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STUDIES ON CYCLIC *vic*-POLYKETONES—II

REACTION OF CYCLOPENTENTRIONES WITH BENZENE

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Abstract—The acid catalyzed reaction of several 1,2-di-substituted cyclopenten-3,4,5-triones with benzene is examined. It is found that the substituents on the cyclopentene ring affect the reaction pathway and the structure of the products. When the both substituents are C_6H_5 or CH_3O, they react only at their central CO group to give 1,2-di-substituted-4,4-diphenylcyclopenten-3,5-diones. When the substituents are OH (croconic acid), condensation with three molar equivalents of benzene occurs to give 1,4,4-triphenyl-2-hydroxycyclopenten-3,5-dione. In this reaction, the intermediacy of 2-hydroxy-1-phenylcyclopenten-3,4,5-trione and the 1,4-diphenyl-allyl cation **16** is proposed. When the substituents are piperidyl, the compound does not condense with benzene, but rearranges intramolecularly to give 1,3-di-piperidylcyclopenten-2,4,5-trione.

MANY aldehydes and ketones are known to condense with benzene or its derivatives in the presence of acidic catalysts to give *gem*-diaryl compounds.[1] Several vicinal polyketones, such as triketohydrindene, alloxane, and diethyloxomalonate, are reported to undergo the same type of condensation only at their central CO groups.[2]

The cyclopenten-3,4,5-triones synthesized and characterized in our previous paper[3] are expected to undergo this type of condensation. In order to investigate the effect of substituents attached to the cyclopentene system, the acid catalyzed condensation of 1,2-disubstituted cyclopenten-3,4,5-triones with various aromatics was carried out. In addition, the preparation of a structurally interesting cyclopentantetrone using the condensate as a synthetic intermediate was attempted.

RESULTS AND DISCUSSION

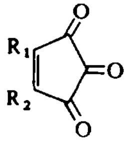
1,2-Diphenylcyclopenten-3,4,5-trione **1** was reacted with benzene in the presence of concentrated sulfuric acid at room temperature. The yellow crystalline condensation product was identified as 1,2,4,4-tetraphenylcyclopenten-3,5-dione **2** (m.p. 189–189·5°, 76%) by UV and IR spectral methods and elemental analysis. It showed IR bands at 1700 and 1740 cm^{-1}, which are characteristic of 5-membered cyclic 1,4-enediones.

2-Hydroxy-1-phenylcyclopenten-3,4,5-trione **3** gave 2-hydroxy-1,4,4-triphenylcyclopenten-3,5-dione **4** (m.p. 191·5°, 82%). The structure of **4** was confirmed by its IR and UV spectra, and by its alkaline degradation products. Its IR spectrum showed two carbonyl bands at 1745 and 1680 cm^{-1}. Its UV spectra exhibited an absorption maxima at 241 nm ($\log \varepsilon = 4{\cdot}28$) and 333 nm ($\log \varepsilon = 4{\cdot}03$) in ethanol. These resemble the spectroscopic properties of 1-hydroxy-2-phenylcyclopenten-3,5,dione [$\nu_{C=O}$, 1741 and 1680 cm^{-1}, λ_{max} in ethanol ($\log \varepsilon$): 234 (4·09), 318 nm (4·06)], in these regions. The presence of an enolic OH group in **4** was ascertained by the formation of a mono acetate which showed a CO band at 1785 cm^{-1}. Alkaline degradation of **4** gave 1,3,3-triphenylacetone.

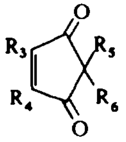
Croconic acid **5** (1,2-dihydroxycyclopenten-3,4,5-trione) condensed with three molecules of benzene to give **4**. Dimethylcroconate **6** gave 1,2-dimethoxy-4,4-diarylcyclopenten-3,5-diones **7a** (m.p. 126·5°), **7b** (m.p. 123–124°), in low yield on heating in benzene or toluene in the presence of phosphorus pentoxide.

1,2-Dipiperidylcyclopententrione **8**, which is a triketone having strong electron donating substituents, did not yield the expected product **17**. But neutralization of the reaction mixture with sodium bicarbonate followed by column chromatography on silica gel gave a red crystalline product **9** (21%), the sodium salt of 2-hydroxy-1-piperidylcyclopenten-3,4,5-trione **10**, and the starting material **8**.

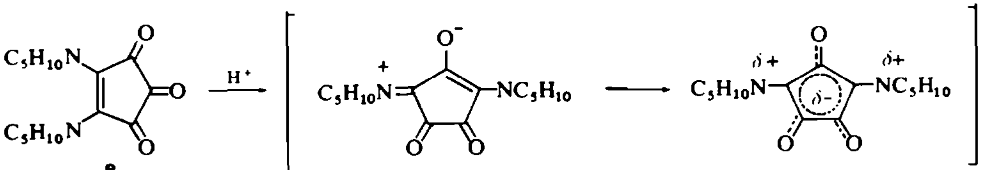
Compound **9** (m.p. 185–185·5°) was isomeric with **8** and was identified as 1,3-dipiperidylcyclopenten-2,4,5-trione on the basis of spectral properties. The CO absorption bands of **9** (1700, 1640, and 1560 cm^{-1}) are of lower frequency than those of **8** (1713, 1673, and 1616 cm^{-1}) and its UV spectrum (λ_{max} in EtOH at 439 nm, log $\varepsilon = 4·54$) is quite similar to those of the aromatic oxocarbon anions $C_nO_n^{2-}$ (n = 4,5,6).[4] In NMR, **9** showed two multiplets at 8·20 (12H) and 5·5 τ (8H), while **8** showed peaks at 8·27 (12H) and 6·25 τ (8H). The lower shift of the protons in **9** relative to those in **8** is explicable if the compound **9** has a mesoionic structure and has more positive charge on nitrogen than the triketone **8**.



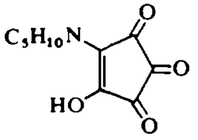
1: $R_1 = C_6H_5, R_2 = C_6H_5$
3: $R_1 = OH, R_2 = C_6H_5$
5: $R_1 = R_2 = OH$
6: $R_1 = R_2 = OCH_3$



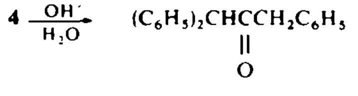
2: $R_3 = R_4 = R_5 = R_6 = C_6H_5$
4: $R_3 = R_5 = R_6 = C_6H_5, R_4 = OH$
7a: $R_3 = R_4 = OCH_3, R_5 = R_6 = C_6H_5$
7b: $R_3 = R_4 = OCH_3, R_5 = R_6 = C_6H_4CH_3$
11: $R_3 = R_5 = R_6 = C_6H_4Cl, R_4 = OH$
12: $R_3 = R_4 = OH. R_5 = R_6 = C_6H_5$
17: $R_3 = R_4 = C_5H_{10}N, R_5 = R_6 = C_6H_5$



8 **9**



10



$$4 \xrightarrow[H_2O]{OH^-} (C_6H_5)_2CH\overset{\displaystyle O}{\overset{\|}{C}}CH_2C_6H_5$$

The sodium salt of **10** (dark brown above 215° without melting) has carbonyl bands at 1700 and 1520 cm^{-1} and its UV absorption maxima (in MeOH) at 398 nm. An attempt to make the free enol **10** was unsuccessful because of the further hydrolysis.

From these experimental results, it is clear that in the condensation of cyclopententrione with benzene, the substituent not only affects the reactivity of the CO groups but also changes the course of the reaction. It appears that electron donating substituents prevent the condensation. 1,2-Dipiperidylcyclopenten-3,4,5-trione, **8**, which has the strongest electron donating substituents in this series does not give the expected condensate due to the decreased reactivity of the CO group caused by the strong electron donation from the substituents.

The rearrangement of 1,2-dipiperidylcyclopententrione **8** to the 1,3-isomer **9** occurs in the absence of benzene, simply by treating the triketone **8** with concentrated sulfuric acid.* Neither dipiperidinium croconate nor piperidinium salt of **10** gave the 1,3-bis-amide **9** by the analogous treatment. An excess of diethylamine present in the reaction mixture had no effect on the formation of **9**. Therefore, this rearrangement is intramolecular and the alternative bimolecular processes involving acidic hydrolysis of the C–N bond of **8** by the water contained in sulfuric acid and condensation of the resulting croconate and piperidine is ruled out. The triketone **8** showed an absorption max at 347 nm (log $\varepsilon = 4{\cdot}13$) in 95% sulfuric acid. But after the solution stood at room temperature 19 hr, this absorption max shifted to 327 nm (log $\varepsilon = 4{\cdot}35$). When the solution was diluted to 70% sulfuric acid concentration, this max disappeared and new maxima appeared at 305 and 365 nm. These new maxima are close to the absorption maxima of **9** (λ_{max} 300 nm, log $\varepsilon = 4{\cdot}10$, and 357 nm, log $\varepsilon = 3{\cdot}90$) in sulfuric acid. From these observations, it seems reasonable to assume that the intermediate in the rearrangement which has an absorption max at 327 nm in sulfuric acid gave **9** and **10** when the solution was neutralized. Unfortunately, further details of this rearrangement have not yet been made clear.

The reaction of croconic acid gave a compound with three benzene groups. If the first and second attacks of benzene took place on the same carbon atom of croconic acid, the intermediate, 1,2-di-hydroxy-4,4-diarylcyclopentene-3,5-dione **12**,[6] would be a very convenient precursor for the systhesis of cyclopentantetrones.

Attempts to stop the reaction at intermediate **12** were unsuccessful. Reaction of croconic acid 5 with 1–3 equivalent of benzene afforded only small amounts of **4** and almost all of croconic acid was recovered. The reaction with a less reactive aryl compound such as chlorobenzene afforded the same type of condensation product **11** (m.p. 188·5–190·5°). A very inert compound such as nitrobenzene did not react.

The reaction of **5** to yield **4** may occur in one of two ways either by Michael type attack at C_1 or by attack at the central CO (C_4). Tetrahydroxy-*p*-benzoquinone and 1,2-dihydroxy-4,4-diphenylcyclopenten-3,5-dione **12** might be expected to react in a Michael fashion, but were found to be unreactive under the reaction conditions. Therefore, **12** is ruled out as an intermediate. Attack by benzene on the central CO giving 2-hydroxy-1-phenylcyclopenten-3,4,5-trione **3** is most reasonable, since **3** afforded the same product **4**, when reacted with benzene. This point was further investigated by reacting substituted benzenes with **3**. 2-Hydroxy-1-phenylcyclopenten-3,4,5-trione **3** was warmed to 110° in anisol for one hour in the presence of *p*-toluene-

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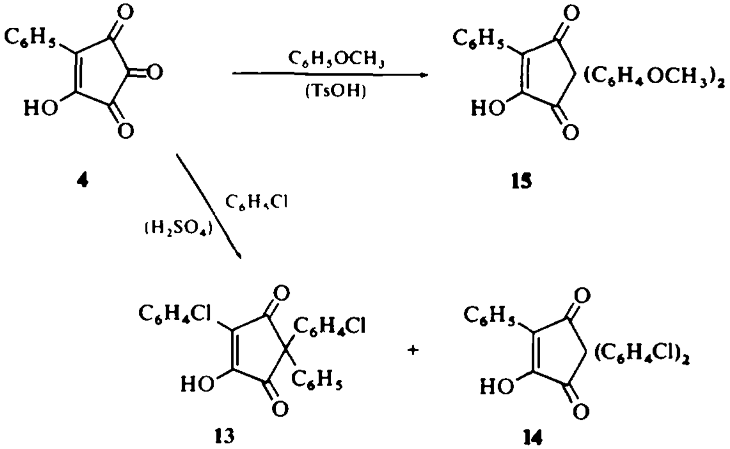
* A similar rearrangement of a polyketone amide is reported for a 1,2-bis-squarate.[5] The mechanism proposed involved hydrolysis of the squarate and through re-condensation of the resulting compounds.



4

15

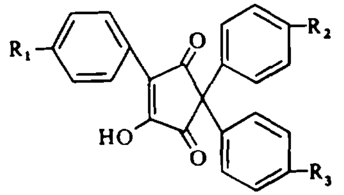
13
(32%)

14
(10%)

sulfonic acid to give 4,4-di-*p*-anisyl-2-hydroxy-1-phenylcyclopenten-3,5-dione **15** (m.p. 154–155°, 67%). Reaction of **3** with chlorobenzene in the presence of sulfuric acid afforded two yellow crystalline products (m.p. 142·5–143°, 32%) and (m.p. 164–165·5°, 10%). From comparison of their UV and NMR spectra with those of other 2-hydroxy-1,4,4,-triarylcyclopenten-3,5-diones, these products were assigned the structure **13**, 1,4-di-*p*-chlorophenyl-2-hydroxy-4-phenylcyclopenten-3,5-dione, and **14**, 4,4-di-*p*-chlorophenyl-2-hydroxy-1-phenylcyclopenten-3,5-dione, respectively.

UV absorption maxima of 2-hydroxy-1,4,4-triarylcyclopenten-3,5-diones are listed in Table 1. The absorption maxima of **13** (330 nm in acidic and 364 nm in basic media)

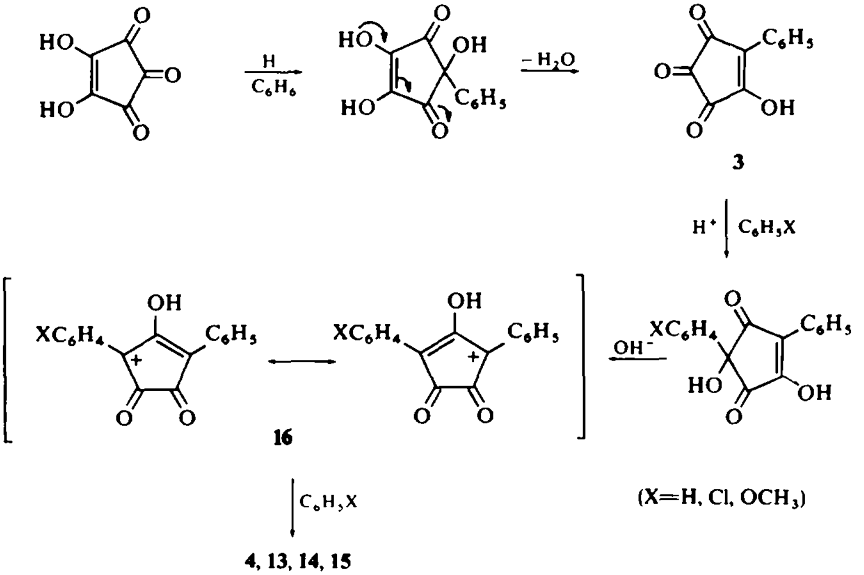
TABLE 1. UV SPECTRA OF 2-HYDROXY-1.4.4-TRIARYLCYCLOPENTENE-3.5-DIONES



Compound	R_1	R_2	R_3	(in EtOH) (neutral)		(acidic)	(basic) nm (log ε)	
4	H	H	H	275 333	(4·03) (4·03)	241 (4·32) 326 (4·17)	275 362	(4·28) (4·08)
11	Cl	Cl	Cl	284 355	(4·17) (4·02)	247 (4·30) 330 (4·15)	283 364	(4·38) (4·20)
13	Cl	H	Cl	283 350	(4·12) (3·90)	248 (4·32) 330 (4·17)	282 364	(4·42) (4·22)
14	H	Cl	Cl	280 342	(4·00) (3·90)	240 (4·28) 328 (4·09)	275–280 363	(4·28) (4·03)
15	H	OCH_3	OCH_3	264–276 327	(4·00) (4·03)	284 (3·81) 323 (4·14)	276 360	(4·37) (4·12)

are approximately in the same region as those of 1,4,4-tri-*p*-chlorophenyl-2-hydroxycyclopenten-3,5-dione **11**. But, these are of longer wave length by 2–7 nm than those of **14** (328 nm in acidic and 363 nm in basic media), 2-hydroxy-1,4,4-triphenylcyclopenten-3,5-dione **4** (326 nm in acidic and 362 nm in basic media), and 4,4-di-*p*-anisyl-2-hydroxy-1-phenylcyclopenten-3,5-dione **15** (325 nm in acidic and 360 nm in basic media). This indicates that **13** has a *p*-chlorophenyl group conjugated with the endione system and **14** does not.

SCHEME 1



Aromatic protons of the triarylcyclopentendiones exhibit two signals at τ 1·5–2·0 (2H) and 2·5–3·5 (11–13H). The lower field peaks are assigned to the ortho hydrogens of the conjugated phenyl groups. In **4**, **14** and **15**, they are multiplets, while those of **11** and **13** are approximately doublets (J = 9cps) indicating the existence of a *p*-Cl atom in the isolated phenyl groups of these compounds.

A pathway consistent with the experimental data is shown in Scheme 1. Aromatic attack at the 1 and 3 positions of the assymmetric cation **16** accounts for the formation of **13** and **14**. The relative amounts of **13** and **14** is determined by the ratio of the contributing canonical structures of **16**. Thus, in the reaction with anisol, almost all of the product is the *gem*-di-*p*-anisyl derivative.

EXPERIMENTAL

Condensation of 1,2-*diphenylcyclopenten*-3,4,5-*trione* **1** *with benzene*

To a soln of **1** (160 mg) in benzene (60 ml) conc H_2SO_4 (4 ml) was added dropwise with stirring. After 15 min the condensation was finished as observed by TLC. After stirring for one night, the mixture was poured into cold water, the benzene layer was separated, and the aqueous layer was extracted with ether. The organic layers were combined, dried over Na_2SO_4, and the solvent was evaporated. The residual yellow crystals (152 mg) were recrystallized from benzene to give 129 mg of **2** as yellow prisms, m.p. 189–189·5°. IR: 1700, 1740 cm^{-1} ($\nu_{C=O}$). (Found: C, 86·91; H, 5·08. Calcd for $C_{29}H_{20}O_2$: C, 86·97; H, 5·03%). Mol. wt. Found (by vapor pressure osmometer) 388·6. Calcd 400·45.

Condensation of 2-hydroxy-1-phenylcyclopenten-3,4,5-trione **3**

(a) *With benzene.* Compound **3** (which possesses ½ equiv of dioxane of crystallization) (0·1 g) was suspended in 10 ml benzene, and conc H_2SO_4 (1 ml) was added dropwise with stirring. The mixture was permitted to stir for 18 hr, and poured into cold water. The benzene layer was separated and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined, washed with water, and dried over Na_2SO_4. After evaporation of the solvent the residual yellow crystals (139 mg) were purified by chromatography on silica gel to give 76 mg of **4** m.p. 191·5°. This compound has one molar equiv of benzene of crystallization. This benzene can be removed by heating to 60° under vacuum. (Found: C, 81·23; H, 4·72. Calcd for $C_{23}H_{16}O_3$: C, 81·16: H, 4·74%).

(b) *With anisol.* To a hot soln of **3** (0·45 g) in dehydrated anisol (30 ml) was added 0·5 g of *p*-toluenesulfonic acid (dehydrated under vacuum at 130° for 2·5 hr), and the solution was warmed to 105–110° for 1 hr. After cooling, the solution was poured into water. The organic layer was separated, washed with water, and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the resulting orange-red oily material (0·79 g) was chromatographed on silica gel to give 0·49 g (67%) of **12** as yellow crystals, which were recrystallized from isopropyl ether to afford 0·17 g of pure **12** (m.p. 154–155°). The second crop produced 0·14 g. (Found: C, 74·78; H, 4·95. Calcd for $C_{25}H_{20}O_5$: C, 74·99; H, 5·03%).

(c) *With chlorobenzene.* A soln of **3** (1·5 g) in chlorobenzene (30 ml) and conc H_2SO_4 (10 ml) was stirred at room temp for 15 hr. The mixture was poured into ice water. After addition of ether, the separated organic layer was washed with water, dried over Na_2SO_4 and the solvent was evaporated under vacuum. The residual yellow oily material was dissolved in 4 ml CCl_4, to which pure crystalline **13** was added. The crystallized crude **13** was collected (0·8 g, m.p. 115–118°), and recrystallized from benzene to yield 0·42 g of pure **13**. Compound **13** thus obtained had one equiv of benzene of crystallization, which can be removed by heating to 80°, m.p. 142·5–143°. (Found: C, 71·56: H, 4·17. Calcd for $C_{23}H_{14}O_3Cl_2C_6H_6$: C, 71·46; H, 4·14. Found: C, 67·60: H, 3·47. Calcd for $C_{23}H_{14}O_3Cl_2$: C, 67·47; H, 3·45%). The CCl_4 filtrate was evaporated to give 0·254 g of **14**. Recrystallization from benzene afforded the pure material (181 mg, m.p. 164–165·5°). (Found: C, 67·88; H, 3·60%). The pure sample of **13** for the crystallization was prepared in another run as follows: the crude mixture was dissolved in K_2CO_3aq and the resulting soln of the K salts was repeatedly extracted with ether. The ether layer was dried over Na_2SO_4 and the solvent was evaporated. The residual yellow mass was recrystallized twice from dioxane to give the salt of **13**. This was dissolved in water and acidified with HCl. Extraction from ether gave crystalline **13**.

Condensation of dimethylcroconate **6** *with benzene*

(a) Dimethylcroconate **6** (1·96 g) was dissolved in 100 ml anhyd benzene in a round-bottomed flask equipped with a Dean–Stark water separator (which contained granulated anhyd $CaCl_2$) and *p*-toluenesulfonic acid (2·5 g, dried at 130° for 2 hr under vacuum) was added. The soln was refluxed for 15 hr. After cooling, the precipitated croconic acid (0·71 g, 47%) was filtered. The filtrate was washed with $NaHCO_3$aq several times and dried over Na_2SO_4. The solvent was evaported and the residual oily material was chromatographed on silica gel (benzene) to give 0·32 g of **7a** as pale yellow needles, m.p. 126·5–127°. The second crop produced 0·14 g, IR: 1750 (w), 1680 (s), ($\nu_{C=O}$), 1637 ($\nu_{C=C}$) cm^{-1}; UV: λ_{max}in EtOH 297 nm ($\log \varepsilon = 3{\cdot}86$). (Found: C, 73·87: H, 5·29. Calcd for $C_{19}H_{16}O_4$: C, 74·01; H, 5·23%).

By analogy, toluene was condensed with **6** to give **7b** in 13% yield after boiling the mixture for 3·5 hr, m.p. 123–124°. (Found: C, 75·16: H, 6·20. Calcd for $C_{21}H_{20}O_4$: C, 74·98; H, 6·19%).

(b) Silver croconate (25 g, dried at 60–70° under vacuum for 5 hr) was placed in a soxhlet extractor equipped on a 500 ml round-bottomed flask and reacted with 70 g MeI in 300 ml anhyd benzene under reflux for 5 hr. The soxhlet extractor was removed and a 25 cm column packed with small glass helices was inserted and unreacted MeI was distilled from the soln. To the resulting soln, 40 g of P_2O_5 and 100 ml anhyd benzene were added and the mixture was refluxed for 14 hr with vigorous stirring. After cooling, the mixture was poured into ice water. The benzene layer was separated and the aqueous layer was extracted with benzene. The organic layers were combined, washed with water and dried over Na_2SO_4. After evaporation of the solvent, the residual red oily mass was chromatographed on silica gel to give 3·3 g of **7a** (n-hexane-methylene chloride 3/2). Recrystallization from n-hexane-methylene chloride afforded pure **7a** (2·9 g).

Condensation of croconic acid **5**

(a) *With benzene.* To a suspension of **5** (0·15 g) in benzene (80 ml) was added conc H_2SO_4 (2 ml) and the mixture was stirred for 2 days. Then this was poured into water, the benzene layer was separated, washed with water, and dried over Na_2SO_4. After evaporation of the solvent, the resulting yellow crystalline product was recrystallized from benzene to give **4** (0·27 g, m.p. 191°). The IR and UV spectra of this sample agreed with the reaction product of benzene and **3**.

(b) *With chlorobenzene.* To a suspension of croconic acid (0·5 g) in chlorobenzene (30 ml) was added conc H_2SO_4 (10 ml). After stirring at 45–50° for 18 hr, the mixture was poured into water. The chlorobenzene layer was separated and the water layer was extracted with benzene. The organic layers were combined, washed with water, and dried over Na_2SO_4. Evaporation of the solvent gave a yellow solid, which was recrystallized from ligroin to give **11** (0·455 g, m.p. 188·5–190·5°). The filtrate was placed on silica gel and eluted with n-hexane-chlorform to yield 0·544 g of **11**. (Found: C, 62·58; H, 2·86. Calcd for $C_{23}H_{13}O_3Cl_3$: C, 62·49; H, 2·97%).

Acetylation of A → **4**

A soln of 160 mg of **4** in 2 ml Ac_2O was warmed on an oil bath to 100–105° for 3 hr. After the reaction had cooled to room temp, water was added and excess Ac_2O was decomposed. The yellow solid was collected and recrystallized from hexane-CH_2Cl_2 to give 112 mg of 2-acetoxy-1,4,4-triphenylcyclopentene-3,5-dione, m.p. 152·5–153·5°; IR: 1785, 1750, 1700 cm^{-1} ($\nu_{C=O}$). (Found: C, 78·26; H, 4·89. Calcd for $C_{25}H_{18}O_4$: C, 78·52; H, 4·74%).

Alkaline degradation of **4**

Compound **4** (0·2 g) was dissolved in a soln of MeOH (5 ml), water (1 ml) and KOH (4 g). After the soln stood at room temp overnight. The precipitated white mass was filtered and the filtrate was poured into water, extracted with ether. The ether layer was washed with water, dried over Na_2SO_4 and the solvent was evaporated. The white residue was chromatographed on silica gel (hexane-benzene) to give 1,3,3-triphenylacetone (27 mg, m.p. 78·5–79·5°). This compound was identical with an authentic sample prepared from benzene and 1-bromo-1,3-diphenylacetone.

Reactions of 1,2-*dipiperidylcyclopenten*-3,4,5-*trione* **8**

Compound **8** (0·1 g) was suspended in 60 ml benzene and 20 ml H_2SO_4. The mixture was stirred at room temp overnight. After the mixture was poured into water, the organic layer was separated. The water layer was twice extracted with benzene. The organic layers were combined, dried over Na_2SO_4, and the solvent was evaporated. The residual solid was recrystallized from isopropyl ether-CH_2Cl_2 to give 27 mg of **9**, m.p. 185–185·5°. (Found: C, 65·08; H, 7·21; N, 10·22. Calcd for $C_{15}H_{20}N_2O_3$: C, 65·19; H, 7·30; N, 10·14%). Mol. wt. Found (by vapor pressure osmometer) 270·6 (Calcd 276·3).

(b) A soln of 1·0 g of **8** in 15 ml of conc H_2SO_4 (d = 1·84) stood at room temp for 41 hr. This was poured into a mixture of 100 ml ice water, 150 ml CH_2Cl_2 and 60 g $NaHCO_3$. After the water layer was washed twice with CH_2Cl_2, the organic layers were combined, dried over $MgSO_4$ and the solvent was evaporated. The residual orange-red crystalline solid (0·49 g) was chromatographed on silica gel (30 g) to afford **9** (0·212 g, 21%, chloroform), and **8** (0·140 g, 14%, 2% MeOH containing $CHCl_3$). The eluent from $CHCl_3$/MeOH (98/2–1/1) was allowed to evaporate slowly to give the Na salt of **10** (40 mg). The aqueous layer of this work up showed absorption max at 398 nm, which indicated the soln contained 2-hydroxy-1-piperidylcyclopententrione. The Na salt of **10** has no m.p., but becomes brown from 215°; UV λ_{max} in EtOH: 398 nm (log ε = 4·16). (Found: C, 47·67; H, 4·76; N, 5·41. Calcd for $C_{10}H_{10}NO_4Na \cdot H_2O$: C, 48·19; H, 4·83; N, 5·65%).

(c) A soln of **8** (50 mg) and diethylamine (0·3 g) in 4 ml of conc H_2SO_4 stood at room temp for 16 hr. After this had been poured into a mixture of ice water and CH_2Cl_2, the organic layer was separated, washed with water, dried over $MgSO_4$ and the solvent was evaporated to give orange-red solid. The NMR showed three multiplets at τ 8·25, 6·25, and 5·5 with relative intensities of 3:1:1, suggesting that this was as 1:1 mixture of **8** and **9**. No signal due to diethylamino group was observed.

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[c] A. W. Dox and A. Thomas, *Ibid.* **45**, 1813 (1923)

[3] T. Yamazaki, T. Oohama, T. Doiuchi and T. Takizawa, *Chem. and Pharm. Bull.* **20**, 238 (1972)

[4] For a discussion of the spectral properties of oxocarbon anions, see Ref 3

[5] J. Gauger and G. Menacke, *Chem. Ber.* **103**, 3553 (1970)

[6] For the synthesis of this compound, see T. Yamazaki and T. Takizawa, *Tetrahedron Letters* 1497 (1970)