organic layer was washed three times with 5% aqueous caustic solution and with water. The 3-ethylcyclohexanone was filtered through filter-aid and dried with anhydrous magnesium sulfate. The yield of light-amber liquid ($n^{20}\text{D}$ 1.4520) was 4268 g. (61%). This product was distilled through the 3-ft. column at a pressure of 34 mm. and 3816 g. (55%) of clear, water-white 3-ethylcyclohexanone was obtained ($n^{20}\text{D}$ 1.4514). A further fractionation of 1300 g. of this latter material in a 6-ft. Podbielniak column (22 mm. diam.) yielded 725 g. of constant refractive index and constant density product for physical constants (m.p. −62.27°, b.p. 193.93°, $d^{20}$ 0.9143 g./ml., $n^{20}\text{D}$ 1.4515).

**1-Benzyl-3-ethylcyclohexanol.**—In a 30-gal. water-cooled, glass-lined reactor, the Grignard reagent from 75 moles (25% excess) of benzyl chloride was condensed with 60 moles of 3-ethylcyclohexanone. After the reaction mixture was hydrolyzed with saturated ammonium chloride solution and the clear ether layer siphoned from the precipitated salts, the ether was allowed to evaporate. The residual ether was removed under vacuum by heating with hot water and 11,107 g. (85% yield) of a yellow, oily liquid was obtained. This product was not purified further.

**Olefins from Dehydration.**—The 1-benzyl-3-ethylcyclohexanol (11,107 g., 50.9 moles) was passed at a rate of 6 ml./min. into a 2.5- by 90-cm. Pyrex column which was packed with 8 to 14 mesh alumina and heated to 250–300°. The alumina was replaced after 2.5-l. of 1-benzyl-3-ethylcyclohexanol had passed through the column. After the water was separated, the product from the dehydration was distilled through the 3-ft. glass column. The material (8385 g.) boiling at 126–140° at 8 mm. was collected. Attempts to separate the individual isomers by fractionation in a 6-ft. Podbielniak column were unsuccessful. The refractive index ($n^{20}\text{D}$ 1.5257–1.5460) and density ($d^{20}$ 0.935–0.941 g./ml.) varied continuously from fraction to fraction. However, dibenzyl was separated in this distillation from the higher-boiling olefins, and the yield of dibenzyl-free olefins was 6433 g. (63%).

**3-Ethyldiphenylmethane.**—Dehydrogenation of 3910 g. of the olefins was accomplished by passing it at a rate of 4 ml./min. into a 2.5- by 90-cm. quartz tube packed with chromia–alumina catalyst and maintained at a temperature of 450–475°. The amber product (3782 g.) was distilled through the 3-ft. column, and the portion distilling at 140–167° at 18 mm. (3197 g.) was fractionated at reduced pressure (3 mm.) in a 6-ft. Podbielniak column. The yield of constant refractive index and constant density 3-ethyldiphenylmethane was 2332 g. (61% based on the amount of olefin dehydrogenated and 17% based on the *m*-ethylphenol). The remainder of the distillation fractions were lower boiling and had lower refractive indices than the desired hydrocarbon. Several of the purest fractions (highest m.p.) of the 3-ethyldiphenylmethane, sufficient to yield the desired 500-ml. quantity, were combined and percolated through silica gel prior to the determination of the final physical properties.

**3-Ethyldicyclohexylmethane.**—A solution of 1209 g. of olefins in an equal volume of methylcyclohexane was mixed with 120 g. of U.O.P. nickel catalyst in a 4.5-l. rocking autoclave and hydrogenated for 15 hours at 200° and an initial pressure of 1400 p.s.i. The solutions from two runs were filtered from the catalyst and the solvent was removed by distillation. The hydrocarbon was distilled *in vacuo* in the 3-ft. column and 2375 g. (94%) of 3-ethyldicyclohexylmethane (b.p. 133–134° at 8 mm., $n^{20}\text{D}$ 1.4753) was obtained. Further purification and separation of isomers was attempted in a 6-ft. Podbielniak column at 2.5 mm. No plateaus of refractive index and density were obtained, and the first 25% (583 g.) and the last 32% (760 g.) of the distilled material were refractionated separately in 6-ft. Podbielniak columns at a pressure of 2 mm. Only the last three fractions (162 g.) of the higher-boiling portion were of constant refractive index and density, and the physical properties listed in Table I were obtained on this material.

CLEVELAND, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY]

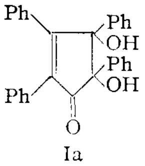
# The Oxidation of Tetracyclone with Nitric Acid

BY PETER YATES AND GEORGE H. STOUT[1]

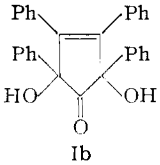
RECEIVED JUNE 1, 1954

The action of nitric acid on tetracyclone in dioxane is shown to yield a 2,3-dihydroxy-2,3,4,5-tetraphenylcyclopent-4-enone as the main product together with smaller amounts of both diastereoisomeric forms of 2,5-dihydroxy-2,3,4,5-tetraphenylcyclopent-3-enone. The structures of the products obtained by further oxidation of these compounds with lead tetraacetate also have been elucidated. The mode of formation and reactions of the compounds are discussed.

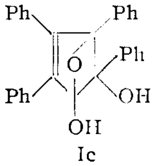
**Introduction.**—During the course of an extensive study of the chemistry of tetracyclone (tetraphenylcyclopentadienone) and related compounds, Dilthey and his school investigated its oxidation with nitric acid.[2,3] Reaction in either acetic acid or dioxane gave a compound $C_{29}H_{22}O_3$ (I), m.p. 191–192° dec. In addition, when acetic acid was the solvent, 3,4,5,6-tetraphenyl-2-pyrone (II) could be isolated from the mother liquor from the crystallization of I.[4] I was shown by the Zerewitinoff method to have two active hydrogen atoms. It could be converted readily by treatment with acid or base, or by heating briefly above the melting point, to 2-benzoyl-3,4,5-triphenylfuran (III). With acetic anhydride in pyridine, it gave a monoacetate which could be converted by the action of hydrogen chloride in methanol to the pyrone II. Both II and III were obtained by heating I with acetic anhydride alone. On the basis of these facts Dilthey concluded that the compound $C_{29}H_{22}O_3$ must be one of the dihydroxytetraphenylcyclopentenones Ia and Ib, or the hemiketal corresponding to Ia, Ic.



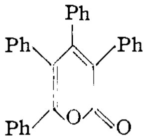
Ia



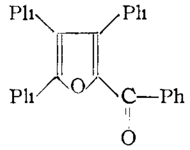
Ib



Ic



II



III

In an attempt to distinguish between these struc-

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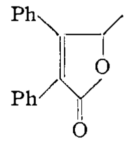
[1] National Science Foundation Predoctoral Fellow, 1953–1954.

[2] R. Pütter and W. Dilthey, (a) *J. prakt. Chem.*, **149**, 183 (1937); (b) **150**, 40 (1937).

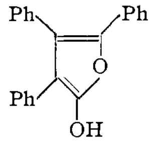
[3] *Cf.* W. Dilthey, S. Henkels and M. Leonhard, *ibid.*, **151**, 97 (1938), for the oxidation of related compounds by other means.

[4] This pyrone was also obtained by peracetic acid oxidation of tetracyclone.

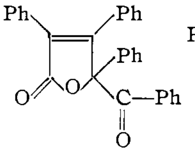
tures he studied the oxidation of I with lead tetraacetate. A colorless product $C_{29}H_{20}O_3$ (IV) was obtained in high yield which was readily hydrolyzed by acid or base to benzoic acid and a compound $C_{22}H_{16}O_2$ (V) shown to be either 4-hydroxy-2,3,4-triphenylcrotonic acid lactone (Va) or its tautomer, 2-hydroxy-3,4,5-triphenylfuran (Vb). IV was, therefore, formulated as having one of the three structures: 4-benzoyl-4-hydroxy-2,3,4-triphenylcrotonic acid lactone (IVa), 2-benzoyl-4-hydroxy-2,3,4-triphenyl-3-butenoic acid lactone (IVb) or 2-benzoyloxy-3,4,5-triphenylfuran (IVc). Originally structure IVc was preferred[2a] on the basis of "the low melting point and ready hydrolysis to V"; subsequently,[2b] either IVa or IVb was considered more likely than IVc since "IV could not be obtained by the action of benzoyl chloride on V."



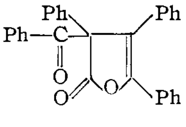
Va



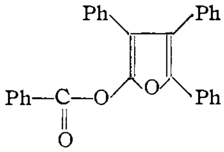
Vb



IVa



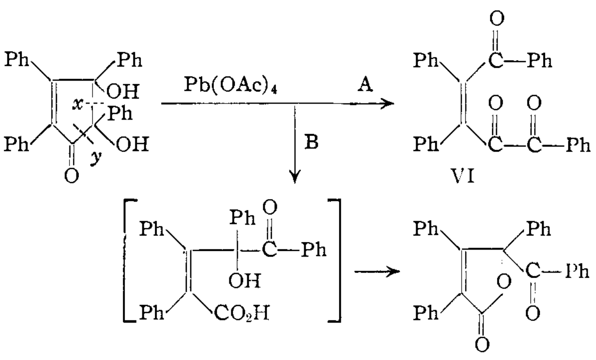
IVb



IVc

Although Dilthey had not established completely the structure of the lead tetraacetate oxidation product, he nevertheless considered that one of its properties enabled him to eliminate Ia as a possible structure for the nitric acid oxidation product I. He argued that Ia on lead tetraacetate oxidation would give the α-diketone VI, which would be colored; since IV was colorless, he concluded that it could not be derived from Ia and that I must, therefore, be represented by the structures Ib or Ic.

Although we considered that the properties of I were in accord with either of the structures Ia or Ib proposed by Dilthey (and also with the less probable structure Ic), his argument for the elimination of Ia appeared to us to rest on two unwarrantable assumptions. First, VI once formed would be isolated as such and would not undergo further reaction to give a colorless product. Second, lead tetraacetate oxidation of Ia would necessarily cleave the bond (*x*) between the carbon atoms bearing the hydroxyl groups leading to the α-diketone VI (path A). The possibility that, due to unfavorable steric factors, cleavage of bond *x* is inhibited and preferential cleavage of the bond between the ketone carbon and that bearing the α-hydroxy group (*y*) occurs cannot be dismissed. Further, such an alternative cleavage would be expected to give rise to IVa by way of the intermediate hydroxyacid VII (path B). We now present the results of a reinvestigation of the structures of the products obtained by the nitric acid oxidation of tetracyclone and their further oxidation products on treatment with lead tetraacetate.



VI

VII

IVa

**2,3-Dihydroxy-2,3,4,5-tetraphenylcyclopent-4-enone.**—Brief treatment of tetracyclone with 65% nitric acid in dioxane on the steam-bath followed by addition to water gave a crude product which on crystallization afforded a compound identical in properties with the compound $C_{29}H_{22}O_3$ (I) described by Dilthey, although in poorer yield. The infrared spectrum of this material in chloroform solution showed a band at 2.80 μ, confirming the presence of one or more hydroxyl groups, and a strong band at 5.86 μ. The presence of this latter band allows the rejection of structure Ic which contains no carbonyl group.[5] Further, its position allows an unequivocal choice between structures Ia and Ib. For Ib contains an unconjugated ketone group in a five-membered ring with an annular β,γ-double bond and would absorb in the neighborhood of 5.7 μ,[6] whereas Ia has an α,β-unsaturated ketone function in a five-membered ring and should absorb in the neighborhood of 5.85 μ.[6,7] Thus the presence of the carbonyl stretching band at 5.86 μ in I shows that it must have structure Ia; in fact, the position of the band is very similar to that reported[8] for the close analog, 2,3,4,5-tetraphenylcyclopent-2-enone (VIII). The ultraviolet spectrum of I is also in accord with this structural designation, showing a maximum at 306 mμ with log ε 4.06.[9]

The nature of the product obtained by lead tetraacetate oxidation of I can also be deduced on the basis of a study of its infrared spectrum. Two bands are present in the carbonyl stretching region at 5.59 and 5.96 μ. Structure IVc is, therefore, untenable since this should show only one carbonyl band—that due to the benzoate function. The band at 5.96 μ can be equated readily with the benzoyl group in either IVa or IVb.[11] The lower band allows a choice between IVa and IVb on the basis of a comparison with the positions of the carbonyl

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(5) The possibility that I might exist as the hemiketal in the solid state and equilibrate to a dihydroxyketone in solution was eliminated by the observation that the infrared spectrum of solid I in Nujol suspension still showed a strong carbonyl band.

(6) *Cf.*, for example, J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

(7) The presence of the β-phenyl group extending the conjugated system might be expected to shift the carbonyl band to longer wave lengths (*cf.* the carbonyl band of anhydroacetonebenzil at 5.90 μ), however, cross-conjugation with the α-phenyl group should effectively oppose this shift.

(8) N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, THIS JOURNAL, **75**, 2283 (1953).

(9) *Cf.* the ultraviolet spectrum of VIII, $\lambda_{max}^{EtOH}$ 295 mμ (log ε 4.13).[8,10]

(10) E. D. Bergmann, *Bull. soc. chim. France*, 703 (1952).

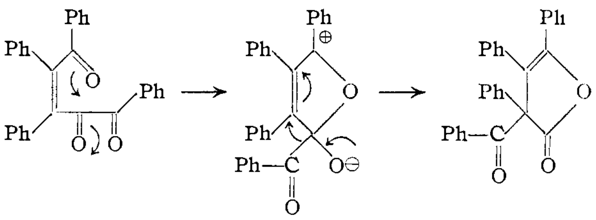
(11) *Cf.* R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

stretching bands in the following compounds[12,13].

| | Infra-red $\lambda_{C=O}$, $\mu$ | Ultra-violet, $\lambda_{\max}^{EtOH}$, m$\mu$ | log $\epsilon$ |
|---|---|---|---|
| 4-Hydroxy-2,2,3,4-tetraphenyl-3-butenoic acid lactone | 5.59 | 280 | 4.110 |
| 4-Hydroxy-2,3,4-triphenylcrotonic acid lactone[14] | 5.71 | 286 | 4.068 |
| 4-Hydroxy-4-methoxy-2,3,4-triphenylcrotonic acid lactone | 5.70 | 293 | 4.024 |

Thus the carbonyl band at 5.59 $\mu$ in the infrared spectrum of IV proves it must be the $\beta,\gamma$-unsaturated lactone IVb and not the $\alpha,\beta$-unsaturated lactone IVa. Possible complicating effects engendered by the presence of the benzoyl group leading to a shift in the position of the carbonyl bands of either (i) IVb or (ii) IVa could be discounted on the following grounds: (i) the position of the lactone carbonyl stretching band of 2-acetyl-4-hydroxybutyric acid lactone (5.64 $\mu$) is essentially the same as that of 4-hydroxyvaleric acid lactone (5.65 $\mu$),[15] showing that an RCO– grouping on the carbon adjacent to the lactone carbonyl affects very little the stretching frequency of the latter; (ii) although the carbonyl stretching bands of ester groups in $\alpha$-acyloxy ketones are displaced to lower wave lengths than those of the corresponding isolated esters, such shifts are always accompanied by concomitant similar shifts of the ketone carbonyl stretching bands[16]; hence, since the higher carbonyl band of IV is at a position characteristic of an isolated benzoyl group,[17] it cannot be argued that the lower band of IV corresponds with the $\alpha,\beta$-unsaturated lactone grouping in IVa displaced to an abnormally low wave length because of the presence of the $\gamma$-benzoyl group. The ultraviolet spectrum of IV showed a maximum at 259.5 m$\mu$ (log $\epsilon$ 4.306), appreciably lower than the ultraviolet maxima of the model compounds listed above. Such changes in the position of maximum absorption in the ultraviolet with the introduction of apparently insulated functional groups have been observed previously.[18,19]

The designation of IVb as the structure of the lead tetraacetate oxidation product of I is not in accord with the cleavage of the ketol linkage (path B, above), but may be rationalized readily on the basis of a reaction scheme involving formation of the triketone VI followed by further reaction to give IVb[19a]



VI IVb

**2,5-Dihydroxy-2,3,4,5-tetraphenylcyclopent-3-enones.**—From the mother liquor from the crystallization of I was obtained material which yielded on fractional crystallization from several solvents a *second substance*, IX, m.p. 226–227.5°, and a *third substance*, X, m.p. 201–202° dec. The composition of both IX and X, $C_{29}H_{22}O_3$, showed them to be isomeric with I. Their infrared spectra showed in both cases an hydroxyl band at 2.81 $\mu$ and a strong carbonyl band at 5.67 $\mu$, but significant differences in the region 7–12 $\mu$. Compound X was shown to contain two active hydrogen atoms by the Zerewitinoff method. It appeared, therefore, very likely that we now had in hand for the first time the two stereoisomeric forms of 2,5-dihydroxy-2,3,4,5-tetraphenylcyclopent-3-enone (Ib), the carbonyl stretching frequency being close to that expected for a $\beta,\gamma$-unsaturated cyclopentenone.[6] Again the ultraviolet spectra (IX, $\lambda_{\max}^{EtOH}$ 255 m$\mu$ (log $\epsilon$ 4.162); X, $\lambda_{\max}^{EtOH}$ 254 m$\mu$ (log $\epsilon$ 4.125) (were of little diagnostic value owing to the lack of suitably close analogs.[20]

These structures were confirmed by subjecting both IX and X to lead tetraacetate oxidation. Each gave the same product, XI, $C_{28}H_{20}O_2$, m.p. 211–212°. This showed a very strong band in its infrared spectrum at 6.03 $\mu$ and had an ultraviolet spectrum identical with that recorded[21] for *cis*-dibenzoylstilbene, with whose properties the other properties of XI are in consonance and with an authentic sample of which it gave no depression of m.p. The formation of *cis*-dibenzoylstilbene is readily explicable in terms of the structure Ib for IX and X.

An attempt to convert Ia into either IX or X by treatment with a dilute solution of hydrochloric

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(12) We are greatly indebted to Professor H. H. Wasserman, Yale University, who supplied us with samples of these compounds (work to be published shortly).

(13) The positions of these bands in the infrared spectrum were calibrated with the water vapor spectrum as were all other carbonyl bands measured during the course of this work. The spectra were taken in chloroform solution on a Perkin–Elmer model 21 spectrophotometer.

(14) This compound proved to be identical with the product V obtained by hydrolysis of IV, thus eliminating the furan structure Vb.

(15) R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

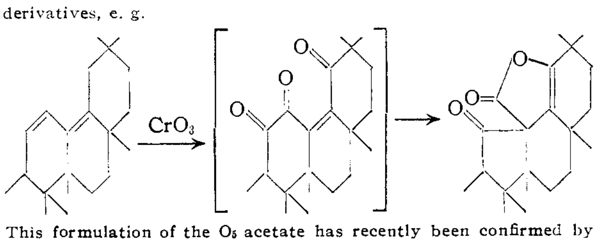
(16) *Cf.*, for example, R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, *ibid.*, **70**, 2024 (1948).

(17) The magnitude of the expected shift in the case of a benzoyl group is illustrated by the positions of the upper carbonyl bands of $\alpha$-benzoyloxyacetophenone and $\alpha$-phenylacetoxyacetophenone, *viz.*, 5.85 $\mu$ in each case.

(18) *Cf.*, for example, W. B. Bennet and A. Burger, THIS JOURNAL, **75**, 84 (1953).

(19) Graphic analysis demonstrated that the ultraviolet absorption curve of IV did not correspond to a simple superimposition of a band in the region of 280 m$\mu$ and a band attributable to an isolated benzoyl group.

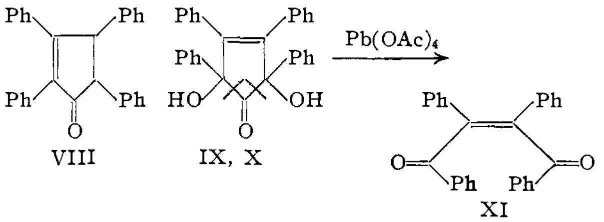
(19a) NOTE ADDED IN PROOF.—Professor R. B. Woodward has pointed out (private communication) that the mechanism here proposed is similar to that which he has advanced for the formation of the so-called $O_5$ acetate obtained by the oxidation of various $\beta$-amyrin derivatives, e. g.



This formulation of the $O_5$ acetate has recently been confirmed by L. C. McKean and F. S. Spring, *J. Chem. Soc.*, 1989 (1954).

(20) The compound claimed by F. R. Japp and G. D. Lander, *J. Chem. Soc.*, **71**, 123 (1897), to be 3,4-diphenylcyclopent-3-enone almost certainly does not have this structure and will be the subject of a further communication.

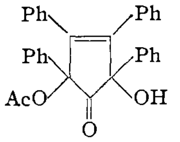
(21) L. P. Kuhn, R. E. Lutz and C. R. Bauer, THIS JOURNAL, **72**, 5058 (1950).



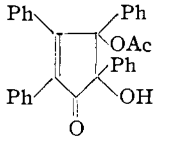
VIII IX, X XI

acid in dioxane gave no evidence of this transformation; the only product isolated was 2-benzoyl-3,4,5-triphenylfuran (III).

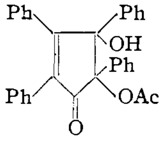
**The Monoacetate of Ia; Furan and Pyrone Formation from Ia.**—Dilthey prepared a monoacetate of Ia by treatment with acetic anhydride in pyridine for several days followed by heating on the steam-bath; he assigned to it the structure XII on the basis of his formulation of I as Ib. We have repeated this preparation and also have found that the same compound may be obtained more expeditiously by direct heating of Ia with acetic anhydride and pyridine for several hours. The product, XIII, has been shown by the Zerewitinoff method to contain one active hydrogen only, confirming its designation as a monoacetate. Its infrared spectrum shows a strong band at 5.83 μ with no sharp band in the 2.8–3.1 μ region. Its ultraviolet spectrum ($\lambda_{\max}^{\mathrm{EtOH}}$ 308 mμ (log $\epsilon$ 4.06)) is very similar to that of Ia. This affords strong evidence that no allylic rearrangement has occurred during the course of acetylation to give a compound of structure XII and that the monoacetate must be either XIIIa or XIIIb.



XII



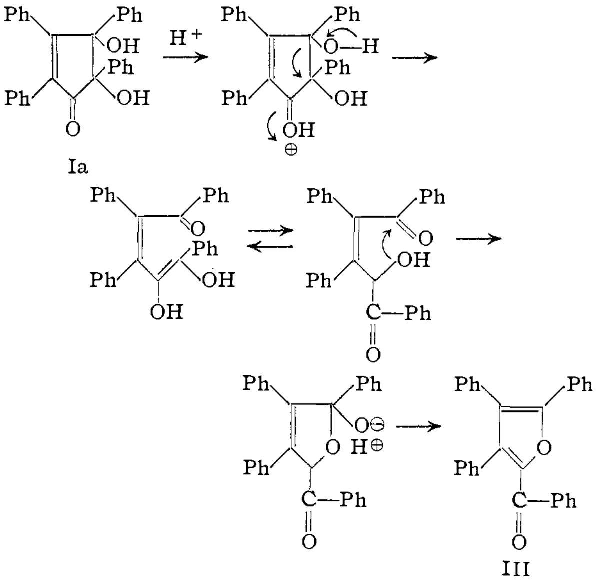
XIIIa



XIIIb

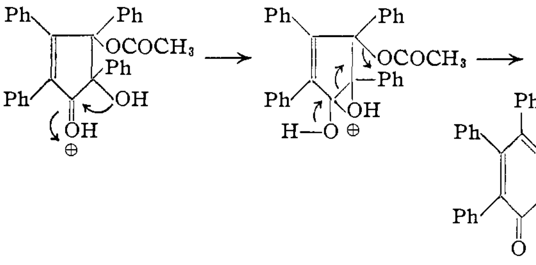
Further, a tentative choice may be made in favor of XIIIa on the following basis. The single strong band at 5.83 μ must represent an overlapping of the acetate and ketone carbonyl stretching bands. As discussed above, it has been observed that an α-acyloxy ketone has both of its carbonyl stretching bands displaced to lower wave lengths compared with the corresponding bands of analogous isolated acyloxy and ketone groups; thus the saturated ketone and ester carbonyl stretching bands of 4-pregnene-21-ol-3,20-dione acetate are at 5.77 and 5.69 μ, respectively, whilst the corresponding ketone band of progesterone is at 5.86 μ and the ester band of steroids with isolated acetate groups is at 5.75 μ.[16,22] The fact, therefore, that the combination carbonyl band of XIII is at the position expected for the superimposition of the carbonyl band of Ia and a normal acetate band indicates that it is not the α-acetoxy ketone XIIIb but possesses the structure XIIIa.

Such an interpretation of the structure of XIII leads to a ready explanation of the fact that whilst Ia is rearranged by acid to the furan III, XIIIa gives the pyrone II on treatment with hydrogen chloride. The formation of III may be represented as



Ia III

Whereas, in the case of XIIIa, the acetylation of the β-OH prevents the reverse aldol reaction and leads to an alternative course[23]



II

**Stereochemistry, Mode of Formation.**—The results of an attempt to gain insight into the *cis* or *trans* relationship of the pairs of hydroxyl groups in I, IX and X by a study of the effect of these substances on the acidity of boric acid solutions[24] were inconclusive. Although a large effect was noted in the case of I, a small effect with IX and no effect with X, the *p*H of the latter two solutions sank on standing and the infrared spectra of material recovered from all the solutions indicated in every case that chemical change had occurred, thus vitiating the results. One piece of evidence is available, however, which makes it possible to make a provisional assignment of the *cis* configuration for Ia. Its cleavage with lead tetraacetate at the glycol bond (*x*) to give IVb rather than at the ketol bond (*y*) to give IVa makes it likely that the glycol has the configuration favorable for cleavage; *i.e.*, the hydroxyl groups are *cis*.[25]

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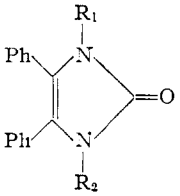
[22] Since *both* carbonyl bands are shifted to shorter wave lengths, this effect must be attributed to a mutual interaction of dipoles through space rather than to an inductive effect.

[23] *Cf.* the analogous formation of isocoumarins in the 2,3-diphenylinden-1-one series: C. F. H. Allen and J. W. Gates, THIS JOURNAL, **65**, 1230 (1943). The formation of an isobenzofuran, analogous to the production of III, has been reported in this series only under basic conditions.

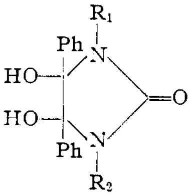
[24] *Cf.* F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, P. N. Gordon, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *ibid.*, **75**, 5455 (1953).

[25] *Cf.* W. A. Waters in H. Gilman, "Organic Chemistry," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 1190.

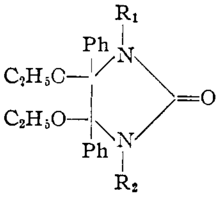
This assignment is concordant with the stereochemistry that may be deduced for the only other recorded cases of 1,2-glycol formation by the action of nitric acid.[26] Biltz[27] treated several imidazolones of the type XIV with nitric acid in acetic acid obtaining glycols of the type XV; in one case ($R_1 = R_2 = CH_3$) he established that the product obtained was identical with that obtained by oxidation with aqueous potassium permanganate. The latter reagent is known ordinarily to give *cis*-glycols[28] and thus nitric acid appears to have effected *cis*-hydroxylation. This view is corroborated by the fact that Biltz found that the action of nitric acid in ethanol yielded diethoxy compounds XVI which, since they were irreversibly converted in boiling ethanol to isomeric diethoxy compounds, must have had the less stable stereochemical configuration and hence have been the result of *cis* addition.



XIV

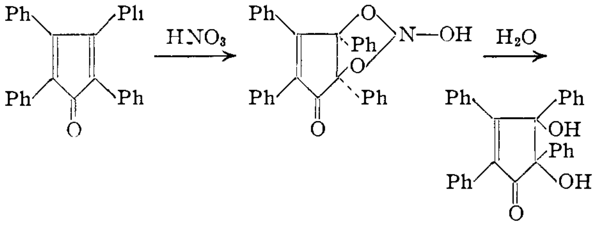


XV



XVI

On the basis of the *cis* configuration for Ia and the formation of diethoxy compounds in the case of the reactions in alcohol studied by Biltz, the formation of 1,2-glycols *via* epoxides may be ruled out. A reasonable hypothesis involves the formation of a cyclic intermediate followed by hydrolysis (or ethanolysis in the case of the reactions in ethanol), *e.g.*[29]



*cis*-Ia

Preliminary attempts have been made to extend this reaction to other ethylenic compounds. Benzalacetophenone and dibenzalacetone were recovered unchanged after treatment with nitric acid in dioxane either on the steam-bath or under reflux. Benzalacetophenone was unchanged by refluxing with nitric acid in acetic acid. Stilbene was unaffected by treatment with nitric acid in dioxane on the steam-bath but reacted when the solution was heated to boiling giving a nitrogen containing product whose infrared spectrum indicated it to be a nitro nitrate[30]; it has not been investigated further.

## Experimental

**Oxidation of Tetracyclone.** (i) **2,3-Dihydroxy-2,3,4,5-tetraphenylcyclopent-4-enone (Ia).**—Tetracyclone (15.0 g.) in dioxane (30 ml.) was heated on the steam-bath and a solution of 65% nitric acid (2.7 ml.) in dioxane (4.5 ml.) was added. After heating had been continued for several minutes, the solution began to boil and its color very rapidly changed from deep red to pale yellow. It was then added to a large volume of cold water giving a yellow gummy mass which was washed thoroughly with water by trituration and decantation, when it solidified. Crystallization of the crude product from dioxane–methanol gave 3.6 g. of Ia, m.p. 188–190° dec. Addition of methanol to the mother liquor gave a further 1.8 g. of less pure Ia which on washing with a small amount of acetone yielded 1.4 g. of pure Ia; total yield of pure material 5.0 g. (31%); other similar preparations of Ia gave yields varying from 30 to 40%. A sample twice-recrystallized from benzene–ligroin gave small needles, m.p. 190–191° dec. (Pütter and Dilthey[2a] give m.p. 191–192° dec.); infrared spectrum ($CHCl_3$), bands at 2.80 and 5.86 μ; ultraviolet spectrum (95% EtOH), $\lambda_{max}$ 306 mμ (log ε 4.06).

(ii) **2,5-Dihydroxy-2,3,4,5-tetraphenylcyclopent-3-enones (IX, X).**—The mother liquor remaining after the removal of the two crops of Ia was evaporated to remove most of the methanol. On addition of acetone 0.38 g. of IX, m.p. 225.5–227°, was deposited; on concentration of the solution a further 0.16 g. of IX, of similar m.p., was obtained; total yield of IX 0.54 g. (3.25%). Two recrystallizations from isopropyl alcohol gave fluffy balls of needles, m.p. 231.2–231.8°; infrared spectrum ($CHCl_3$), bands at 2.81 and 5.67 μ; ultraviolet spectrum (95% EtOH), $\lambda_{max}$ 255 mμ (log ε 4.162).

*Anal.* Calcd. for $C_{29}H_{22}O_3$: C, 83.23; H, 5.30. Found: C, 82.90; H, 5.40.

The mother liquor remaining after the removal of the two crops of IX was freed of dioxane by adding water in excess, extracting with benzene and washing the benzene extract with water. The extract was dried and concentrated. Addition of petroleum ether and cooling led to the deposition of 2.13 g. of solid. This was crystallized from benzene to give 1.61 g. (9.9%) of X, m.p. 191–193° dec.[31] Several recrystallizations from both aqueous methanol and benzene gave cubes, m.p. 201–202° dec.; Zerewitinoff determination: Calcd. for 2 active H: 12.05 ml. $CH_4$. Found: 11.15 ml. $CH_4$. Infrared spectrum ($CHCl_3$), bands at 2.81 and 5.67μ; ultraviolet spectrum (95% EtOH), $\lambda_{max}$ 254 mμ (log ε 4.125).

*Anal.* Calcd. for $C_{29}H_{22}O_3$: C, 83.23; H, 5.30. Found: C, 82.94; H, 5.40.

**Lead Tetraacetate Oxidation of Ia. 2-Benzoyl-4-hydroxy-2,3,4-triphenyl-3-butenoic Acid Lactone (IVb).**—Ia was oxidized with lead tetraacetate in pyridine–acetic acid in the manner described by Pütter and Dilthey.[2a] The product was obtained as needles, m.p. 110.5–112° (Pütter and Dilthey give m.p. 114°); infrared spectrum ($CHCl_3$), bands at 5.59 and 5.96 μ; ultraviolet spectrum (95% EtOH), $\lambda_{max}$ 259.5 mμ (log ε 4.306).

**Lead Tetraacetate Oxidation of IX and X.** ***cis*-Dibenzoylstilbene.**—X (0.21 g.) was ozidized with lead tetraacetate (0.25 g.) in pyridine-acetic acid as above. After standing for 21 hours the crystalline deposit was filtered and washed with a little hot water giving 0.155 g. (80%) of crude *cis*-dibenzoylstilbene, m.p. 200–206°. Recrystallization from ethanol yielded 0.100 g. (51%) of needles, m.p. 211.5–212°, undepressed by admixture with an authentic sample prepared by the nitric acid oxidation of tetraphenylfuran[29]; infrared spectrum ($CHCl_3$), band at 6.03 μ; ultraviolet spectrum (95% EtOH), $\lambda_{max}$ 256 mμ (log ε 4.45).

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[26] In addition to the cases here cited, Simonsen and Owen have proposed that a glycol is formed as the first step in the nitric acid oxidation of camphene to ketopinic acid, but this has not been confirmed experimentally: "The Terpenes," Vol. II, Second Edition, Cambridge University Press, 1949, p. 302.

[27] H. Biltz, *Ann.*, **368**, 156 (1909).

[28] *Cf.* W. A. Waters, ref. 24, p. 1212.

[29] The preparation of *cis*-dibenzoylstilbene by the nitric acid oxidation of tetraphenylfuran, N. Zimin, *J. prakt. Chem.*, **101**, 160 (1867), may be formulated as involving the formation of a similar cyclic intermediate followed by loss of nitrous acid.

[30] *Cf.* C. E. Anagnostopoulos and L. F. Fieser, THIS JOURNAL, **76**, 532 (1954).

[31] Although the m.p. of this material is some 10° lower than that recorded for the analytical sample, the infrared spectrum was essentially identical with that of the analytical sample. The absence of any Ia also is shown by the fact that no coloration occurs on decomposition at the melting point whilst Ia gives an intense red color on melting.

*Anal.* Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.09; H, 5.43.

Similar oxidation of X (0.100 g.) gave 0.060 g. (65%) of product, m.p. 210.5–211.5°, undepressed by admixture with the product from IX and with identical spectral properties.

**Attempted Conversion of Ia to IX and X.**—Ia (0.50 g.) was dissolved in dioxane (25 ml.) and two drops of concentrated hydrochloric acid were added. The solution was heated on the steam-bath and samples were removed after 3, 9, 18 and 36 hours. Infrared spectroscopic examination of the material from these samples showed that although extensive changes were occurring no IX or X was formed. After 57 hours the solution was poured into excess water and the mixture extracted with ether. The extract was dried and freed of solvent yielding an oil which solidified on trituration with ethanol. Crystallization from ethanol gave very pale yellow plates, m.p. 166.5–167°; infrared spectrum band at 6.09 μ. This was shown to be 2-benzoyl-3,4,5-triphenylfuran by direct comparison with a sample obtained by heating Ia above its melting point for five minutes[2a] (Pütter and Dilthey[2a] give m.p. 166° for this compound). Attempts to obtain other crystalline products from the crude reaction mixture were unsuccessful.

**Monoacetate of Ia (XIII).**—Ia (1.5 g.) was dissolved in a mixture of pyridine (20 ml.) and acetic anhydride (10 ml.) and the solution was heated on the steam-bath for 3 hours. It was then poured into excess cold water when a sticky brown tar separated. This solidified on washing with water by trituration and decantation. The solid was taken up in methanol and was partially precipitated as a dark tar by addition of water. The solution was decanted and treated twice in the cold with Norit. By treating the hot solution with water and cooling very slowly, there was obtained 0.30 g. of pale yellow crystals, m.p. 137–142°. The dark tar which had separated from the original aqueous methanol solution was crystallized from aqueous methanol using the same technique with seeding. The further 0.10 g. of crystalline material thus obtained was combined with the 0.30 g. of crystals and the combined product was crystallized from ether–petroleum ether. There was thus obtained 0.31 g. of a crystalline powder, m.p. 142–144°; by working up all the mother liquors an additional 0.13 g. of product of similar m.p. was obtained; total yield 0.44 g. (27%). On recrystallization from aqueous methanol and from ether–petroleum ether, the acetate was obtained as microcrystals, m.p. 144.2–145.2° (Pütter and Dilthey[2a] give m.p. 145°). Zerewitinoff determination: Calcd. for 1 active H: 5.5 ml. $CH_4$. Found: 4.4 ml. $CH_4$. Infrared spectrum ($CHCl_3$), band at 5.83 μ; ultraviolet spectrum (95% EtOH) $\lambda_{max}$ 308 mμ (log ε 4.06).

*Anal.* Calcd. for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25. Found: C, 80.54; H, 5.51.

**Boric Acid Acidity Measurements.**—Solutions containing 0.1 millimole of Ia, IX and X in 5-ml. portions of a 0.500 *M* solution of boric acid in methanol were made up. To each of these solutions and to 5 ml. of the boric acid solution was added 1 ml. of water and the *p*H of the resulting solutions was measured with a glass electrode using a Coleman *p*H meter. The following data were obtained:

| | *p*H | *p*H after standing overnight |
|---|---|---|
| Ia | 3.01 | 3.01 |
| IX | 4.72 | 3.50 |
| X | 4.63 | 3.94 |
| Blank | 4.72 | 4.74 |

After standing overnight Ia, IX and X could not be recovered from their solutions: the infrared spectra of the recovered materials differed considerably from those of the starting materials.

**Action of Nitric Acid on Other Unsaturated Compounds.**—Benzalacetophenone, dibenzalacetone and stilbene were each treated with nitric acid in dioxane under identical conditions to those used for the nitric acid oxidation of tetracyclone. In every case the starting material was recovered quantitatively. When the reactions mixtures containing benzalacetophenone and dibenzalacetone were boiled under reflux for ten minutes, the starting materials were still recovered in 92–99% yield. On heating the stilbene solution to boiling for ten minutes, reaction did occur and on working up the mixture in the usual manner a crystalline, nitrogenous product was obtained, infrared spectrum bands at 6.05 and 6.40 μ.

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# The Application of the Principle of Vinylogy to the Chemistry of γ-Pyrone Derivatives

BY ALEXANDER SCHÖNBERG, MAHMOUD MOHAMED SIDKY AND GAMIL AZIZ

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Whether aromatic thioketones containing the group $-\overset{S}{\overset{\|}{C}}-CH_3$ will undergo condensations of the aldol type cannot be determined directly, because of the sensitivity of these compounds toward alkali and their tendency to polymerize; however, it was found that the methyl group in 2-methyl-4-thiochromones, which may be regarded as vinylogs of the above thioacetyl compounds condenses with aromatic aldehydes as well as with aromatic nitroso compounds in the presence of a base to form 2-styryl-4-thiochromones and nitrons, respectively. The thermoinstability of 2,6-diphenyl-4-thiopyrone and the easy hydrolysis of the methoxy group in visnagin are discussed in the light of the principle of vinylogy.

No condensation of the aldol type with thioketones containing $CH_3-\overset{S}{\overset{\|}{C}}-$ have been reported, probably due to the instability of such substances, thus thioacetophenone readily forms a trimer as does thioacetone. To determine whether the group $CH_3-\overset{S}{\overset{\|}{C}}-$ in thioketones is capable of condensing with aromatic aldehydes in the presence of a base, the vinylogs of these compounds were investigated. The principle of vinylogy[1] gives an explanation for the condensation of 2-methylchromone[2] and 2,3-dimethylchromone[3] with aromatic aldehydes, *e.g.*, benzaldehyde, since both chromones may be regarded as vinylogs of Ar–CO–$CH_3$.

We have found that 2-methyl-4-thiochromone (I), 2,3-dimethyl-4-thiochromone (II) and 2,3-

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(1) R. C. Fuson, *Chem. Revs.*, **16**, 1 (1935).

(2) U. Cheema, K. Gulati and K. Venkataraman, *J. Chem. Soc.*, 925 (1932).

(3) I. Heilbron, H. Barnes and R. Morton, *ibid.*, 123, 2559 (1923).