[Contribution from the Department of Chemistry and Biology, the Polytechnic]

Condensation of *o*-Phthalaldehyde with Ketones. I. The Formation and Structures of Some 4,5-Benztropones

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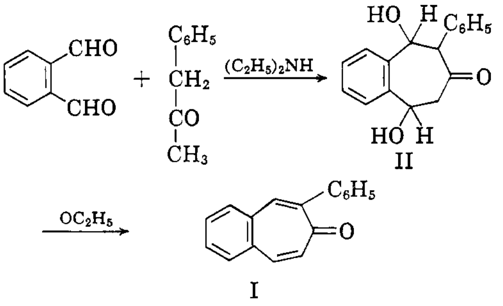
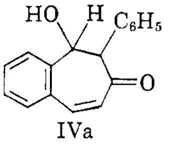
Condensation of *o*-phthalaldehyde with appropriate ketones, using diethylamine as catalyst, has yielded aldols, which have been dehydrated to the corresponding benztropones. The dehydration of the aldols under acid and alkaline conditions has been studied and the reactions and structures of the products investigated by chemical and spectroscopic methods. Diels-Alder adducts of certain compounds have been prepared and investigated. Oxidation studies of reaction products were carried out to assist in the assignment of structure.

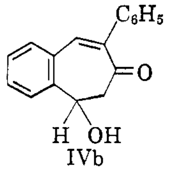
Systems containing the 4,5-benztropone nucleus were synthesized by Thiele *et al.*[2] by condensation of *o*-phthalaldehyde with aliphatic ketones containing the R—CH$_2$ —CO—CH$_2$—R′ chain, (where R = CH$_3$ or C$_6$H$_5$; R′ = H or C$_6$H$_5$). Recently Treibs and Lippmann,[3] and also Reid and Schwenecke,[4] have used the same approach for troponoid systems. The present work describes some similar condensations using straight chain ketones of the same type R—CH$_2$—CO—CH$_2$—R′ where R′ = C$_6$H$_5$, or CH$_3$—CO. The condensation of *o*-phthalaldehyde with 1-phenylpropan-2-one was carried out following the method of Tarbell and Bill.[5] The expected product 2-phenyl-4,5-benztropone I was formed in low yield and the isolation of a pure product was difficult. A condensation attempted with acetylacetone and *o*-phthalaldehyde under the same conditions as used for the tropone I gave only impure products on isolation. Thiele used ethanol as solvent and potassium hydroxide as catalyst and reported fast reactions and high yields; application of this method to 1-phenylpropan-2-one and acetylacetone gave a poor yield of the tropone with the former ketone, and failed completely in the case of the latter. The most suitable approach was the preparation of the intermediate aldol which could subsequently be dehydrated by alkaline catalysts to the desired tropone. On condensation of *o*-pthalaldehyde with 1-phenylpropan-2-one and acetylacetone using diethylamine as catalyst the aldols II and III could be isolated.

The aldol, 3,6-dihydroxy-2-phenyl-4,5-benzcyclohept-4-ene-1-one, (II) can be dehydrated smoothly by sodium ethoxide in ethanol to the tropone (I).[3] The effect of acid-catalyzed dehydration on the aldol II was examined next, and the reaction was carried out using *p*-toluenesulfonic acid in benzene when a single product, C$_{17}$H$_{14}$O$_2$ (IV) was obtained. This product showed absorption maxima at 235 mμ and 316 mμ (log ε 4.0 and 4.3 respectively) in the ultraviolet region. The infrared spectrum of compound IV showed carbonyl absorption at 1639 cm.$^{-1}$, and two strong C=C stretching bands at 1600 cm.$^{-1}$ and 1587 cm.$^{-1}$. A structural assignment to IV became more difficult on the basis of these results, as the carbonyl band at 1639 cm.$^{-1}$ would point to a structure such as IVa or IVb. Comparison of these infrared bands with those of the tropone I, the absorptions of which lie at 1626 cm.$^{-1}$, 1613 cm.$^{-1}$, and 1587 cm.$^{-1}$ show points of resemblance. The band exhibited by I at 1626 cm.$^{-1}$ is attributed to the carbonyl frequency, and the 1613 cm.$^{-1}$ and 1587 cm.$^{-1}$ peaks to C=C stretching. A comparison of the infrared bands of IV in the C=C stretching region with those of the tropone I would support either IVc or IVd, whereas

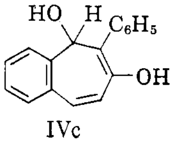




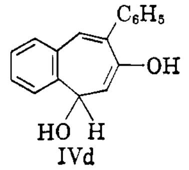
IVa



IVb



IVc



IVd

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[2] J. Thiele and J. Schneider, *Ann.*, **369**, 287 (1908); *cf.* also J. Thiele and E. Weitz, *Ann.*, **377**, 1 (1910).

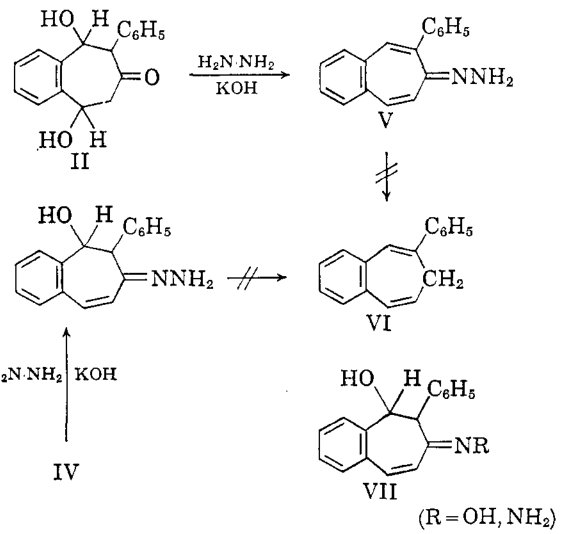
[3] W. Treibs and E. Lippmann, *Chem. Ber.*, **91**, 1999 (1958). Reported with ultraviolet spectrum λ_{max} 235,274 mμ, but no analytical data.

[4] W. Reid and H. J. Schwenecke, *Chem. Ber.*, **91**, 566 (1958).

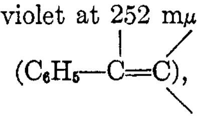
[5] D. S. Tarbell and J. C. Bill, *J. Am. Chem. Soc.*, **74**, 1234 (1952).

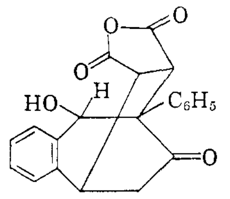
the similarity of the carbonyl stretching frequency of IV and I indicates structures IVa or IVb. The ultraviolet spectrum of IV is not fully consistent with the individual structures IVa–d, and if the ultraviolet spectrum of I is taken as a criterion for comparison, then the spectrum of IV would indicate structures lying between the pairs IVa and IVc, IVb and IVd respectively. Essentially, the problem resolves into two parts, whether IV is indeed a mixture of keto and enol forms and if so does it react as an equilibrium mixture or as one species completely independent of the other.

Comparison of the ketonic activity of the tropone I and the product IV showed that the tropone was nonketonic whereas IV formed a stable oxime and hydrazone. The product obtained on Wolff-Kishner reduction of the aldol II was the hydrazone of 2-phenyl-4,5-benztropone(V). This hydrazone could not be prepared directly by reaction of the tropone (I) with hydrazine hydrate. Presumably the hydrazone of the aldol (II) is formed initially and dehydration to V occurs because of the high reaction temperature. The product (V) could not be converted to the hydrocarbon 2-phenyl-4,5-benzcycloheptatriene (VI) even on prolonged heating with an excess of potassium hydroxide. In a similar experiment with compound IV a hydrazone (VII. R = NH_2) was obtained after Wolff-Kishner reduction, and this compound was identical in all respects with that prepared directly by reaction of IV with hydrazine hydrate. Attempted conversions of the hydrazone (VII) to the hydrocarbon (VI) could not be achieved under conditions which were identical with those used for the decomposition of the hydrazone (V) to the hydrocarbon (VI). Therefore, it appears that compound IV reacts in the keto form with hydroxylamine and hydrazine to give compounds formulated as VII.

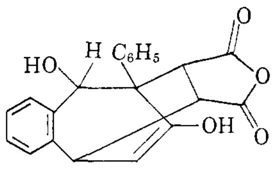


The compounds formulated as IVc and IVd should form adducts with dienophiles, if these enolates represent a possible structure for compound IV. Diels-Alder reaction of IV with maleic anhydride in dry benzene at room temperature gave two crystalline products, m.p. 188° (VIII) and 142° (IX) respectively. Analyses of compounds VIII and IX showed that they were isomers of $C_{21}H_{16}O_5$. Each compound showed benzenoid absorption in the ultraviolet.

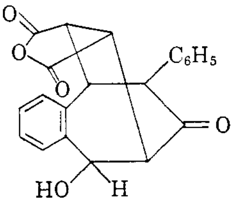
Four isomers can be formulated for the Diels-Alder adducts of structures IVc and IVd with maleic anhydride. These are represented as Xa and Xb derived from IVc, and Xc and Xd derived from IVd. Examination of the structures Xc and Xd shows that if these two isomers are formed in the reaction, one of them (Xc) should show a peak in the ultraviolet at 252 mμ characteristic of styryl residues  $(C_6H_5{-}C{=}C)$, whereas both VIII and IX showed only benzenoid absorption.



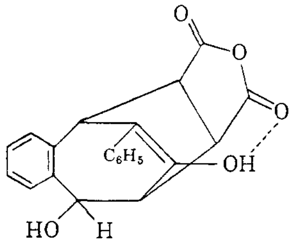
Xa VIII



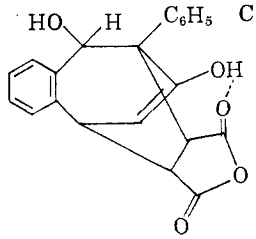
Xb IX



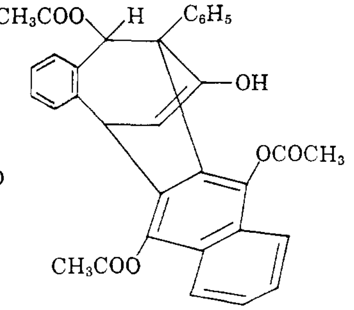
Xd



Xc



IX



XI

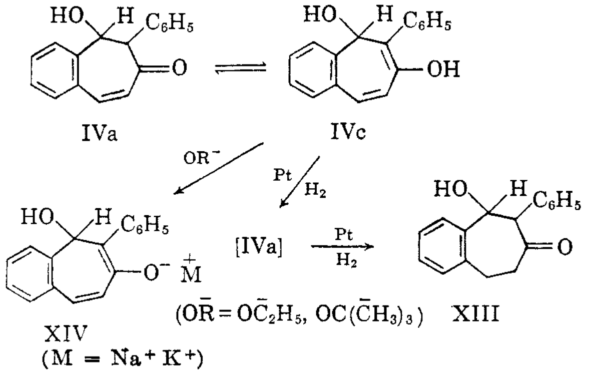
The formation of the adducts VIII and IX must be regarded as having originated from one parent compound, either IVc or IVd. Hence consideration of the infrared data should lead to a pair of isomers derived from IVc or IVd which satisfies the requirements of Xa and Xb or Xc and Xd. Compound VIII showed bands at 1859 cm.$^{-1}$, 1786 cm.$^{-1}$ (carbonyl stretching of the anhydride group) and a sole peak at 1721 cm.$^{-1}$ (stretching mode of saturated ketone), but there was no absorption in the 1600 cm.$^{-1}$ region. The adduct IX showed a band at 3012 cm.$^{-1}$ (absorption associated with =C—H stretching) and two bands at 2667 cm.$^{-1}$, 2632 cm.$^{-1}$ presumably due to hydrogen bonding of the tertiary hydroxyl group of the enolate with the carbonyl of the anhydride ring. The carbonyl anhydride absorptions of IX were doublets at 1869 cm.$^{-1}$, 1839 cm.$^{-1}$ and 1786 cm.$^{-1}$, 1704 cm.$^{-1}$ and strong —C=C—stretching bands were shown at 1639 cm.$^{-1}$ and 1600 cm.$^{-1}$

Considering the pair of isomers Xa and Xb, structure Xa should show a saturated carbonyl stretching peak outside the range exhibited by the carbonyl stretching of the anhydride grouping, and there should be no absorption in the C=C stretching region (1620–1600 cm.$^{-1}$). The enolate type isomer (Xb) should not have any carbonyl absorption apart from the carbonyl anhydride peaks, but absorptions corresponding to $=\overset{|}{\mathrm{C}}\text{—H}$ stretching at 3015 cm.$^{-1}$ and C=C stretching in the 1620 cm.$^{-1}$ region should be shown. The structure of Xc would fulfill all the infrared requirements of the adduct IX with the exception of the $=\overset{|}{\mathrm{C}}\text{—H}$ band at 3013 cm.$^{-1}$ which would be absent. Furthermore, the ultraviolet spectrum of Xc could show styryl absorption at 252 mμ, whereas both adducts obtained gave benzenoid type spectra. Consequently, formulation Xc cannot be considered as representing compound IX. Neither can Xd account for the adduct VIII, as both adducts must have the same precursor, either IVc or IVd. On the basis of these results the adducts VIII and IX are formulated as corresponding with structures Xa and Xb respectively.

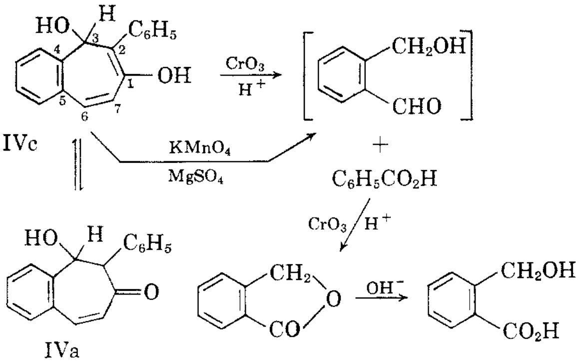
Further work showing the reactivity of compound IV towards dienophiles was exemplified using 1,4-naphthoquinone in glacial acetic acid, when a crystalline adduct formulated as the triacetate XI was obtained.

Certain observations regarding the validity of the enolate structure assigned to IV can be made on the basis of rearrangement reactions that were attempted. Essentially the question arises as to whether the compound reacts in the enol form, being produced from its tautomeric keto under reaction conditions, or if the enol exists independently of the keto form. Rearrangement of the enolate should give reversion to the keto form which under suitable reaction conditions would dehydrate to the known 2-phenyl-4,5-benztropone (I). Irradiation of IV using a mercury arc lamp and iodine as catalyst caused no rearrangement, and the starting material could be recovered. Treatment of IV with potassium *tert*-butoxide in *tert*-butyl alcohol, or with sodium ethoxide in ethanol caused no rearrangement, and compound IV was recovered unchanged. The solutions formed on dissolving IV in alkoxide-containing media were deeply colored, and this color was destroyed on subsequent modification. It is possible, therefore, that the stable enolate anion (XIV) is produced under anhydrous conditions when IV is dissolved in a medium containing alkoxide ion. However, compound IV formed a stable oxime and hydrazone in alkaline medium, and neither of these products undergoes Diels-Alder addition with 1,4-naphthoquinone in glacial acetic acid, as does the parent compound IV. Therefore the evidence for the independent existence of the enol form of IV is no longer valid.

Hydrogenation of IV in the presence of Adam's platinum catalyst ceased after the absorption of one mole of hydrogen. The product XIII obtained from this reaction showed benzenoid absorption in the ultraviolet region, and the infrared spectrum showed the presence of a saturated ketone (band at 1705 cm.$^{-1}$) and no C=C stretching in the 1620–1600 cm.$^{-1}$ region. On the basis of this evidence it may be deduced that one of the enolates (IVb or IVd) reverted to the keto form (IVa or IVc) and the double bond was subsequently reduced. However, the Diels-Alder adducts VIII and IX tend to support the view that the reacting species is IVc, and the formation of ketonic derivatives from IV support structure IVa. The mechanism leading to the formation of the keto alcohol XIII on hydrogenation of IV may possibly be an enol-keto charge catalysed by H$^+$ produced from the hydrated platinum oxide catalyst. The infrared spectrum of IV showed carbonyl absorption, whereas the ultraviolet spectrum supported an aromatic type system (IVc or IVd) rather than an α,β-unsaturated ketone (IVa or IVb). Therefore the foregoing reactions of IV may possibly be interpreted as those of a tautomeric mixture, and the structures which offer a reasonable explanation for these are IVa and IVc. Hence the following reaction scheme is proposed, treating compound IV as a mixture of IVa ketone $\rightleftharpoons$ IVc enol.

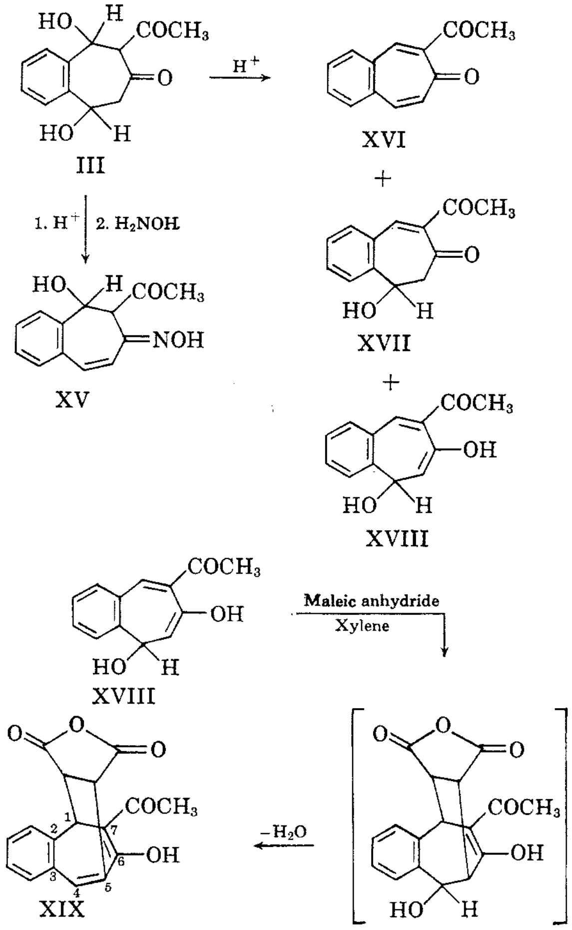


The products obtained on oxidation of compound IV using chromium trioxide in aqueous acetic-sulfuric acid were phthalide and benzoic acid. Oxidation of IV with potassium permanganate in acetone containing magnesium sulfate to give a "neutral" medium gave a single product, elemental analysis of which indicated the formula $C_8H_8O_2$. This product was shown to be 1-hydroxymethylbenzaldehyde[6] by oxidation with chromium trioxide to the corresponding acid, 1-hydroxymethylbenzoic acid (prepared by hydrolysis of phthalide). The sole product obtained on oxidizing IV with potassium permanganate in acidic medium was benzoic acid. If compound IV is a tautomeric mixture and the equilibrium lies on the enolic side (IVc), the mechanism whereby the oxidation products, benzoic acid, phthalide and 1-hydroxymethylbenzaldehyde are formed can be considered in the following way. In the presence of chromium trioxide, scission of bonds C-1, C-2, and C-3 forms benzoic acid; oxidation of the residual fragment at C-6 and C-7 forms the aldehyde group, giving rise to 1-hydroxymethylbenzaldehyde as an intermediate, further oxidation of which forms phthalide.



The condensation of *o*-phthaldehyde and acetylacetone to form the aldol (III) has been discussed earlier. In this series difficulty was encountered in dehydrating the aldol (III) with basic catalysts, and no pure products could be isolated. Consequently, acid-catalyzed dehydration of III was attempted; in one reaction the acidic catalyst was removed from the reaction mixture, and in another identical dehydration no attempt was made to eliminate the catalyst prior to isolation of the products. The reason for avoiding removal of acid from the reaction mixture in the second dehydration attempted on III was that when a benzene solution of the reaction products was washed with dilute alkali most of the organic product passed into the basic phase.

The product obtained on acid-catalyzed dehydration of III after removal of acid from the reaction mixture was converted into the oxime XV. A structural assignment to the oxime XV is made on the basis of its ultraviolet spectrum, λ_{max} 222 mμ (log ϵ 3.5), and this product proved to be important as a comparison with the products obtained on acid-catalyzed dehydration of the aldol III, where no attempt was made to eliminate the catalyst from the reaction mixture. Acid-catalyzed dehydration of III was effected using *p*-toluenesulfonic acid in benzene, and in this reaction (where no attempt was made to eliminate the catalyst) three products were obtained. The first of these, 2-acetyl-4,5-benztropone (XVI), was identified by its ultraviolet and infrared spectra. The infrared spectrum of XVI showed a band at 1681 cm.$^{-1}$ (carbonyl stretching of $-CO-CH_3$ group) and another carbonyl absorption at 1616 cm.$^{-1}$ because of the carbonyl stretching of the seven-membered aromatic rings, two C=C stretching bands also characteristic of tropone systems occurred at 1575 cm.$^{-1}$ and 1550 cm.$^{-1}$ Analysis of the other two products obtained in this reaction indicated that they were isomers of $C_{13}H_{12}O_2$ designated as XVII and XVIII, respectively. Structural assignment to XVII is made on the basis of its ultraviolet spectrum, λ_{max} 253 mμ (log ϵ 3.9) typical of an α-substituted α,β-unsaturated ketone, and the infrared spectrum 1689 cm.$^{-1}$ (α,β-unsaturated ketone). Furthermore XVII formed a bi-2,4-dinitrophenylhydrazone in contrast to the acetylbenztropone (XVI) which formed a monophenylhydrazone. The keto group of the tropone ring is inactive as shown for the tropone I discussed earlier. A comparison may be drawn between the ultraviolet spectra of the half-aldol XVII and the oxime XV, as the position of the absorption maxima 222 mμ for XV and 253 mμ for XVII indicates the position of the double band in



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[6] O. Hessert, *Chem. Ber.*, **10**, 1448 (1903). 1-Hydroxymethylbenzaldehyde reported as a yellow sweet-smelling oil, yielding phthalic acid on alkaline potassium permanganate oxidation.

the seven-membered ring, and consequently locates the hydroxyl group on C-3 in XV and C-6 in XVII.

As assignment of structure to compound XVIII requires treatment similar to that extended for explaining the reactions of compound IV. The analytical data of XVIII indicate a half-aldol structure, (α,β-unsaturated cyclic ketone), but the ultraviolet spectrum which exhibits maxima at 239 mμ, 281 mμ, 285 mμ (log ϵ, 3.98), when compared with the spectra of XV and XVII does not support the evidence for a simple α,β-unsaturated cyclic ketone, but points rather to a fully conjugated ring. A possible formulation to XVIII could be assigned by comparing this material with compound IV, and showing that XVIII is the enolic form of XVII and should therefore be capable of forming adducts with dienophiles. Diels-Alder reaction of XVIII with maleic anhydride in xylene formed an adduct $C_{17}H_{12}O_5$ (XIX). This product corresponds to the addition of one molecule of maleic anhydride and the loss of a molecule of water. Presumably, because of the high temperature and anhydrous reaction conditions, dehydration occurs after the addition of the dienophile. The ultraviolet spectrum of XIX showed λ_{max} 237–238 mμ, (log ϵ 4.7 and 4.2), a spectrum very similar to that of a benzcycloheptatriene[7]; the infrared spectrum showed strong bands at 1835, 1818, and 1770 cm.$^{-1}$ due to carbonyl stretching of the anhydride group. As XVIII forms a Diels-Alder adduct with maleic anhydride, there is similarity with compound IV, the reactions of which are interpreted as those of a tautomeric ketoenol mixture (IVa $\rightleftharpoons$ IVc) the enolic form of which also forms Diels-Alder adducts. The difference between XVIII and IV lies in the fact that whereas IV appears to be a tautomeric mixture, compounds XVII (keto form) and XVIII (enol form) appear to exist independently, as each was isolable from the same reaction mixture. Hence XVIII is formulated as the enol form of the half-aldol XVII (2-acetyl-6-hydroxy-4,5-benzcyclohept-2-ene-1-one). The Diels-Alder adduct XIX is formulated as a derivative of 7-acetyl-6-hydroxy-2,3-benzcycloheptatriene.

EXPERIMENTAL

Melting points are uncorrected. The light petroleum refers to the fraction having a b.p. of 60–80°, unless otherwise stated. Ultraviolet spectra were measured in 96% ethanol using a Union SP 500 Spectrophotometer. Infrared spectra were measured in potassium bromide discs with a double beam Grubb-Parson Spectrophotometer.

3,6-Dihydroxy-2-phenyl-4,5-benzcyclohept-1-one (II). 1-Phenylpropan-2-one (0.01 mole), 2.68 g., and 2.68 g. of *o*-phthalaldehyde (0.01 mole) were mixed and warmed on the steam bath to 50°, 0.5 cc. of diethylamine was added, the mixture shaken thoroughly and the flask stoppered. The resulting red solution was allowed to stand at room temperature for 2 days. Addition of benzene to the mixture and shaking induced crystallization, and the product was filtered, washed with benzene and dried. Crystallization from benzene afforded 3.85 g. (73%) of colorless prisms, m.p. 120–121° of the aldol II. $\lambda_{max}^{C_2H_5OH}$ 262 mμ (log ϵ 2.89) 269 mμ (log ϵ 2.82).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.5; H, 6.3.

2-Phenyl-4,5-benztropone (I). To a solution of sodium ethoxide in ethanol was added 2 g. of the aldol II (prepared from 400 mg. of sodium in 100 cc. of ethanol), and the mixture was refluxed for 1.5 hr. The solution was cooled and was then poured into 300 cc. of water, and a pale yellow solid separated which was filtered off and dried *in vacuo.* Crystallization from light petroleum–ethyl acetate yielded pale yellow plates, 1.25 g. (72%) of 2-phenyl-4,5-benztropone (I), m.p. 142–143°. $\lambda_{max}^{C_2H_5OH}$ 238 mμ (log ϵ 4.4) 277 mμ (log ϵ 4.5); γ_{max}^{KBr} 1626 cm.$^{-1}$ (S) (carbonyl stretching of seven-membered aromatic ring); 1613 cm.$^{-1}$ (S) 1587 cm.$^{-1}$ (S) (C=C stretching of tropones systems).

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 87.6; H, 5.1.

Compound IV. The aldol II (1.8 g.) was dissolved in 150 cc. of benzene and 10 mg. of *p*-toluenesulfonic acid was added, and the mixture was refluxed under a Dean-Starck apparatus for 1.5 hr. On cooling the reaction mixture was washed with 5% sodium carbonate solution, and then with water to neutrality, and the organic phase was dried (magnesium sulfate) and evaporated. Crystallization of the residue from light petroleum–ethyl acetate gave the *compound* IV as yellow prisms (82%), 1.38 g., 82%, m.p. 127–128°, $\lambda_{max}^{C_2H_5OH}$ 235 mμ (log ϵ 4.01) 316–319 mμ (log ϵ 4.29). γ_{max}^{KBr} 1639 cm.$^{-1}$ (S) (carbonyl stretching), 1600 cm.$^{-1}$ (S) 1587 cm.$^{-1}$ (S) (C=C stretching), 1089 cm.$^{-1}$ (S) (—OH deformation).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.6; H, 5.5.

The *oxime of* IV was prepared by standard procedure. The product crystallized as yellow needles from methanol, m.p. 195–196°. $\lambda_{max}^{C_2H_5OH}$ 312–314 mμ (log ϵ 4.1). γ_{max}^{KBr} 3155 cm.$^{-1}$ (m) (—OH stretching), 1626 cm.$^{-1}$ (S) (C=N stretching of $>$C=NOH group), 1093 cm.$^{-1}$ (S) (—OH deformation).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.7; N, 5.3. Found: C, 76.8; H, 5.16; N, 5.3.

The *hydrazone of* IV was prepared by standard procedure. The product crystallized from ethanol in white prisms, m.p. 222–224°. $\lambda_{max}^{C_2H_5OH}$ 232 mμ (log ϵ 4.23) 235 mμ (log ϵ 4.23).

Anal. Calcd. for $C_{17}H_{16}N_2O$: C, 77.3; H, 6.1; N, 10.6; mol. wt., 264. Found: C, 77.6; H, 6.1; N, 10.2; mol. wt., 255.

The *picrate of the hydrazone* crystallized from benzene-ethanol as bright yellow prisms, m.p. 119–120°.

Anal. Calcd. for $C_{23}H_{19}N_5O_8$: C, 56.0; H, 3.9; N, 14.2. Found: C, 56.2; H, 4.0; N, 14.1.

The hydrazone of 2-phenyl-4,5-benztropone (V). To 660 mg. of the ketone II in 20 cc. of ethylene glycol were added 3.5 cc. of 78% hydrazine hydrate, and 500 mg. of potassium hydroxide in 2 cc. of water. The mixture was refluxed for 6 hr. and after 1.5 hr. the internal temperature was raised to 200°. The mixture was allowed to cool, poured into 100 cc. of water, and the solid which separated was filtered and dried *in vacuo.* Crystallization from light petroleum gave bronze needles of the *hydrazone* (V) (320 mg.) 53%, m.p. 127–128°. $\lambda_{max}^{C_2H_5OH}$ 236 mμ (log ϵ 4.11), 244 mμ (log ϵ 4.10), 278 mμ (log ϵ 4.20).

Anal. Calcd. for $C_{17}H_{14}N_2$: C, 82.9; H, 5.17; N, 11.4. Found: C, 82.6; H, 5.9; N, 11.6.

The picrate of V was prepared by refluxing 190 mg. of V and 110 mg. of picric acid in benzene. Three crystallizations from benzene gave 110 mg. (30%) of the *picrate* as bright yellow prisms, m.p. 198–199°.

Anal. Calcd. for $C_{23}H_{17}N_5O_7$: C, 58.1; H, 3.6; N, 14.7. Found: C, 58.0; H, 3.6; N, 15.0.

Attempted decomposition of V *to 2-phenyl-4,5-benzcyclo-*

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(7) *Cf.* ref. 3. 2,7-Substituted 4,5-benztropones have two maxima in the region 230–244 mμ, 270–290 mμ.

heptatriene (VI). To a solution of 100 mg. of compound V in 5 cc. of ethylene glycol was added 150 mg. of potassium hydroxide in 1 cc. of water and the mixture was refluxed for 4 hr. The reaction mixture was poured into 25 cc. of water and the solid which separated the filtered and dried *in vacuo.* Crystallization from light petroleum gave bronze needles, m.p. 127–128°, alone or mixed with compound V.

Wolff-Kishner reduction of compound IV. To 960 mg. of compound IV in 20 cc. of ethylene glycol were added 4.5 cc. of 78% hydrazine hydrate and 750 mg. of potassium hydroxide in 2 cc. of water, and the mixture was refluxed for 6 hr. The internal temperature was raised to 200° after 1.5 hr. The mixture was allowed to cool and was poured into 100 cc. of water, the crystalline material which separated was filtered and dried *in vacuo.* Crystallization from ethanol gave 750 mg. (77%) of colorless prisms, m.p. 222–224°, and gave no depression on admixture with the hydrazone of compound IV.

The Diels-Alder adducts VIII *and* IX. A mixture of 500 mg. of maleic anhydride (0.05 mole) and 1.30 g. of compound IV (0.05 mole) was dissolved in 5 cc. of dry benzene and allowed to stand at room temperature for 3 hr. On concentration of the solution a semicrystalline material was obtained, trituration of which with light petroleum–ethyl acetate afforded 220 mg. of a colorless crystalline solid, 12%, m.p. 138–140°. Repeated crystallization from light petroleum–ethyl acetate gave IX as colorless prisms m.p. 140–141°. $\lambda_{\max}^{C_2H_5OH}$ 258 mμ (log ε 2.82) 262 mμ (log ε 2.63). $\gamma_{\max}^{KBr}$ 3012 cm.$^{-1}$ (m) (=C—H stretching) 2667 cm.$^{-1}$ (m) 2632 cm.$^{-1}$ (m) (H— bonded —OH group) 1869 cm.$^{-1}$ (m) 1835 cm.$^{-1}$ (m) 1786 cm.$^{-1}$ (s) 1704 cm.$^{-1}$ (s) (carbonyl stretching of the anhydride), 1639 cm.$^{-1}$ (s) 1600 cm.$^{-1}$ (s) (C=C stretching).

Anal. Calcd. *for* $C_{21}H_{16}O_5$: C, 72.4; H, 4.6. Found: C, 72.0; H, 5.0.

The mother liquors from the original extraction, and those from the crystallizations of IX, were concentrated to give another colorless crystalline solid, m.p. 180–184° (110 mg.) Repeated crystallization from light petroleum–ethyl acetate gave *compound* VIII (95 mg.) as colorless prisms, 6%, m.p. 187–188°. $\lambda_{\max}^{C_2H_5OH}$ 260 mμ (log ε 2.82) 264 mμ (log ε 2.84). $\gamma_{\max}^{KBr}$ 1859 cm.$^{-1}$ (m) 1786 cm.$^{-1}$ (S) (carbonyl stretching of anhydride), 1721 cm.$^{-1}$ (s) (carbonyl stretching of ketone).

Anal. Calcd. for $C_{21}H_{16}O_5$: C, 72.4; H, 4.6. Found: C, 72.2; H, 4.4.

Diels-Alder adduct XI. To a solution of 230 mg. of compound IV in 10 cc. of glacial acetic acid was added 160 mg. of 1,4-naphthoquinone and the mixture maintained at 100° for 5 hr. A deep red crystalline solid separated on cooling; this was filtered off and dried *in vacuo.* Crystallization of the product from glacial acetic acid gave 120 mg. of deep red needles of *the adduct* XI, 24% m.p. 334–336°. $\lambda_{\max}^{C_2H_5OH}$ 262 mμ (log ε 4.95).

Anal. Calcd. for $C_{33}H_{26}O_7$: C, 74.1; H, 4.9. Found: C, 74.2; H, 5.0.

Chromium trioxide oxidation of compound IV. To 700 mg. of IV dissolved in 15 cc. of acetic acid was added 1 g. of chromium trioxide dissolved in 5 cc. of acetic acid and 2 cc. of 10% sulfuric acid with stirring during 1 hr. and the mixture was allowed to stand at room temperature for 36 hr. The resulting solution was extracted with four 50-cc. portions of ether, and the organic layer was washed with four 25-cc. portions of 20% sodium hydroxide, and finally with three 10-cc. portions of water to neutrality. The combined alkaline and aqueous solutions were acidified with concentrated hydrochloric acid and extracted with four 25-cc. portions of ether, and the organic layer washed with three 10-cc. portions of water to neutrality, dried (magnesium sulfate), and evaporated to give the "acid" fraction. Crystallization of the residue from light petroleum gave 80 mg. of colorless prisms (28%), m.p. 120–121°. Undepressed on admixture with authentic benzoic acid.

The original ethereal extract of the reaction mixture, the "neutral" fraction, was dried (magnesium sulfate) and evaporated. Crystallization of the residue from ether gave 36 mg. of colorless crystals (9%) m.p. 71–72°, mixed melting point with authentic phthalide showed a m.p. of 71–72°.

Neutral potassium permanganate oxidation of compound IV. To a solution of 5 g. of compound IV in 60 cc. of aqueous acetone (5:1 acetone/water v./v.) were added 2 g. of magnesium sulfate and the mixture shaken while solid potassium permanganate was added in small portions during 4 hr., *until a permanent pink color was obtained.* The solution was filtered and the precipitate washed with warm acetone (50 cc.) and then with ether (25 cc.). The filtrate was diluted with 30 cc. of water, and extracted with six 30-cc. portions of ether, and the aqueous layer was rejected. The ethereal extract was washed with 4% sodium hydroxide and then with water to neutrality, dried (magnesium sulfate) and evaporated to give 750 mg. of a yellow oil. Repeated distillation through a short path Vigreux column gave 580 mg. of a yellow oil (21%) b.p. 104–105°/0.6 mm. $n_D^{19.5}$ 1.5355, 1-hydroxymethylbenzaldehyde.

Anal. Calcd. for $C_8H_8O_2$: C, 70.6; H, 5.9; mol. wt., 136. Found: C, 70.8; H, 6.1; mol. wt., 142 (Rast).

1-Hydroxymethylbenzaldehyde (250 mg.) was dissolved in 5 cc. of acetic acid containing 1 cc. of sulfuric acid, and 300 mg. of chromium trioxide in 5 cc. of acetic acid was added. The mixture was allowed to stand at room temperature for 2 hr., and was then diluted with 25 cc. of water and extracted with three 10-cc. portions of ether. The organic layer was washed with 4% sodium hydroxide (3 × 25 cc.) and then with water to neutrality, dried (magnesium sulfate), and evaporated, and no residue was obtained from the "neutral" fraction. The aqueous and alkaline washings were combined and acidified with 7% hydrochloric acid and chilled in ice, to give a white crystalline precipitate which was filtered and dried. Crystallization from water gave 220 mg. of 1-hydroxymethylbenzoic acid as colorless needles (84%), m.p. 118–120°. Authentic 1-hydroxymethylbenzoic acid was prepared by hydrolysis of phthalide with 50% sodium hydroxide, and showed a m.p. of 118–120°. Mixed melting point with the oxidation product showed a m.p. of 119–120°.[8]

Oxidation of IV *with concentrated nitric acid.* Treatment of 2.2 g. of IV at 0°, with 22 cc. of concd. nitric acid (*d.* 1.42), induced immediate reaction with evolution of oxides of nitrogen. The mixture was kept at 0° for 1 hr., and was then heated on a steam bath for 1 hr. until the evolution of nitrogen oxides ceased. On chilling in ice a pale yellow solid crystallized, which was filtered and washed with water, and dried *in vacuo.* Crystallization from benzene–ethyl acetate gave 970 mg. of *p*-nitrobenzoic acid, pale yellow plates (67%), m.p. 238–239°, alone or mixed with authentic *p*-nitrobenzoic acid.

The keto alcohol (XIII). Compound IV (1 g.) was dissolved in 50 cc. of ethanol and hydrogenated over 25 mg. of Adam's (platinum oxide) catalyst at atmospheric pressure and room temperature. Absorption ceased after the uptake of 85 cc. (1.1 moles) in 1 hr. Filtration of the catalyst and evaporation of the solvent yielded a colorless oil. Crystallization was induced by trituration with light petroleum and gave 920 mg. of *3-hydroxy-2-phenyl-4,5-benzcyclohept-4-ene-1-one*, colorless needles (91%), m.p. 93–94°. $\lambda_{\max}^{C_2H_5OH}$ 259 mμ (log ε 3.26) 265 mμ (log ε 3.31) 272 mμ (log ε 3.27). $\gamma_{\max}^{KBr}$ 3367 cm.$^{-1}$ (w) (—OH stretching) 1704 cm.$^{-1}$ (s) (carbonyl of saturated ketone).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.6; H, 6.0.

Attempted rearrangements of IV. (1) To a solution of potassium *tert*-butoxide in dry *tert*-butyl alcohol (from 80 mg. of potassium and 8 cc. of *tert*-butyl alcohol) was added

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[8] P. R. Jones, *J. Org. Chem.*, 23 (9), 1386 (1958). 1-Hydroxymethylbenzoic acid, m.p. 111–112°, prepared by alkaline hydrolysis of phthalide.

500 mg. of IV. A deep red color developed immediately and the solution was heated at 100° for 36 hr. On cooling, the solution was poured into water, acidified with dilute hydrochloric acid, and the precipitated solid was filtered and dried *in vacuo*. Crystallization from light petroleum–ethyl acetate gave 450 mg. of yellow prisms (90%), m.p. 126–127°, alone or mixed with authentic IV.

(2) To a solution of sodium ethoxide in dry ethanol (from 20 mg. of sodium in 10 cc. of ethanol) was added 300 mg. of IV with the formation of a deep green solution. The mixture was refluxed for 24 hr., cooled, and poured into water, acidified with dilute hydrochloric acid, and the precipitated solid filtered and dried *in vacuo*. Crystallization from light petroleum–ethyl acetate gave 275 mg. of yellow prisms (91%), m.p. 126–127°, alone or mixed with authentic IV.

2-Acetyl-3,6-dihydroxy-4,5-benzcyclohept-4-ene-1-one (III). A mixture of 2.68 g. of *o*-phthalaldehyde (0.01 mole) and 2 g. of acetylacetone was heated to 50° on a water bath, 6 drops of diethylamine was added, and the resulting mixture was allowed to stand at room temperature or 24 hr. The resulting clear yellow gum was shaken with 15 cc. of benzene, which caused separation of a colorless crystalline solid, which was filtered and dried. Crystallization from benzene gave colorless prisms of the aldol III (3.83 g., 85%), m.p. 116–117°. $\lambda_{max}^{C_2H_5OH}$ 265 mμ (log ϵ 2.49) 272 mμ (log ϵ 2.45).

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.7; H, 6.2. Found: C, 67.2; H, 5.8.

Acid-catalyzed dehydration of III. A crystal of *p*-toluenesulfonic acid was added to 1 g. of the aldol III dissolved in 50 cc. of benzene and the mixture was heated in a Dean-Starck apparatus for 1 hr. (Any attempt at washing the organic phase with dilute sodium hydroxide resulted in most of the organic product passing into the alkaline phase.) The solvent was evaporated and the residue dissolved in 30 cc. of ethanol, a mixture of 1 g. of hydroxylamine hydrochloride and 1 g. of sodium carbonate in 5 cc. of water was added and the solution was refluxed for 1 hr. On cooling, the mixture was poured into water, and the precipitated solid filtered and dried. Crystallization of the *oxime* from aqueous ethanol gave 150 mg. of XV (15%), m.p. 119–120°. $\lambda_{max}^{C_2H_5OH}$ 222 mμ (log ϵ 3.54).

Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.5; H, 5.9; N, 6.1. Found: C, 67.2; H, 5.7; N, 6.5.

Dehydration of III *to compounds* XVI–XVIII of the aldol III (1.5 g.) was effected with benzene and *p*-toluene sulfonic acid. Distillation of the resulting oil through a short path Vigreux column gave three fractions. (1) A pale yellow oil, b.p. 90°/1.6 mm. (2) A viscous deep yellow oil, b.p. 159–162°/1.0 mm. (3) A thick colorless oil, b.p. 188–190°/1.0 mm.

Fraction (1). Crystallization of the oil from light petroleum ether (b.p. 40–60°) gave pale yellow needles of *2-acetyl-6-hydroxy-4,5-benzcyclohept-2-ene-1-one* (XVII) (185 mg., 11%) m.p. 52–53°. $\lambda_{max}^{C_2H_5OH}$ 253 mμ (log ϵ 3.90). γ_{max}^{KBr} 1689 cm.$^{-1}$ (S) (α,β-unsaturated ketone).

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.6. Found: C, 71.9; H, 5.8.

The *bi-2,4dinitrophenylhydrazone* was prepared by standard procedure, and formed orange prisms form chloroform-ethanol, m.p. 195–197°.

Anal. Calcd. for $C_{25}H_{20}N_8O_9$: C, 50.9; H, 4.4; N, 19.5. Found: C, 50.6; H, 4.2; N, 19.1.

Fraction (2). Crystallization of the oil from light petroleum (b.p. 40–60)-ether gave yellow prisms of XVIII (440 mg. 26%) m.p. 79–80°. $\lambda_{max}^{C_2H_5OH}$ 239 mμ (log ϵ 3.98) 281 mμ (log ϵ 3.97) 285 mμ (log ϵ 3.96). γ_{max}^{KBr} 3390 (m) (—OH group) 3058 (m) (H bonded hydroxyl group) 1695 (v.s.) (carbonyl of acetyl group) 1653 (S) 1613 cm.$^{-1}$ (s) (C=C stretching).

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.6. Found: C, 72.6; H, 5.3.

Fraction (3). The oil crystallized from light petroleum-ether to give white needles of *2-acetyl-4,5-benztropone* (XVI) (120 mg., 6.8%), m.p. 89–90°. $\lambda_{max}^{C_2H_5OH}$ 235 mμ (log ϵ 4.4) 275 mμ (log ϵ 4.6). γ_{max}^{KBr} 1681 (s) (carbonyl of acetyl group) 1613 (s) (carbonyl of seven-membered aromatic ring) 1575 (s) 1550 cm.$^{-1}$ (s) (C=C stretching of aromatic seven-membered ring).

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.8; H, 5.1. Found: C, 78.9; H, 5.2.

The *monophenylhydrazone* of XVI was prepared by standard procedure, and formed prisms from aqueous ethanol, m.p. 111–112°.

Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 79.1; H, 5.6; N, 9 7. Found: C, 78.8; H, 5.4; N, 9.6.

Diels-Alder adduct XIX. A mixture of 240 mg. of XVIII and 70 mg. of maleic anhydride was dissolved in dry xylene (5 cc.), and refluxed for 5 hr. The crystalline material which separated on cooling (80 mg.) was crystallized from benzene–ethyl acetate to give colorless needles of the adduct XIX, (2.4%), m.p. 268–270°. $\lambda_{max}^{C_2H_5OH}$ 237–238 mμ (log ϵ 4.73), 286 mμ (log ϵ 4.19). γ_{max}^{KBr} 1835 (s) 1818 (s) 1770 (s) (carbonyl of anhydride group) 1610 (s) 1600 cm.$^{-1}$ (s) (aromatic C=C stretching).

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.9; H, 4.1. Found: C, 69.2; H, 4.1

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND BIOLOGY, THE POLYTECHNIC]

Condensation of *o*-Phthalaldehyde with Ketones. II

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Condensation of *o*-phthalaldehyde with appropriate ketones has led to the formation of benzotropolones and these products have been investigated by chemical and spectroscopic methods. Metal complexes of certain benztropolones have also been prepared. Some bromobenztropones and benztropolone-*O*-methyl ethers have been synthesized and certain of their reactions studied.

The condensation of *o*-phthalaldehyde with ketones of the type R—CH_2CO—CH_2R' (where R' = C_6H_5, —CO—CH_3, and R = H) leads to the formation of troponoid systems.[2] The 4,5-benztropolone *O*-methyl ether(II) was prepared by Tarbell

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