Oxidation Conditions.—In general the oxidations were carried out in 50-ml. reactors which were immersed in a running water-bath at 20 to 25°. The reactors were attached to a suitable gas measuring system and the sample (2–5 g.) was stirred vigorously with a magnetic stirrer. Normal variation in stirring rate did not affect the rate of oxidation. The photosensitizer was commercial oil-soluble chlorophyll stated to contain 4% of chlorophyll in oil. In most cases 3 mg. of this product was added per gram of substrate and there was no further addition of catalyst. One or more 300 watt reflector spot lights placed about 10 cm. from the reactor were used as the source of light.

In a typical case, 2.004 g. (0.0147 mole) of myrcene containing 0.006 g. of crude chlorophyll illuminated with one 300 watt light absorbed 0.0147 mole of oxygen in 150 minutes. The product had a peroxide number of 11,400 meq. per kilogram or 96% of theoretical. Ultraviolet and infrared spectral characteristics are given in Tables II and III. Similar products were obtained by removing unreacted myrcene from partially oxidized products by evaporation *in vacuo* at below 35°.

Spectrophotometric Measurements.—The ultraviolet spectra were run in isoöctane solution on a manual Beckman[11] DU spectrophotometer. The infrared, spectra were recorded on a Perkin-Elmer 21[11] double beam spectrophotometer with NaCl optics. All samples were run neat in 0.027-mm. cells. Quantitative curves were made with slit program 927, suppression 8, speed 0.4 micron/min., scale 5 cm./micron and normal gain. The curves given in Figs. 1 and 2 were made with slit program 927, suppression 5, speed 0.7 micron/min., scale 2 cm./micron, slightly less than normal gain to suppress noise and 50% attenuation (1 cm./10% transmission). Paper calibrated in absorbance was used and values were read directly from the curves.

Reduction of Myrcene Hydroperoxide.—A portion (1.00 g.) of the 96% hydroperoxide was hydrogenated in a conventional quantitative hydrogenator at 25° using 25 mg. of platinum oxide as the catalyst. Two moles of hydrogen per mole was absorbed in 2.5 hours, an additional 0.7 mole per mole was absorbed during the next 3 hours and a total of 2.81 moles after 20 hours. The ethyl acetate was removed under vacuum at *ca.* 50° and the product was steam distilled and isolated by ether extraction. The infrared spectral characteristics are given in Table III (alcohol 2).

A sample of myrcene hydroperoxide (26 g. of 80% purity) was reduced by stirring it at room temperature with 1.75 g. of $NaBH_4$ dissolved in 15 ml. of ethanol and 10 ml. of water for about 16 hours. The product (10 g.) was isolated by adding water, extracting with ether and distilling at 0.1 mm. after removal of the ether. This is "alcohol 1" in Table 3. This product, which was water-white, had $n^{20}D$ 1.4857. Distillation through a 6-inch long column packed with protruded nickel at 0.2 mm. gave fractions boiling from 47 to 74° with only slight separation of isomers. With increasing boiling point absorbance at 10.26 μ decreased from 0.70 to 0.50 while absorbance at 6.05 μ increased from 0.16 to 0.28.

Tetrahydromyrcene Hydroperoxide.—Tetrahydromyrcene (2.25 g.) containing 6 mg. of crude chlorophyll per gram was illuminated with three 300 watt lamps and oxidized in the usual way. It absorbed 0.85 mole of oxygen per mole in 54 minutes, at which time the rates decreased rapidly and the reaction was stopped. The product contained 0.82 mole of hydroperoxide per mole. Removal of unoxidized material left a residue having a peroxide number of 12,400 (theory is 11,600 for the monohydroperoxide) and characteristic infrared absorption at 11.1 μ — baseline-corrected absorbance (A) = 0.74, 10.30 μ — A = 0.74, 8.8 μ — A = 0.43, 6.07 μ — A = 0.15, and 2.95 μ — A = 1.23.

OLUSTEE, FLA.

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[11] Trade names are given as experimental detail and do not constitute recommendation of these instruments over any other.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

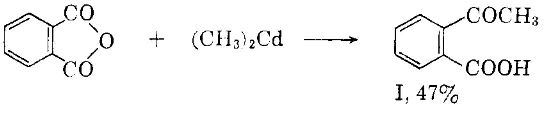
Investigation of an Abnormal Organocadmium Reaction[1]

BY PAUL R. JONES AND STEPHEN L. CONGDON

RECEIVED FEBRUARY 2, 1959

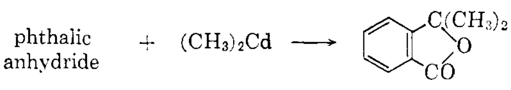
The reaction of the methylcadmium reagent with phthalic anhydride has been investigated with regard to the reaction time and the nature and quantity of the organometallic reagent. The expected product, *o*-acetylbenzoic acid (I), predominates in reactions of relatively short duration, while the formation of 3,3-dimethylphthalide (II) is enhanced with an increase in time or quantity of cadmium compound. I is relatively inert toward the methylcadmium reagent except during a prolonged reflux period. These results are consistent with the conclusion that I exists, under the conditions of this reaction, not as the ring tautomer (3-methyl-3-hydroxyphthalide) but as the open chain ketoacid. Infrared spectra of I in various media serve to corroborate this point of view.

Acid anhydrides, as well as acid chlorides, are generally considered to be convenient starting materials for the preparation of ketones by means of an organocadmium reaction.[2] de Benneville[3] has described the synthesis of a series of *o*-acylbenzoic acids from phthalic anhydride and the appropriate alkyl- or arylcadmium compound, yields ranging from 47 to 67%. Dimethylcadmium, for example, leads to *o*-acetylbenzoic acid (I).



I, 47%

In striking contrast to these results, it was later reported that dimethylcadmium, when used in excess, converted phthalic anhydride to 3,3-dimethylphthalide (II) in 60% yield.[4]



II, 60%

In an attempt to reconcile these two conflicting reports, we have investigated the nature of the products from the interaction of phthalic anhydride and the methylcadmium reagent with variation in the time and the nature and quantity of the cadmium compound. The results, given in Table II (Experimental section), are consistent with several conclusions. Both *o*-acetylbenzoic acid (I) and 3,3-dimethylphthalide (II) are formed even when the reaction time is relatively short; but the amount of II, by comparison with I, is increased

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[1] This work was generously supported by a Frederick Gardner Cottrell grant from the Research Corporation of New York.

[2] J. Cason, *Chem. Revs.*, **40**, 15 (1947).

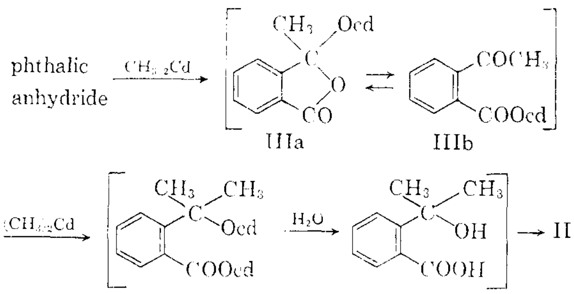
[3] P. L. de Benneville, *J. Org. Chem.*, **6**, 462 (1941).

[4] C. H. Wang, R. Isensee, A. M. Griffith and B. E. Christensen, THIS JOURNAL, **69**, 1909 (1947).

as the time is lengthened. For example, after six hours, the yield ratio of II:I was 0.5, while the same ratio after one-half hour was 0.02. When the reaction time was extended to seventeen hours, II was the only isolable product.

A differentiation is made in the present work between "dimethylcadmium" and "monomethylcadmium chloride" on the basis of the stoichiometry of their formation. While such a distinction may be artificial, since little attention has been given to the relative stabilities of the two species, there is an apparent difference in their reactivities with phthalic anhydride. The highest conversion to products was achieved with two equivalents of monomethylcadmium chloride rather than with one equivalent of dimethylcadmium. As might be expected, the use of one equivalent of monomethylcadmium chloride led to the formation of I as the only product. The superior reactivity of the latter reagent may be a purely mechanical phenomenon, however, for when it was employed, the mixture remained sufficiently fluid so that stirring could be maintained throughout the reaction period. This is to be contrasted with the mechanical difficulties usually encountered in organocadmium reactions.[2]

It might be concluded from the experimental results that the salt of I (IIIa ar IIIb) is formed rapidly from phthalic anhydride and converted less readily, in the presence of additional cadmium reagent, to the lactone II. The reaction could be represented by the following series of transformations. According to this scheme, compound I would be formed by hydrolysis of IIIa or IIIb.



("cd" = 1/2 Cd or its equivalent)

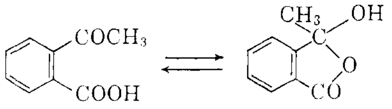
If the salt of *o*-acetylbenzoic acid IIIb were indeed an intermediate in the formation of II, this reaction would be a striking exception to the generalization that aldehydes and ketones are relatively inert toward organocadmium reagents. By comparison, benzaldehyde, when placed in a sealed tube with diethylcadmium for five months, was converted to the corresponding carbinol in only 32% yield.[5]

In order to test the above conclusion, we have subjected *o*-acetylbenzoic acid to the action of the methylcadmium reagent (Table III). Under conditions that led to formation of the lactone II from phthalic anhydride, the acid I is clearly unreactive. In fact, after being heated with an excess of cadmium compound for six hours, compound I was recovered to the extent of 93%.

Consequently it is highly likely that the initial product from anhydride, which is undoubtedly IIIa, is not identical to the salt formed by treatment of I with the methylcadmium reagent. The suggestion is therefore advanced that the structure of the salt from I is IIIb, which, unlike IIIa, is relatively inert toward reaction with additional dimethylcadmium or monomethylcadmium chloride; and it follows from this that there is not a rapid equilibrium between IIIa and IIIb.

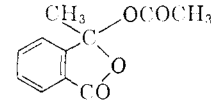
The details of the transformation of IIIa to II without participation of IIIb are not clear. Since no intermediate could be intercepted when acetyl chloride was added to a reaction mixture from phthalic anhydride and methylmagnesium iodide, it is possible that the unstable hydroxyacid corresponding to II is not involved in the reaction, and the product is a result of direct displacement on IIIa.

Because the cadmium salt formed from I and the first equivalent of organocadmium reagent is IIIb and not IIIa, it seems likely that I reacts as the chain tautomer Ia rather than the ring tautomer Ib.



Ia Ib

Grove and Willis have previously concluded, on the basis of infrared spectroscopy, that *o*-acetylbenzoic acid exists predominantly as Ib in the solid state.[6] Our own infrared data, however, are better accommodated by structure Ia, which is consistent with the chemical evidence. In three determinations in different media, solid *o*-acetylbenzoic acid exhibits two bands in the carbonyl region rather than one. The one at highest frequency is found at 1735 cm.$^{-1}$, which is in good agreement with that reported by Grove and Willis (1732 cm.$^{-1}$). This value seems unusually low to be attributed to a five-membered lactone; by comparison, the corresponding band in the spectrum of 3-acetoxy-3-methylphthalide (IV) is found at 1780 cm.$^{-1}$ in the same medium.



IV

Although Grove and Willis attribute the low carbonyl band for Ib to a bathochromic shift exerted by the 3-OH group, we suggest the spectra are consistent with the assignment of structure Ia for *o*-acetylbenzoic acid and that it exists primarily as monomer rather than dimer. Thus the band at about 3300 cm.$^{-1}$ and the higher of the two carbonyl bands may be attributed to monomeric-COOH on the basis of values previously reported for this functional group.[7] The remaining carbonyl band can be ascribed to the ketone function on the assumption, previously suggested,[8] that an

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(5) H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

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

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 140.

(8) P. R. Jones, *J. Org. Chem.*, **23**, 1386 (1958).

TABLE I

INFRARED SPECTRA OF *o*-ACETYLBENZOIC ACID

Medium	Bands, cm.$^{-1}$	
Nujol	3280	1735 (sh.)
		1725
Halocarbon	3280	1735 (sh.)
		1725
KBr	3250	1725 (broad)
		1685 (sh.)
5% $CHCl_3$	3570	1755 (broad)
	3350	1697
5% dioxane	3320	1770
1% diethyl ether	3320	1726
		1710

TABLE II

Moles of Cd reagent	Nature of reagent	Time, hr.	Yield, %	
			Of I	Of II
1	$(CH_3)_2Cd$	1.5	33	17
1	$(CH_3)_2Cd$	1.5[b]	57	12
1	$(CH_3)_2Cd$	6	52	25
1	CH_3CdCl	1.5	18[a]	..
1	CH_3CdCl	1.5[b]	29	..
1	CH_3CdCl	1.5[b]	50	*ca.* 1
2	CH_3CdCl	0.5	51	1
2	CH_3CdCl	1.5	80	12
2	CH_3CdCl	17	..	34

[a] Phthalic anhydride recovered, 14%. [b] Duplicate experiments.

acyl or carboxy group in the *o*-position exerts an hypsochromic shift on the absorption of its neighboring substituent.

The spectrum of I in diethyl ether is of great interest because the cadmium reactions were carried out in this solvent. After correction is made for the strong absorption caused by ether itself, it is evident that there are at least two bands in the carbonyl region and one in the OH-stretching region. In dioxane solution, in which acids are very probably monomeric,[9] *o*-acetylbenzoic acid likewise exhibits a band at about 3300 cm.$^{-1}$ and one at 1770 cm.$^{-1}$. The latter is in good agreement with the value of 1760 cm.$^{-1}$ previously quoted as the mean value for the carbonyl stretching frequency of monomeric acids in dilute solution.[6]

It is interesting that *o*-benzoylbenzoic acid was assigned the normal keto structure by Newman and Muth,[10] while *o*-phthalaldehydic acid recently has been assigned the tautomeric ring structure in the solid state.[11] In the spectrum of the latter, determined in Nujol, there are also two carbonyl bands similar to those we found in the spectra of I. On the basis of our present results, we believe this acid should be considered as the open chain tautomer in the solid state.

In accord with its structure, *o*-benzoylbenzoic acid, like I, is unresponsive to the cadmium reagent, as evidenced by its recovery to the extent of 87%. Although diethylcadmium converts phthalic anhydride to *o*-propionylbenzoic acid, the yield of product is considerably lower than that from the methyl reagent under comparable conditions.

Experimental[12]

Action of Methylcadmium Reagent on Phthalic Anhydride.—The cadmium reagent was prepared, essentially as described by deBenneville[3] and others, by the addition of solid, anhydrous cadmium chloride to a solution of methylmagnesium iodide in 100 ml. of ether. The addition required 15 minutes, and stirring was continued for 30 minutes. This "formation time" of 45 minutes was not varied throughout the experiments. The Gilman test[13] for the presence of Grignard reagent was usually negative after the first 30 minutes. A slight excess of methyl iodide was employed, and either one or one-half molar equivalent of cadmium chloride was used. As indicated in Table II, the reagent was considered to be, respectively, "dimethylcadmium" or "monomethylcadmium chloride."

The reaction mixture was cooled by means of an ice-bath; solid phthalic anhydride (freshly sublimed) was added, with stirring, in several portions. The subsequent reflux period was varied as indicated in the table. Decomposition of the mixture was effected with dilute, aqueous sulfuric acid in excess. The ether layer was removed and combined with ether washings of the water layer. The organic phase was extracted with several portions of saturated, aqueous sodium carbonate. After the basic solution had been acidified, it was refrigerated. The *o*-acetylbenzoic acid separated as tiny clusters of needles, m.p. 114–115°. Additional fractions of acid were obtained by repeated concentration and cooling of the filtrate.

Anal. Calcd. for $C_9H_8O_3$: mol. wt., 164. Found: mol. wt. (Rast), 152, 173.

By removal of solvent from the ether layer solid 3,3-dimethylphthalide was obtained. It was recrystallized from cyclohexane in the form of colorless prisms, m.p. 69–70°. A mixture melting point with an authentic specimen showed no depression. The infrared spectrum (Nujol) contains a typically strong band at 1750 cm.$^{-1}$ attributable to a lactone carbonyl function.

Action of Ethylcadmium Reagent on Phthalic Anhydride.—Diethylcadmium reagent was prepared from 0.045 mole of magnesium, 0.058 mole of ethyl iodide and 0.026 mole of anhydrous cadmium chloride. It was treated with phthalic anhydride (0.024 mole) as previously described, and the mixture was heated under reflux, with stirring, for 6 hours. The only product isolated, in addition to a small amount of unchanged anhydride, was *o*-propionylbenzoic acid. After recrystallization from ligroin it was in the form of fine, white needles, m.p. 85.0–85.3°, yield 0.6 g. (14%).

Action of Methylcadmium Reagent on *o*-Acetylbenzoic Acid.—The preparation of the cadmium reagent was carried out as described in the reactions with phthalic anhydride. Solid *o*-acetylbenzoic acid was added in several portions to the mixture, cooled by means of an ice-bath, in 15 to 20 minutes. Stirring was continued throughout the reaction period, and the mixture was decomposed and worked up as described above. Results of several experiments are presented in Table III.

TABLE III

Moles of Cd reagent	Nature of reagent	Time, hr.	Yield of II, %	Recovery of I, %
1	$(CH_3)_2Cd$	6[a]	4	76
2	$(CH_3)_2Cd$	2[b]	6	58
1	$(CH_3)_2Cd$	17.5[a]	46[c]	..
2	CH_3CdCl	1.5[b]	..	85
2	CH_3CdCl	6[a]	..	93

[a] Mixture heated at reflux temperature. [b] Mixture stirred at room temperature. [c] A mixture of unidentified oils was obtained in addition.

3-Methyl-3-phenylphthalide.—To a cold slurry of dimethylcadmium, prepared in ether from 0.09 mole of magnesium, 0.116 mole of methyl iodide and 0.051 mole of anhydrous cadmium chloride, was added 0.048 mole of solid, anhydrous *o*-benzoylbenzoic acid in several portions.

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(9) M. S. C. Flett, *J. Chem. Soc.*, 962 (1951).

(10) M. S. Newman and C. W. Muth, THIS JOURNAL, **73**, 4627 (1951).

(11) D. D. Wheeler, D. C. Young and D. S. Erley, *J. Org. Chem.*, **22**, 547 (1957).

(12) Infrared spectra were determined with a Perkin-Elmer model 21 recording double-beam spectrophotometer with sodium chloride optics. The combustion analysis was performed by Galbraith Laboratories, Knoxville, Tenn. All melting points are uncorrected.

(13) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

The mixture was heated under reflux for 6 hr., and decomposed with dilute HCl; the ether layer was separated and combined with ether washings of the water layer. The organic layer was washed with saturated, aqueous potassium carbonate, dried over magnesium sulfate and concentrated. By repeated extraction of the residual oil with hot ligroin and concentration of the extract, 3-methyl-3-phenylphthalide, m.p. 75–77°, was obtained. It was recrystallized from ligroin in the form of white needles, m.p. 76–77°, yield 0.6 g. (5.6%). The melting point of 3-methyl-3-phenylphthalide has been reported[14] as 80–81°. The infrared spectrum (KBr) contains a lactone carbonyl band at 1765 cm.$^{-1}$. By acidification of the potassium carbonate solution, there was obtained 10.15 g. (87% recovery) of *o*-benzoylbenzoic acid monohydrate.

Action of Diphenylcadmium on *o*-Acetylbenzoic Acid.—Powdered *o*-acetylbenzoic acid (0.018 mole) was added in five minutes, with stirring, to a cold slurry of diphenylcadmium, prepared in ether from 0.034 mole of magnesium, 0.044 mole of bromobenzene and 0.019 mole of anhydrous cadmium chloride. The ice-bath was removed and the mixture heated under reflux, with stirring, for 6 hr. When the mixture was decomposed and worked up as previously described, 2.0 g. (68% recovery) of *o*-acetylbenzoic acid was isolated. The small amount of neutral, oily product obtained did not contain any 3-methyl-3-phenylphthalide, since it was miscible in all proportions with ligroin.

Attempted Isolation of 2-Carboxy-α,α-dimethylbenzyl Acetate.—The Grignard reagent was prepared from magnesium (0.09 mole) and methyl iodide (0.116 mole) in 100 ml. of ether. The flask was cooled, and phthalic anhydride (0.048 mole) was added over a period of 15 minutes, with stirring. The mixture was heated under reflux, with stirring for 1.5 hr. The flask was cooled and acetyl chloride (0.1 mole) added in 20 minutes. After a reflux period of 15 minutes, 85 ml. of water was added. The two layers were separated, and ether washings of the water layer were combined with the ether layer. The ether phase was washed with a 20% potassium carbonate solution and, when concentrated, deposited 3,3-dimethylphthalide (5.8 g., 75%). The basic solution was acidified with 20% sulfuric acid and the solution extracted with ether. No product was found on evaporation of the solvent.

In a second experiment, in which the acetyl chloride was added very rapidly, the only product found was 3,3-dimethylphthalide (4.2 g., 54%).

3-Acetoxy-3-methylphthalide, Method A.—Two grams of *o*-acetylbenzoic acid was mixed with 1.0 g. of powdered, fused, sodium acetate and 10 ml. of acetic anhydride. The mixture was heated on a steam-bath for 3 hr. and then poured into 60 ml. of ice-water. The mixture was allowed to stand, with occasional stirring, until the excess acetic anhydride had been hydrolyzed. The precipitate was collected on a filter and then mixed with hot potassium carbonate solution. The mixture was cooled and extracted repeatedly with ether. The solid material remaining after evaporation of the ether was recrystallized four times from *n*-heptane, m.p. 68.5–69.5°. The infrared spectrum (Nujol mull) contains carbonyl bands at 1780 and 1745 cm.$^{-1}$, attributable, respectively, to lactone and unconjugated ester functions. The typical hydroxyl and carboxyl bands are absent.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89. Found: C, 63.88; H, 4.82.

Method B.—A solution of 2 g. of *o*-acetylbenzoic acid, 8 g. of acetic anhydride and 20 ml. of anhydrous pyridine was heated under reflux for 5 minutes. It was poured into 60 ml. of ice-water and the precipitate collected on a filter. The crude product, m.p. 63–65°, was recrystallized twice from 95% ethanol, m.p. 68–69°. A mixture melting point with the 3-acetoxy-3-methylphthalide obtained from method A showed no depression.

DURHAM, N. H.

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[14] J. Tirouflet, *Bull. soc. sci. Bretagne*, No. **26**, 63 (1951); *C. A.* **47**, 8694 (1953).

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

The Chemistry of Derivatives of 2-Benzaltetralone. IV.[1] The Synthesis, Spectra and Ring Cleavage Reactions of Some Spiroepoxyketones

BY NORMAN H. CROMWELL, RONALD E. BAMBURY AND RAYMOND P. BARKLEY

RECEIVED FEBRUARY 5, 1959

Several 2-benzal-1-tetralone oxides have been obtained either by the epoxidation of various 2-benzal-1-tetralones or from a Darzens type condensation of a 2-bromo-1-tetralone and an aromatic aldehyde. The ultraviolet and infrared spectra of these new compounds are reported in connection with a discussion of their stereo structures and conjugation factors. These spiroepoxy ketones were found to be resistant to ring cleavage by bases while acid-catalyzed reactions with hydrogen chloride and methanol were realized. The rearrangement of 2-benzal-4,4-dimethyl-1-tetralone oxide to 2-benzoyl-4,4-dimethyl-1-tetralone with sodium amide constitutes a new base-catalyzed rearrangement of epoxyketones to 1,3-diketones.

In previous investigations[2,3] in this Laboratory it was found that spiroepoxyketones were readily obtained by the direct epoxidation[4] of 2-benzal-1-tetralones, or by a Darzens type condensation[5] of 2-bromo-1-tetralones with aromatic aldehydes. These methods have now been employed to prepare a series of these interesting compounds for a continuation of our studies of the stereochemistry of epoxyketones.[6]

The necessary 2-benzal-1-tetralones were obtained in good yields from the condensation of various aromatic aldehydes with 1-tetralone and 4,4-dimethyl-1-tetralone, employing base[2] or acid[7] catalysis. A comparison of the ultraviolet and infrared absorption spectra of these new 2-benzal-1-tetralones, reported in the Experimental section, with the spectra of analogous *trans*-chalcones[8] and the previously reported 2-benzal-1-tetralones,[2] clearly indicates that these new compounds should be assigned an exocyclic α,β-unsaturated ketone structure, with the substituted β-phenyl groups *trans* to the carbonyl group.

In general there are two or three ultraviolet absorption maxima which are associated with compounds of the chalcone type. The shortest wave length bands (below *ca.* 240 mμ) are due to second-

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[1] For paper III, see A. Hassner and N. H. Cromwell, THIS JOURNAL, **80**, 901 (1958).

[2] A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958).

[3] A. Hassner, N. H. Cromwell and S. J. Davis, *ibid.*, **79**, 230 (1957).

[4] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

[5] S. Bodforss, *ibid.*, **51**, 192 (1918).

[6] For our previous papers in this field see, N. H. Cromwell and R. A. Setterquist, THIS JOURNAL, **76**, 5752 (1954), and references cited therein.

[7] V. L. Bell and N. H. Cromwell, *J. Org. Chem.*, **23**, 789 (1958).

[8] (a) For example see ref. 2 and 6, and (b) W. Black and R. Lutz, THIS JOURNAL, **77**, 5134 (1955).