50**, 265 (1930) (*Chem. Abstr.*, **24**, 4046 (1930)).

LOS ANGELES, CALIFORNIA
RECEIVED SEPTEMBER 12, 1945

[COMMUNICATION NO. 1060 FROM THE KODAK RESEARCH LABORATORIES]

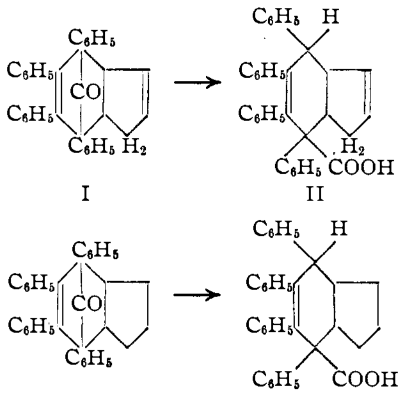
The Action of Alkaline Reagents upon Carbonyl Bridge Compounds. I

BY C. F. H. ALLEN, J. E. JONES AND J. A. VANALLAN

It has been found that in tricyclic carbonyl bridge compounds of the indenone group, the carbonyl bridge is cleaved at one end by the action of strongly alkaline reagents.[1,2] The reaction consists in the addition of one molecule of water, the carbonyl group being converted to a carboxyl group. Since the generality of this reaction had not been determined, all the available carbonyl bridge compounds were submitted to alkaline treatment. These compounds may be placed in two series; one is highly phenylated, whereas in the other, the two phenyl groups at the ends of the bridge are replaced by methyl groups. In this paper the results of treating the first, phenylated series with alkaline reagents are described.

The reaction appears to be fairly general. The action of alkaline reagents upon highly phenylated carbonyl bridge compounds results in the cleavage of the bridge at one end, with consequent formation of a carboxylic acid. Most of the substances treated had simpler structures than the indenones, and fewer functional groups. In spite of this, many secondary reactions often reduce the yield of the primary product. However, quantitative measurements showed that exactly one equivalent of alkali was used for the carbonyl bridge.

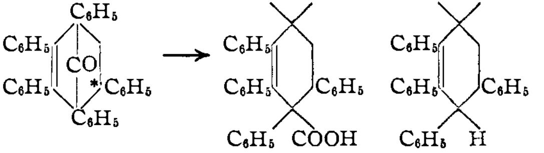
The interpretation of the reaction involved in the action of alkaline reagents on indenones containing carbonyl bridges was complicated by the possibility that the indenone keto group might be the one cleaved.[1] The behavior of the compounds, II and III, with alkali indicates, however, the correctness of the earlier interpretation that the keto group in the side chain was not involved. The tetraphenylindene derivative, I,[3] gives a practically quantitative yield of the acid, II, with either alcoholic potassium hydroxide or sodium ethoxide, and the corresponding indane derivative, III, gives the analogous carboxyindane, IV.



I II

III IV

The pentaphenylated bicyclic ketone, V, gave a mixture of two acids, VI or VII, with potassium hydroxide in ethanol or dioxane, but in methanol a mixture of the two corresponding methyl esters was obtained.



V VI VII

The esters were also formed from the mixed acids by treatment with thionyl chloride, followed by methanol. When piperidine was used, piperidine salts of the acid were formed, but about 10% of an isomeric ketone, Va, was also found. This suggests that the ketone, V, is really a mixture of

[1] Allen and Gates, THIS JOURNAL, **64**, 2120 (1942).

[2] Allen and VanAllan, *J. Org. Chem.*, **10**, 333 (1945).

[3] Grummitt, Klopper and Blenkhorn, THIS JOURNAL, **64**, 604 (1942).

stereoisomers, one of which reacts more easily with this base. Since the substances have decomposition points rather than true melting points, analytical data serve only to indicate the freedom of the ketone from impurities; it does not exclude the presence of isomers.

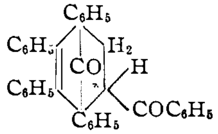
The available evidence affords no basis for conclusion as to whether the two acids are stereoisomers or the position isomers, VI and VII. The latter possibility is favored (barring an unlikely inversion), since the acids are obtained from a cyclic compound which has no hydrogen available in the position *alpha* to the carbonyl group. The esters could not be interconverted, or hydrolyzed even by Newman's procedure.[4]

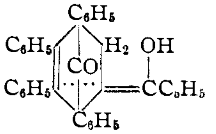
Secondary products of the reaction between the ketone, V, and alkali were negligible. When heated by themselves, the acids underwent decarboxylation, both forming the known pentaphenyldihydrobenzene,[5] which was dehydrogenated by means of bromine to pentaphenylbenzene. The latter hydrocarbon was also formed by oxidation of the acids, VI and VII. The production of a dihydrobenzene from the tetrahydro acid can be accounted for by (a) a decarboxylation, followed by a dehydrogenation, or (b) a transannular elimination of formic acid.

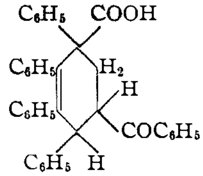
This isomeric ketone, Va, which is unaffected by piperidine, affords a mixture of acids with sodium alkoxide; its behavior thus parallels that already described.

Four stereoisomeric acids are possible, two from each ketone. The ketones differ only in the relation of the two phenyl groups marked with an asterisk. In one case they will be *cis*, and in the other, *trans*. Insufficient evidence makes it impossible to write detailed configurations.

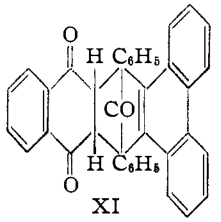
The benzoylated ketone, VIII,[7] presents an interesting case. Since formation of an enolate is possible, any asymmetry due to the *-carbon atom disappears, and hence fewer isomers would be expected than with the ketone, V, just discussed. Furthermore, in the enolate, IX, there is a new double bond between the side chain and the ring. This double bond, and the one already present between the two phenyl groups, in accordance with our interpretation[8] of the cleavage of the carbonyl bridge in the light of Schmidt's double-bond rule, would both act on the same bond of the bridge; cleavage would be expected to take place on one side only, and but one acid, X, should result. This predicted behavior was gratifyingly observed; a single acid is formed in a yield of over 90%.

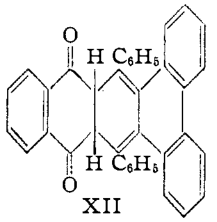

VIII


IX

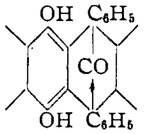

X

The polynuclear compound, XI,[9,10] when treated with alcoholic potassium hydroxide, loses the bridge, forming the known[10] dihydroquinone, XII; the yield is much higher using this procedure. This reaction is apparently analogous to the formation of the pentaphenyldihydrobenzene already described.

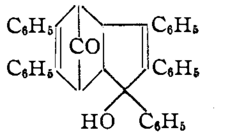

XI

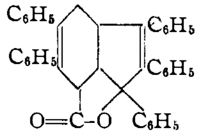

XII

A plausible alternative explanation should be mentioned. In an enolate, XIa, which might be formed by the action of alkali, there would be two double bonds *beta* to the carbonyl bridge. This would facilitate its cleavage in accordance with the double-bond rule.


XIa

Finally, the tricyclic carbinol, XIII,[11] was examined; it likewise reacted with alcoholic potassium hydroxide. The product appears to be the lactone, XIV, for it shows two additions without evolution of gas, when treated quantitatively with methylmagnesium iodide.


XIII


XIV

Experimental

The general procedure employed was to reflux a mixture of carbonyl bridge compound and alkaline reagent until solution was complete. When quantitative results were desired, standard alkali was used, the excess determined

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[4] Newman, THIS JOURNAL, 63, 2431 (1941).

[5] Abramov and Mitropolytanskaya, *J. Gen. Chem. U. S. S. R.*, 10, 207 (1940): *C. A.*. 34, 7284 (1940). This is the substance, m. p., 158°, formed in a yield of 1%, but unrecognized at the time, on p. 1387 (ref. 6).

[6] Allen and VanAllan, THIS JOURNAL, 65, 1384 (1943).

[7] Allen, Bell, Bell and VanAllan, *ibid.*, 62, 656 (1940).

[8] Allen, *Chem. Rev.*, 37, 209 (1945).

[9] Arbuzov, Abramov and Devyatov, *J. Gen. Chem. U. S. S. R.*, 9, 1559 (1939); *C. A.*, 34, 2839 (1940).

[10] Dilthey and Leonhard, *Ber.*, 73, 430 (1940).

[11] Allen and Gates, THIS JOURNAL, 64, 2120 (1942).

and time noted. The alkaline solution was then added to excess mineral acid, and the products were worked up by appropriate manipulation.

A. Indene Series.—Four grams of the indene derivative, I,[12] gave 3.4 g. (82%) of 7-carboxy-4,5,6,7-tetraphenyl-3a,4,7,7a-tetrahydroindene, II, m. p. 274°, when treated with either 10% alcoholic potassium hydroxide or sodium ethoxide; solution was complete in twenty minutes. The analysis is given in Table I. A portion of this acid gave tetraphenylphthalic anhydride upon permanganate oxidation; its identity was shown by comparison with a specimen at hand.

TABLE I

No. or	substance	M. p., °C.	Empirical formula	Analyses, % Calcd. C	H	Found C	H
	II	274	$C_{34}H_{28}O_2$	87.3	6.0	87.3	6.2
XV	Hydrocarbon	204	$C_{33}H_{28}$	93.4	6.6	93.1	6.5
XVI	Acid	256–258	$C_{37}H_{30}O_2$	87.7	5.9	87.8	6.2
XVII	Ester	201–202	$C_{38}H_{32}O_2$	87.7	6.2	87.9	6.4
XVIII	Ester	169–170	$C_{38}H_{32}O_2$	87.7	6.2	87.6	6.2
XIX	Piperidine salt[a]	268	$C_{42}H_{41}NO_2$	85.2	7.0	85.1	7.1
XX	Acid	155–160	$C_{37}H_{30}O_2$	87.7	5.9	87.8	6.0
	Va[b]	201–203	$C_{37}H_{28}O$	91.0	5.8	90.8	6.0
	X	291–293	$C_{38}H_{30}O_3$	85.3	5.6	85.4	5.5
	XII	344	$C_{38}H_{24}O_2$	89.0	4.7	88.9	4.9
	XIV[c]	250	$C_{40}H_{30}O_2$	88.6	5.5	88.2	5.5

[a] Calcd.: N, 2.4. Found: N, 2.4. [b] Calcd.: no active hydrogen, 1 addn. Found: O, 1.1. [c] Calcd.: no active hydrogen, 2 addn. Found: O, 1.8.

The remainder of the acid was distilled; it boiled at 280–300° at 3 mm., with loss of carbon dioxide. The distillate solidified when triturated with methanol; it was recrystallized from xylene. The white hydrocarbon, probably 4,5,6,7-tetraphenyl-2,3,4,7-tetrahydroindene, XV, melted at 204°. It does not add maleic anhydride, evolved hydrogen bromide when treated with bromine, and decolorized a warm acetone solution of permanganate. No definite substance could be isolated from its reaction with sulfur. Lack of material prevented further study.

In a similar manner, the reduced indene derivative, III, dissolved in alkaline potassium hydroxide to give a product completely soluble in water. The acid was oily and was not analyzed since there was not enough for purification.

B. Phenylated Bridged Ketone, V.—The highly arylated bridged ketone, V, had completely dissolved in hot 10% alcoholic potassium hydroxide after three hours of refluxing. An acid, XVI, m. p. 256–258°, was isolated in a yield of 29%; the residual oil, that failed to crystallize, was distilled at 2 mm.—there was no residue. Upon crystallization, dihydropentaphenylbenzene, m. p. 156–157°, was obtained; a mixed melting point with an authentic specimen showed no depression. The solid acids likewise gave this hydrocarbon, indicating that the action of the alkali was practically quantitative.

A portion of the acid was converted to the methyl esters by means of thionyl chloride, followed by methanol. The esters were partially separated by fractional crystallization by using acetic acid, ligroin (70–90°) and butanol. The high-melting ester, XVII, m. p. 201–202°, separated in rosets of needles, whereas the lower-melting isomer, XVIII, formed prisms, m. p. 169–170°. Both failed to react with methyl magnesium iodide, presumably because of the high degree of hindrance. The mixed esters, m. p. 150–165°, distilled unchanged, b. p. 280–340° (2 mm.).

If the bridged ketone, V, was refluxed with methanolic potassium hydroxide, solution was not complete until four days had elapsed. This difference in the rate of reaction, attributed to the difference in boiling point, is very marked. After acidification, the reaction product, in this case, is solid; 15 g. of starting material give 15.6 g. of product. From this, by fractional crystallization, there was isolated 1.5 g. of the high-melting ester. When the acid, m. p. 256–258°, was treated with thionyl chloride, followed by methanol, it gave the low-melting ester. All attempts to hydrolyze the esters failed.

When 10 g. of V and 70 cc. of piperidine were heated on the steam-bath, all the ketone had dissolved after one hour; after two hours, a solid began to deposit from the red solution. This was the piperidine salt, XIX, of the acid, VI; it was obtained in a 75% yield. The solution gave 1 g. (10% yield) of the isomeric ketone, Va, after appropriate manipulation. It forms slightly pink needles, which melt with decomposition. Upon pyrolysis, it gave tetracyclone and styrene. The acid mixture, XX, was isolated after alkaline treatment and after one crystallization from butanol melted at 155–160°.

Upon acidification with hydrochloric acid and crystallization from butanol, the piperidine salt gave an acid, m. p. 155–165° dec.; this was different from the mixed acid above (m. p. 155–160°) for the mixture melted at 140–150° with previous sintering. This mixture of acids was converted to the mixed methyl esters by the procedure already described; only the high-melting ester could be separated in a pure condition.

C. Benzoylated Bridged Ketone, VIII.—When this ketone was treated with ethanolic potassium hydroxide or sodium ethoxide, 2-benzoyl-1,4,5,6-tetraphenyl-1,2,3,4-tetrahydrobenzoic acid, X, was obtained in a yield of 96%; it melts at 291–293° with decomposition.

D. Polynuclear Quinone, XI.—This quinone was suspended in 10% ethanolic potassium hydroxide and refluxed for four hours, added to 200 cc. of water, and boiled a few minutes, after which the solid was filtered; there was no alkali-soluble fraction. The solid was recrystallized several times from trichlorobenzene, after which it melted at 344°; the yield was 70%. Its behavior is identical with that described in the literature.[9]

E. The Carbinol, XIII.—This carbinol, which has no substituents at the bridgeheads, gave a 35% yield of a lactone after three hours of refluxing in 10% ethanolic potassium hydroxide and suitable manipulations. It recrystallized well from acetic acid and from butanol; the latter solvent is preferred. It melts at 250°.

Summary

The reactions of certain phenylated carbonyl bridge compounds with alkaline reagents are described. The bridge is cleaved at one end, so that an acid or its decomposition products result.

ROCHESTER 4, N. Y. RECEIVED DECEMBER 15, 1945

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[12] We are indebted to Dr. Grummitt for all the available addition product, I, and reduced compound, III. Their behavior in the Grignard machine was determined; both showed addition of one mole of reagent without any evolution of gas. Camphorquinone, also examined, showed two additions and no active hydrogen.