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

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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).

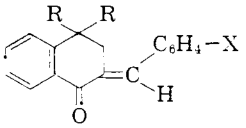
[4] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

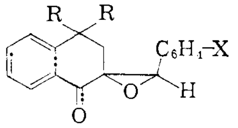
[5] S. Bodforss, *ibid.*, **51**, 192 (1918).

[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).





Ia	R, H; X, *p*-Cl	IVa
b	R, CH_3; X, *p*-Cl	b
IIa	R, H; X, *m*-NO_2	Va
b	R, CH_3; X, *m*-NO_2	b
IIIa	R, H; X, *p*-NO_2	VIa
b	R, CH_3; X, *p*-NO_2	b
VIIa	R, H; X, *o*-NO_2	VIIIa
b	R, CH_3; X, *o*-NO_2	b

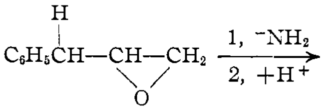
ary absorption of the main chromophore, the middle wave length bands (250–270 mμ) are probably due to an independent chromophore (benzoyl or acrylophenone group) while the main chromophoric group absorbs usually above 280 mμ.[8b] The main chromophoric group may be either the cinnamoyl portion of the molecule or the molecule as a whole.[2,8b]

The six benzaltetralones, Ia, Ib, IIa, IIb, IIIa and IIIb all have a strong ultraviolet absorption band between 280 and 314 mμ and no bands in the 250–270 mμ region of the spectrum, showing the relationship of these structures to that of the related *trans*-chalcones. On the other hand, the benzaltetralones VIIa[2] and VIIb have only weak shoulders between 308 and 318 mμ with major bands at 272–273 mμ. It is probable that these major bands are due to an acrylophenone chromophore just as is the case for *trans*-*o*-nitrochalcone. Steric inhibition of resonance caused by the *o*-position of the nitro group in these compounds prevents the cinnamoyl chromophore from engaging in strong absorption. In the infrared spectrum carbonyl stretching bands were found for all of these compounds which were comparable with those of the parent 2-benzal-1-tetralone[2] and 2-benzal-4,4-dimethyl-1-tetralone[2] (*i.e.*, between 1667–1676 cm.$^{-1}$).

The spiroepoxides IVa, IVb, Va, Vb, VIa, VIb and VIIIa were all produced by an alkaline hydrogen peroxide epoxidation of the corresponding benzaltetralones while VIIIb was obtained from a Darzens type condensation of 2-bromo-4,4-dimethyl-1-tetralone with *o*-nitrobenzaldehyde. The ultraviolet spectra of these epoxides were all quite similar, with a maximum between 258 and 268 mμ and often an inflection of low intensity between 295 and 305 mμ. A comparison of these results with the spectra which have been reported for the chalcone oxides[6,9] and for the parent 2-benzal-1-tetralone oxides[2,3] suggests that three-ring carbonyl hyperconjugation takes place in the excited state of these molecules. All of these spiroepoxyketones probably have a *trans* configuration[2] (side chain aromatic group *trans* to the carbonyl). These spiroepoxyketones showed a relatively high frequency carbonyl stretching vibration in their infrared spectra between 1687 and 1697 cm.$^{-1}$. This indicates, as has been pointed out previously,[6] that the epoxide ring does not interact electrically with the attached carbonyl group through hyperconjugation in the ground state.

The epoxide ring in these spiroepoxyketones was found to be remarkably resistant to ring cleavage by basic reagents, such as amines or sodium methoxide, even after considerable heating. It has been shown that *trans*-chalcone oxide[10] reacts readily with heterocyclic secondary amines through an S$_N$2 type of attack at the β-carbon atom to produce β-amino-α-hydroxyketones. An examination of models indicates that a backside attack by a nucleophilic reagent at the β-carbon atom in these spiroepoxyketones would be subject to considerable steric crowding. It was found previously[10] that the reaction of *trans*-chalcone oxide with amines was quite sensitive to the steric requirements of the attacking reagent (*i.e.*, diethylamine would not react).

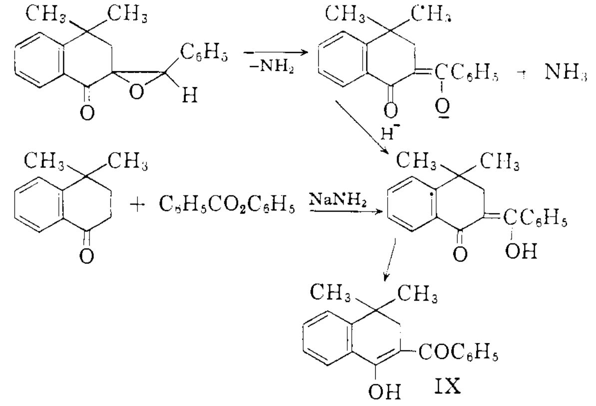
Sodium amide has not been employed often in reactions with epoxides. Haynes[11] treated 1,2-epoxy-3-phenylpropane with sodium amide in liquid ammonia to obtain cinnamyl alcohol, the apparent mechanism being an attack on a benzyl hydrogen by the amide ion and a subsequent rearrangement of the carbonion formed.



$$\overset{H}{\mathrm{C_6H_5CH}}-\underset{\diagdown\ \mathrm{O}\ \diagup}{\mathrm{CH-CH_2}} \xrightarrow[2,\ +H^+]{1,\ ^-NH_2}$$

$$NH_3 + C_6H_5CH{=}CHCH_2OH$$

Recently Cope and co-workers[12] have reported on the rearrangement of some epoxides with a strong base, lithium diethylamide, in which carbanions seem to be involved. 2-Benzal-4,4-dimethyl-1-tetralone oxide rearranged to 2-benzoyl-4,4-dimethyl-1-tetralone (IX) when refluxed with a benzene solution of sodium amide. A possible course for this rearrangement would involve a carbanion mechanism and further studies with other epoxyketones are being carried out.



The base-catalyzed rearrangement of the epoxides of α,β-unsaturated ketones having an α-hydrogen usually leads to 1,2-diketones.[13] Since the benzaltetralone oxides have no α-hydrogen available for such a change it is not surprising that a β-hydrogen is removed instead, even though it may be somewhat less acidic. The formation of the 1,3-diketone appears to be the most facile change available to the resulting carbanion.

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[9] H. H. Wasserman and N. E. Aubrey, THIS JOURNAL, **77**, 590 (1955).

[10] N. G. Barker and N. H. Cromwell, *ibid.*, **73**, 1051 (1951).

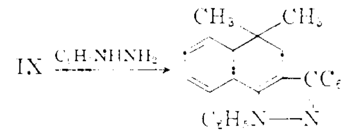
[11] L. J. Haynes, *et al.*, *J. Chem. Soc.*, 1583 (1947).

[12] A. C. Cope, P. A. Trumbull and E. R. Trumbull, THIS JOURNAL, **80**, 2844 (1958).

[13] S. Winstein in Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, Vol. 1, p. 52.

The general nature of this rearrangement product IX was established by a comparison of its physical properties with an authentic sample of 2-benzoyl-4,4-dimethyl-1-tetralone which was prepared by a modification of the procedure used by Hauser[14] to prepare 2-benzoyl-1-tetralone. The infrared spectra of IX, prepared by these two methods, were superimposable and indicated extensive chelated conjugation,[15] similar to that found for dibenzoylmethane. It seems probable that this compound in carbon tetrachloride exists mainly as the enol tautomer as implied by structure IX.

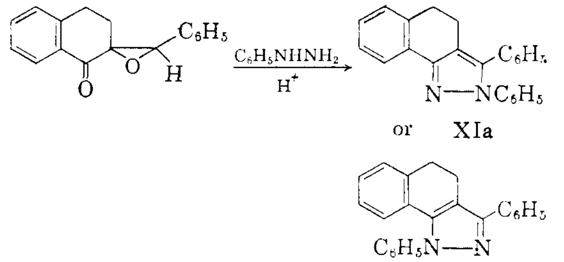
The 1,3-diketone enol IX reacted normally with phenylhydrazine to produce a pyrazole which is tentatively assigned structure X on the basis of the assumed structure for the enol IX and the expected course of such reactions.[16]



X

The ultraviolet absorption spectra of X showed a strong peak at 262 mμ and is quite similar to the spectra of 1,3,5-triarylpyrazoles previously studied.[17]

2-Benzal-1-tetralone oxide reacted with phenylhydrazine to produce a product which has an elemental analysis and ultraviolet absorption spectrum which suggests[17] that it is a 1,3,5-triarylpyrazole, of structure XIa or possibly XIb.

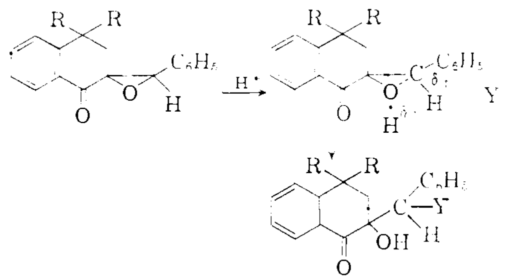


or XIa

XIb

Because of the resistance of the epoxide ring in these spiroepoxyketones to SN2 attack by bases, attention was turned to acid-catalyzed ring cleavages in which SN1 type mechanisms might be available and expected to involve a less sterically crowded partially positive β-carbon atom. Ionization should take place most readily at the β-carbon atom since the α-carbon to oxygen bond should be the stronger bond, and, moreover, the partial positive charge should be most readily supported at the β-carbon atom in the transition state by resonance with the β-aryl group.[18]

2-Benzal-4,4-dimethyl-1-tetralone oxide reacted with dry hydrogen chloride in an ether–benzene mixture or ethanol solution to give a halohydrin which is assigned structure XII. The halohydroxyketone gave no release of iodine from an acidified potassium iodide solution, a reaction expected for α-haloketones.[19] Treatment of the halohydrin XII with bases converted it to an epoxyketone identical with the precursor of XII. This result indicates that ring cleavage involves a transition state in which the ring oxygen atom maintains steric control at the β-carbon atom with the chlorine ion attacking this position with inversion. It does not necessarily follow, however, that the cleavage is an SN2 reaction. These studies are being continued. A similar reaction has been discussed in detail for the ethylenimine ketones.[18]



XII, R, CH_3; Y, Cl
XIII, R, H; Y, OCH_3
XIV, R, CH_3; Y, OCH_3

The ultraviolet and infrared absorption spectra of XII are in agreement with this structural assignment. The infrared spectrum in carbon tetrachloride showed an OH band at 3530 cm.$^{-1}$, and also one at 3480 cm.$^{-1}$, and a broad carbonyl band (1680–1695 cm.$^{-1}$) which implied hydrogen bonding of the α-hydroxyl group with the ketone carbonyl. At reduced concentrations in carbon tetrachloride this broad carbonyl band was resolved into a band at 1690 cm.$^{-1}$ with a shoulder at 1682. In chloroform solution external hydrogen bonding with the solvent changed the carbonyl band into a single, strong symmetrical band at 1687 cm.$^{-1}$.

Both 2-benzal-1-tetralone oxide and 2-benzal-4,4-dimethyl-1-tetralone oxide reacted at room temperature with methanol containing a small amount of sulfuric acid to produce the 2-hydroxy-2-(α-methoxybenzyl)-1-tetralone, XIII and XIV, respectively. The odor of benzaldehyde in these reaction mixtures indicated that some more extensive reaction than simple ring cleavage also occurs. The ultraviolet and infrared spectra of XIII and XIV were quite similar. The infrared spectra of both compounds showed OH bands between 3570 and 3530 cm.$^{-1}$ and between 3515 and 3480 cm.$^{-1}$, and split carbonyl bands at 1690–1680 and 1677 cm.$^{-1}$. These studies seem to indicate that carbonyl-hydroxyl hydrogen bonding takes place with these compounds in carbon tetrachloride solution. The assignment of the structures XIII and XIV to these hydroxymethoxyketones is mainly based upon the elemental analysis, the absorption spectra and the expected course of such reactions.[20] The more extensive change which produces some benzaldehyde in these reactions is under further investigation in this Laboratory.

Acknowledgment.—This investigation was supported in part by a grant from the National Cancer Institute, U. S. Public Health Service, CY 2931.

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[14] C. R. Hauser, *et al.*, THIS JOURNAL, **69**, 2649 (1947).

[15] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *ibid.*, **71**, 1068 (1949).

[16] N. H. Cromwell and G. D. Mercer, *ibid.*, **79**, 3819 (1957).

[17] N. H. Cromwell and H. Hoeksema, *ibid.*, **71**, 716 (1949).

[18] See N. H. Cromwell, *et al.*, *ibid.*, **75**, 5384 (1953), who studied hydrogen chloride ring cleavage reactions with the related ethylenimine ketones.

[19] N. H. Cromwell and R. A. Wankel, *ibid.*, **70**, 1320 (1948).

[20] W. Baker and R. Robinson, *J. Chem. Soc.*, 1798 (1932).

Experimental[21]

Substituted 2-benzal-1-tetralones were prepared either by an acid-catalyzed condensation[7] (method A) or a base-catalyzed condensation[2] (method B) of the substituted benzaldehyde with 1-tetralone or 4,4-dimethyl-1-tetralone.[7]

2-(*p*-Chlorobenzal)-1-tetralone (Ia), method **B**, 97% yield, m.p. 138–139°, recrystallized from benzene and 60–70° b.p. petroleum ether; λ_{max} 231, 310 mμ (ϵ 12,800, 18,400); $\gamma_{C=O}$ 1673/93, $\gamma_{ArC=C}$ 1605–1610/89.

Anal. Calcd. for $C_{17}H_{13}OCl$: C, 75.98; H, 4.88. Found: C, 76.08; H, 5.08.

2-(*p*-Chlorobenzal)-4,4-dimethyl-1-tetralone (Ib), method **B**, 98% yield, m.p. 136–137°, recrystallized from benzene and petroleum ether; λ_{max} 233, 287(sh), 314 mμ (ϵ 13,200, 11,000, 14,800); $\gamma_{C=O}$ 1674/85, $\gamma_{ArC=C}$ 1605–1610/80.

Anal. Calcd. for $C_{13}H_{17}OCl$: C, 76.89; H, 5.77. Found: C, 76.96; H, 5.76.

2-(*m*-Nitrobenzal)-1-tetralone (IIa), method **B**, 71% yield, m.p. 142–143°, recrystallized from benzene and ethanol; λ_{max} 281 mμ (ϵ 21,700); $\gamma_{C=O}$, 1674/71 (1660/68 in Nujol), $\gamma_{ArC=C}$ 1600–1610/51 (1610/58 in Nujol).

Anal. Calcd. for $C_{17}H_{13}O_3N$: C, 73.11; H, 4.69. Found: C, 72.90; H, 4.79.

2-(*m*-Nitrobenzal)-4,4-dimethyl-1-tetralone (IIb), method **B**, 96% yield, m.p. 93–94.5°, recrystallized from benzene and petroleum ether; λ_{max} 280 mμ (ϵ 21,000); $\gamma_{C=O}$ 1675/85 (1685/30 in Nujol), $\gamma_{ArC=C}$ 1600/70 (1595/25 in Nujol).

Anal. Calcd. for $C_{19}H_{17}O_3N$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.65; H, 5.63; N, 4.66.

2-(*p*-Nitrobenzal)-1-tetralone (IIIa), method **B**, 63% yield, m.p. 192–193°, recrystallized from a benzene–ethanol solution; λ_{max} 310 mμ (ϵ 21,300); $\gamma_{C=C}$ 1665/63 (in Nujol), 1667/56 (in dioxane), $\gamma_{ArC=O}$ 1595–1615/60 (in Nujol), 1597–83 (in dioxane).

Anal. Calcd. for $C_{17}H_{13}O_3N$: C, 73.11; H, 4.69. Found: C, 73.15; H, 4.97.

2-(*p*-Nitrobenzal)-4,4-dimethyl-1-tetralone (IIIb), method A, 94% yield, m.p. 183–184°, recrystallized from acetone and water; λ_{max} 313 mμ (ϵ 20,200); $\gamma_{C=O}$ 1675/70 (1660/45 in Nujol), $\gamma_{ArC=C}$ 1660/65, 1610/40 (in Nujol). Attempts to prepare this unsaturated ketone by method **B** were not successful.

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 74.25; H, 5.58. Found: C, 74.21; H, 5.64.

Substituted 2-Benzal-1-tetralone oxides were prepared either by the epoxidation of the corresponding 2-benzal-1-tetralone with alkaline hydrogen peroxide, method C,[2,4] or by means of a Darzens type condensation of the substituted benzaldehyde with the required 2-bromo-1-tetralone, method D.[2,5]

2-(*p*-Chlorobenzal)-1-tetralone oxide (IVa), method C, 97% yield, m.p. 137–138°, recrystallized from benzene–methanol and then benzene and petroleum ether, λ_{max} 258, 304(sh) mμ (ϵ 17,300, 2,400); $\gamma_{C=C}$ 1694/93, γ_{ar} 1604/67.

Anal. Calcd. for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60; Cl, 12.45. Found: C, 71.85; H, 4.69; Cl, 12.41.

2-(*p*-Chlorobenzal)-4,4-dimethyl-1-tetralone oxide (IVb), method C, 91% yield m.p. 156–157°, recrystallized from benzene and petroleum ether; λ_{max} 260, 296 (sh), mμ (ϵ 17,300, 3,000); $\gamma_{C=O}$, 1693/85, γ_{Ar} 1603/55.

Anal. Calcd. for $C_{19}H_{17}O_2Cl$: C, 72.96; H, 5.48. Found: C, 73.00; H, 5.46.

2-(*m*-Nitrobenzal)-1-tetralone oxide (Va), method C (30% hydrogen peroxide added to reaction mixture over a 90-minute period), 76% yield, m.p. 152–153°, recrystallized from benzene–ethanol solution; λ_{max} 259, 305 (sh) mμ (ϵ 21,500, 3,300); $\gamma_{C=O}$ 1695/62 (1681/56 in Nujol) (1687/56 in dioxane), γ_{Ar} 1603/30 (1602/34 in Nujol) (1605/58 in dioxane).

Anal. Calcd. for $C_{17}H_{13}O_4N$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.21; H, 4.63; N, 4.58.

2-(*m*-Nitrobenzal)-4,4-dimethyl-1-tetralone oxide (Vb), method C, 99% yield, m.p. 200–201, recrystallized from benzene and petroleum ether; λ_{max} 258, 297 mμ (ϵ 24,400, 3,600); $\gamma_{C=O}$ 1693/30 (satd. CCl_4 soln.) (1670/70 in Nujol), γ_{Ar} 1595/55 (in Nujol).

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 70.57; H, 5.30. Found: C, 70.89; H, 5.51.

2-(*p*-Nitrobenzal)-1-tetralone Oxide (VIa).—The usual conditions of method C gave only traces of product. To 2.0 g. (0.00716 mole) of IIIa in 350 ml. of a warm mixture of methanol and isopropyl alcohol was added dropwise a mixture of 7 ml. of 6.5% methanolic sodium hydroxide and 45 ml. of 30% hydrogen peroxide over a 6-hour period. Neutralization of this solution with dil. hydrochloric acid and dilution with cold water produced an oil which was crystallized from benzene and ethanol, m.p. 195–196°, in 75% yield; λ_{max} 264 mμ (ϵ 20,700); $\gamma_{C=O}$ 1685/87 (in Nujol) (1687/90 in dioxane), γ_{Ar} 1602/76 (in Nujol) (1603/67 in dioxane).

Anal. Calcd. for $C_{17}H_{13}O_4N$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.41; H, 4.58; N, 4.91.

2-(*p*-Nitrobenzal)-4,4-dimethyl-1-tetralone Oxide (VIb).—This spiro epoxide was not obtained by the usual conditions of method C. To a hot solution of one liter of methanol containing 3.06 g. (0.009 mole) of IIIb was added 0.9 g. of potassium hydroxide dissolved in 100 ml. of methanol and then 55 ml. of 30% hydrogen peroxide. The solution was stirred for 4 hours at 55–60° and allowed to cool to room temperature overnight. Neutralization with hydrochloric acid and dilution with water produced a 94% yield of the oxide, m.p. 190–191°, recrystallized from benzene and petroleum ether; λ_{max} 268 mμ (ϵ 22,900); $\gamma_{C=O}$ 1697/55 (1675/20 in Nujol), γ_{Ar} 1600/40 (1600/15 in Nujol).

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 70.57; H, 5.30. Found: C, 70.88; H, 5.57.

2-(*o*-Nitrobenzal)-1-tetralone Oxide (VIIIa).—The conditions described for the *p*-nitro isomer VIa produced an 86% yield of this spiroepoxyketone VIIIa starting with 2-(*o*-nitrobenzal)-1-tetralone[2] (VIIa); m.p. 148–149°, recrystallized from benzene–ethanol; λ_{max} 258, 302(sh) mμ (ϵ 21,100, 4,500); $\gamma_{C=O}$ 1697/79, γ_{Ar} 1606/44.

Anal. Calcd. for $C_{17}H_{13}O_4N$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.36; H, 4.59; N, 4 60.

2-(*o*-Nitrobenzal)-4,4-dimethyl-1-tetralone Oxide (VIIIb).—Attempts to epoxidize the corresponding benzaltetralone (VIIb)[7] with hydrogen peroxide by method C returned only the starting material. A Darzens type reaction, method D, was successful. A 1.25-g. (0.005 mole) sample of 2-bromo-4,4-dimethyl-1-tetralone[2] and 0.76 g. (0.005 mole) of *o*-nitrobenzaldehyde were dissolved in 10 ml. of a 2:1 mixture of methanol and dioxane. Sodium (0.5 g.) dissolved in 7 ml. of methanol was added with stirring, keeping the temperature of the solution near 10°. After 10 min. the crystalline product which had formed was filtered and washed with water. Neutralization of the filtrate with 50% acetic acid produced an additional crop of solids, total wt. 1.6 g. (99% yield), m.p. 154–156°, recrystallized from benzene; λ_{max} 260, 297(sh) mμ (ϵ 20,300, 5,000); $\gamma_{C=O}$ 1695/65 (1680/70 in Nujol), γ_{Ar} 1597/65 (in Nujol).

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 70.57; H, 5.30; N, 4.33. Found: C, 70.47; H, 5.36; N, 4.64.

2-Benzal-1-tetralone Oxide and 2-Benzal-4,4-dimethyl-1-tetralone Oxide with Basic Reagents. A. With Amines.—Refluxing benzene solutions of these benzaltetralone oxides with 1–15 molar equiv. of piperidine, morpholine or cyclohexylamine gave only non-crystallizable red oils with 2-benzal-1-tetralone oxide[3] and returned the starting material in the case of 2-benzal-4,4-dimethyl-1-tetralone oxide[2] in 90% amounts. Likewise, anhydrous ammonia solutions in ethanol after standing for several days with these spiroepoxides returned only the starting materials. Also 2-benzal-4,4-dimethyl-1-tetralone oxide failed to react on refluxing a methanol solution with two molar equiv. of piperidine for 3.5 hr. Refluxing this spiroepoxyketone with only

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(21) Melting points are corrected. The ultraviolet spectra were determined between 200 and 400 mμ with a Cary ultraviolet recording spectrophotometer, model 11MS, employing matched 1-cm. fused silica cells and 10^{-4} molar methanol solutions of the compounds unless otherwise indicated. The measurements of the infrared spectra were determined with a Perkin–Elmer model 21 double-beam recording spectrophotometer employing sodium chloride optics over a frequency range of 4000 to 600 cm.$^{-1}$ using spectro grade solvents and matched 1-mm. sodium chloride cells for the solution studies, and recorded as γ, cm.$^{-1}$/approximate relative % absorption in CCl_4 solution unless otherwise indicated.

piperidine for 9 hours or allowing it to stand in cyclohexylamine at room temperature for 24 days returned only the starting material. Similar experiments with the *m*-nitro analogs Va and Vb and the *p*-chloro derivative IVa gave similar results.

B. With sodium methoxide, in methanol 90% of 2-benzal-4,4-dimethyl-1-tetralone oxide was recovered after 8 hours reflux.

C. With Sodium Amide (a Base-catalyzed Rearrangement).—A 2.8-g. (0.01 mole) sample of 2-benzal-4,4-dimethyl-1-tetralone oxide and 0.8 g. (0.02 mole) of finely ground sodium amide in 100 ml. of benzene were refluxed for 5.5 hours to produce a green colored solution. The reaction mixture was cooled and stirred with cold dilute hydrochloric acid. From the benzene layer was obtained 1.1 g. (40% yield) of a pale yellow product IX, m.p. 125.5–126.5°, recrystallized from benzene and petroleum ether; λ_{max} 353, 304, 293(sh), 247, 238(sh) mμ (ϵ 15,700, 6,000, 4,600, 9,600, 9,400) run in 2,2,4-trimethylpentane solution; $\gamma_{C=O}$ (chelated) 1613/90 (broad) (1610/35 broad in Nujol). *Anal.* Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.32. Found: C, 81.81; H, 6.57.

2-Benzoyl-4,4-dimethyl-1-tetralone (IX).—A modification of Hauser's[13] directions for 2-benzoyl-1-tetralone was employed. To a warm (50°), stirred benzene solution of 1.16 g. (0.0067 mole) of 4,4-dimethyl-1-tetralone was added 0.52 g. (0.013 mole) of sodium amide. After stirring this slurry for 15 minutes, 1.38 g. (0.007 mole) of phenyl benzoate in 25 ml. of benzene was added over an interval of 5 min. After refluxing the mixture for 4.5 hours it was mixed with cold dilute hydrochloric acid. From the benzene layer an oil was obtained which after crystallization from isopropyl alcohol and water and then ethanol and water gave 0.4 g. (21% yield), m.p. 125–130°; mixed with IX obtained from the epoxide rearrangement, m.p. 125–130°. The infrared spectra of this material in CCl_4 was superimposable on that of IX obtained from the rearrangement of the spiroepoxide.

Reaction of IX with Phenylhydrazine.—A 0.3-g. sample of IX was dissolved in 3 ml. of a 50-50 ethanol–chloroform mixture and one molar equivalent of phenylhydrazine and a drop of gl. acetic acid added. After standing at room temperature for 5 days, concentration of the reaction mixture gave 0.36 g. (93.5% yield) of the colorless pyrazole X, m.p. 132.5–134°, recrystallized from ethanol and water, λ_{max} 262, 282(sh), 292(sh), 302(sh) mμ (ϵ 22,400, 20,200, 18,000, 15,600), run in spectro grade 2,2,4-trimethylpentane. *Anal.* Calcd. for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.22; H, 6.21; N, 8.39.

Reaction of 2-Benzal-1-tetralone Oxide with Phenylhydrazine.—A 1.5-g. (0.006 mole) sample of the oxide was dissolved in 6 ml. of chloroform and 2 ml. of gl. acetic acid and 0.65 g. (0.006 mole) of phenylhydrazine added. After refluxing for 4 hours, the solution was washed with dilute hydrochloric acid and then sodium bicarbonate solution, dried and concentrated to produce an oil. Crystallization of the oil from benzene and petroleum ether and then gl. acetic acid gave 1.04 g. (53% yield) of the colorless crystalline pyrazole XI, m.p. 141.5–142°; λ_{max} 257, 277(sh), 298 mμ (ϵ 19,900, 17,700, 17,800).

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.87; H, 5.64; N, 8.82.

2-Benzal-1-tetralone Oxide and 2-Benzal-4,4-dimethyl-1-tetralone Oxide in Acidic Media. A. With Dry Hydrogen Chloride.—A 5.5-g. (0.02 mole) sample of 2-benzal-4,4-dimethyl-1-tetralone oxide was dissolved in 75 ml. of benzene and 50 ml. of ether and the cooled solution saturated with dry hydrogen chloride. After standing at room temperature for 12 hours the reaction mixture was washed with water and 5% sodium carbonate. After drying the solution over anhyd. magnesium sulfate, concentration produced 5.82 g. of the crude product, m.p. 140–160°. Recrystallization from benzene and petroleum ether gave 4.5 g. (71% yield), m.p. 164–165.5°, of the pure halohydrin XII; λ_{max} 253, 293 (broad) mμ (ϵ 13,300, 2,200); γ_{OH} 3530/21, 3480/24 (12 mg./l. ml. CCl_4); $\gamma_{C=O}$ 1680–1695/60 (12 mg./l. ml. CCl_4), 1690/67 and 1682(sh)/66 (6 mg./l. ml. CCl_4), 1687/85 (12 mg./l. ml. $CHCl_3$).

Anal. Calcd. for $C_{19}H_{19}O_2Cl$: C, 72.49; H, 6.08. Found: C, 72.27; H, 5.89.

The halohydrin XII did not release iodine when warmed with an acidified acetone solution of potassium iodide.[18] This same halohydrin XII resulted when the epoxide was treated with dry hydrogen chloride in ethanol. A methanol solution of potassium hydroxide quantitatively converted the halohydrin XII at room temperature in 10 minutes to the corresponding epoxide. When XII was refluxed for 9 hours with a benzene solution of 2 molar equiv. of morpholine, or heated on a steam-bath with excess morpholine for one hour, 80–90% yields of the epoxide were produced.

B. With Methanol and Sulfuric Acid. 2-Hydroxy-2-(α-methoxybenzyl)-1-tetralone (XIII).—A 2.0-g. (0.008 mole) sample of 2-benzal-1-tetralone oxide was dissolved in 20 ml. of methanol and 3 drops of 96% sulfuric acid added. After standing at room temperature for six weeks the odor of benzaldehyde was detected. Concentration of the solution, washing with sodium carbonate solution, and cooling produced a colorless product XIII which was recrystallized from methanol; wt. 0.84 g. (37%), m.p. 91–92°; λ_{max} 251, 296(sh) mμ (ϵ 13,300, 1,700); γ_{OH} 3570/16 and 3515/36; $\gamma_{C=O}$ 1680–1690/89 and 1677/90.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.24; H, 6.58.

2-Hydroxy-2-(α-methoxybenzyl)-4,4-dimethyl-1-tetralone (XIV) was produced in 32% yield from 2-benzal-4,4-dimethyl-1-tetralone oxide in a manner similar to that described for the preparation of XIII. The reaction mixture stood at room temperature for 11 days. Again the odor of benzaldehyde was observed and a residual oil gave a purple-brown color with ferric chloride solution. Recrystallization of the solid material from methanol gave the pure product XIV, m.p. 139–140°; λ_{max} 252, 287 (broad) mμ (ϵ 13,400, 2,200); γ_{OH} 3530/30 and 3480/20; $\gamma_{C=O}$ 1685/80 and 1677/90.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.66; H, 7.20.

Absorption spectra for 2-(*o*-nitrobenzal)-4,4-dimethyl-1-tetralone (VIIb)[7]: λ_{max} 273, 318(sh) mμ (ϵ 19,700, 7,300); $\gamma_{C=O}$ 1676/40 (satd. CCl_4 soln.), 1674/55 (in Nujol); $\gamma_{ArC=C}$, 1626/50 (in Nujol).

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