to contain the nortricyclyl chloride if any were present. The infrared spectrum showed no trace of any of the prominent bands of nortricyclyl chloride.[19] A very small amount of *anti*-7-*exo*-2-dichloronorbornane was found. The bulk of the material was a viscous black oil which would not distill.

Dipole Moment Measurements.—All compounds were recrystallized to constant melting point. The solvent was thiophene-free benzene which was dried just prior to use by azeotropic distillation of a trace of water. All data were taken at 25° and collected in Table II. In all cases the plot of $e - n^2$ *vs.* concentration gave a line with no detectable curvature.

The dipole moments were derived from the dielectric constants and refractive indices of benzene solutions by the Guggenheim method of initial slopes.[20] Values of the dielectric constants were obtained using a heterodyne beat apparatus similar to that of Smyth and Lewis.[21]

---

(20) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

(21) C. P. Smyth and G. L. Lewis, *J. Chem. Phys.*, **7**, 1085 (1939).

NEWARK, DELAWARE

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

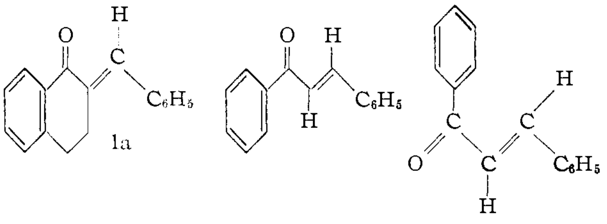
The Chemistry of Derivatives of 2-Benzaltetralone. II. Absorption Spectra and Stereostructure

BY ALFRED HASSNER[1a] AND NORMAN H. CROMWELL[1b]

RECEIVED APRIL 27, 1957

trans-2-Benzal-4,4-dimethyl-1-tetralone (Ib) and its endocyclic unsaturated isomer IXb were synthesized in good yields and characterized by their chemical properties and absorption spectra. The structure of 2-benzal-4,4-dimethyl-1-tetralone oxide (VIIb) obtained by alkaline epoxidation of Ib was verified by synthesis through a Darzens condensation. The advantage of 80% sulfuric acid in the condensation of *o*-nitrobenzaldehyde with 1-tetralone and 1-indanone was demonstrated. Analogies between 2-benzal-1-tetralones, 2-benzal-1-indanone and chalcones are pointed out and a discussion is presented of the effect of conjugation, α-bromo substitution and 4-*gem*-dimethyl substitution in 1-tetralones in terms of conformational analysis, ultraviolet and infrared absorption characteristics.

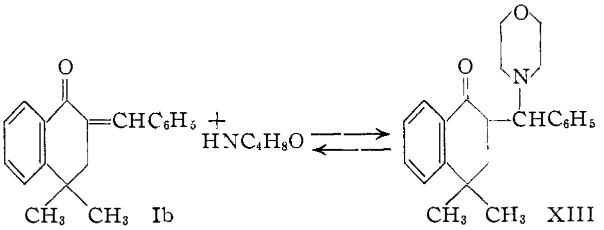
In connection with our study of the chemical behavior of cyclic aromatic ketones[2,3] we have synthesized and examined the stereostructure and absorption spectra of several 2-substituted tetralones and indanones. The 2-benzal-1-tetralones are structurally related to the chalcones in the open chain series, the chemistry of which has been the subject of several investigations.[4] For the cyclic ketones, however, the conformation of the ring and of the substituents are additional aspects to be considered. Moreover, in these exocyclic α,β-unsaturated ketones there exists a fixed *s-cis* conformation of the C=C with respect to the C=O bond, while in the open chain chalcone types the *s*-conformation is labile.[5]



s-cis-trans *s-cis-trans*-chalcone *s-trans-trans*

As in the case of 2-benzal-1-tetralone (Ia),[2] the 4,4-dimethyl analog Ib was obtained from a base-catalyzed condensation of the corresponding 1-tetralone with benzaldehyde. Only one of the two possible stereoisomers of 2-benzal-4,4-dimethyl-1-tetralone (Ib) was isolated (presumably the *trans* form). It showed the same chemical inertness against acids and bases as did 2-benzal-1-tetralone (Ia).[2]

A careful study of the reactivity of Ib with morpholine revealed the existence of the equilibrium



The morpholinoketone XIII was formed in yields of about 10% when 2-benzal-4,4-dimethyl-1-tetralone (Ib) was allowed to stand for one day with three molar equivalents of morpholine. The equilibrium outlined above may be approached from either side. Thus 2-[α-(N-morpholino)-benzyl]-4,4-dimethyl-1-tetralone (XIII) was converted back to Ib in 40% yield upon standing with excess morpholine alone or in benzene solution. This facile change probably involves a quasi six-membered ring with the morpholine serving as a proton transfer agent to give this α,β-unsaturated ketone with a fixed *s-cis* conformation.

The preparations of 2-(*o*-nitrobenzal)-1-tetralone (Xa) and 2-(*o*-nitrobenzal)-1-indanone (Xc) were accomplished in high yields by employing 80% sulfuric acid or a sulfuric–acetic acid mixture as the condensing agent. With boiling acetic anhydride the synthesis of pure Xc[6] was accomplished in 36% yield while with 80% sulfuric acid as the solvent-catalyst the yield was 73%.

Selective hydrogenation of 2-benzal-4,4-dimethyl-1-tetralone (Ib) over platinum oxide af-

---

(1) (a) Monsanto Research Fellow, 1954–1955; 1955–1956; (b) to whom correspondence concerning this article should be addressed.

(2) A. Hassner, N. H. Cromwell and S. J. Davis, THIS JOURNAL, **79**, 230 (1957).

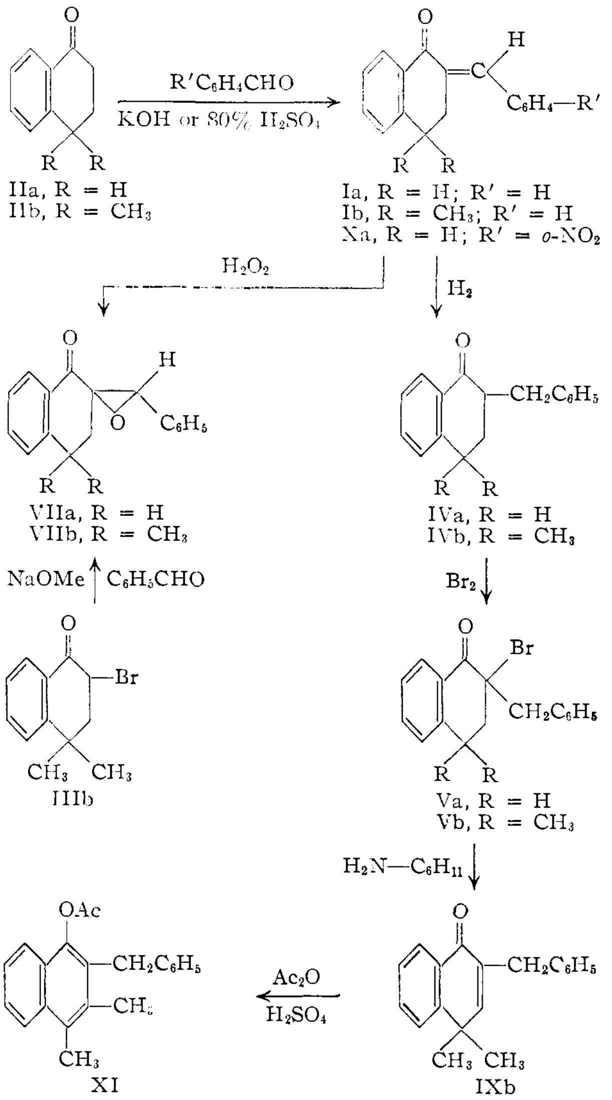
(3) N. H. Cromwell, H. H. Eby and D. B. Capps, *ibid.*, **73**, 1230 (1951).

(4) For example see N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

(5) (a) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955); (b) E. A. Braude and C. J. Timmons, *ibid.*, 3766 (1955).

(6) G. Singh and J. N. Ray, *J. Indian Chem. Soc.*, **7**, 638 (1930), failed to effect the reaction of 1-indanone with *o*-nitrobenzaldehyde in the presence of bases but obtained low yields of 2-(*o*-nitrobenzal)-1-indanone (Xc) by using boiling acetic anhydride.

forded 2-benzyl-4,4-dimethyl-1-tetralone (IVb), which in turn was brominated in chloroform solution to the 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (Vb). On treatment with cyclohexylamine[7] Vb was dehydrobrominated in 70% yield to 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IXb), the endocyclic unsaturated isomer of Ib. The preferential loss of H as HBr from the ring, rather than from the side chain, presents a convenient route for the preparation of this isomer of 2-benzal-4,4-dimethyl-1-tetralone (Ib). The structure of IXb was evident from its chemical and physical properties. Unlike the benzal compound Ib, it is a colorless solid with ultraviolet absorption characteristics similar to those of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VIIIb). Catalytic reduction of IXb to IVb in 90% yield suggested that IXb was not a cyclopropyl compound. This was confirmed by the spectra studies; see Table I.

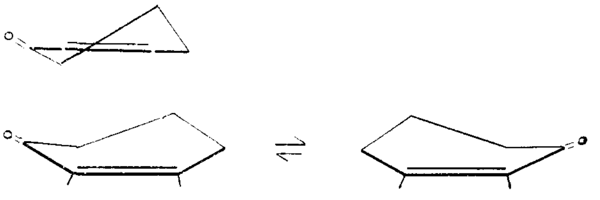


The failure of 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IXb) to add amines under ordinary conditions is in accord with its rigid *s-trans* conformation of C=O with respect to C=C. A study of models suggests this ring structure can exist only in a stable quasi-boat conformation. Reaction of IXb with alkaline hydrogen peroxide led mainly to recovery of starting material. Upon standing in acetic anhydride solution in the presence of sulfuric acid for 36 hours, IXb underwent the dienone–phenol rearrangement to the naphthol acetate XI in 95% yield, as would be expected for the endocyclic unsaturated isomer of Ib. The benzal compound Ib failed to rearrange under analogous conditions even when the reaction time was extended to 8 days. No interconversion between Ib and IXb was observed.[8]

The only structure for the acid-rearrangement product of IXb which is consistent with the known path of the dienone–phenol rearrangement as well as with the elemental analysis and spectral data for XI, is 2-benzyl-3,4-dimethyl-1-naphthol acetate. Alkaline hydrolysis of the acetate XI, followed by careful acidification, allowed the isolation of a free naphthol, probably 2-benzyl-3,4-dimethyl-1-naphthol. This product was very difficult to purify, gave a weak ferric chloride test and exhibited absorption spectra characteristic[2] of 2-benzyl-1-naphthols.

In analogy with 2-benzal-1-tetralone (Ia),[2] the 4-*gem*-dimethyl derivative Ib served as the starting material for a spiroepoxide VIIb. Similarly 2-benzal-1-indanone (Ic) reacted readily with alkaline hydrogen peroxide to give its oxide VIIc in good yield. A few spiroepoxyketones have been described in the literature.[9] We have now unambiguously verified the structure of such oxides by an independent synthesis of 2-benzal-4,4-dimethyl-1-tetralone oxide (VIIb) employing the Darzens reaction. Steric controls operating[14b] in the transition state for the formation of the intermediate halohydrin anion favor kinetically the thermodynamically more stable *dl-erythro* form which produces the *trans*-epoxyketone in Darzens reactions. Rearrangement to the *cis* form *via* enolization is not possible with these spiroepoxyketones.

Conformation and Spectra.—The 1-tetralones should exist in a staggered quasi-chair conformation, the carbonyl group forming a small angle with the plane of the unsaturated system. An examination of models indicates that in the quasi-boat conformation this angle is widened and would not allow for as complete an orbital overlap. Carbon atoms 6 and 5, respectively, will be below



Staggered quasi-chair conformations for cyclohexenones.

---

[7] A more extensive discussion of the reaction of Vb with amines is presented in a forthcoming paper by A. Hassner and N. H. Cromwell.

[8] If IXb and Ib had been stereoisomers, the rearrangement of one form to the other should have taken place in sulfuric acid. In such media α,β-unsaturated ketones form mesomeric systems in which the fixed C=C no longer exists.

[9] (a) J. Reese, *Ber.*, **75**, 384 (1942); (b) H. O. House and R. L. Wasson, THIS JOURNAL, **78**, 4394 (1956).

and above the plane in which carbons 1,2,3,4 are located.[10] By comparing the intensities of ultraviolet absorption of 1-tetralone and acetophenone, Braude[5a] deduced the interplanar angle between the benzene ring and the carbonyl group in the former to be 22°. For indanone this angle was calculated to be 17°.

In 2-benzal-1-tetralone, the introduction of an additional trigonal carbon atom into the cyclohexenone system will cause the molecule to assume a rather flat conformation. Undoubtedly, the opportunity for orbital overlap between the carbonyl π-orbital, through the π-electrons of the olefinic double bond, with the π-orbital of the side-chain phenyl group contributes to the high stability exhibited by the 2-benzal-1-tetralones. Their electronic absorption spectra indicate an extensive molecular orbital characteristic of *trans*-chalcones. The approach to coplanarity in the cyclic compounds (I) in the excited state is done at the expense of a small amount of energy (Franck–Condon principle) and the result is shown in the decreased molar extinction coefficients of Ia and Ib with respect to *trans*-chalcone (Table I). In the language of Braude[5] this would indicate that the nature of the transition from ground to excited energy states in Ia and Ib and *trans*-chalcone are nearly identical, but the transition probability for reaching the excited states in Ia and Ib has been reduced. One might possibly expect the fixed *s-cis-trans* conformation-configuration in compounds I to lead to a lowering of intensity in contrast with the value for the labile *s*-conformations of chalcones.[5b] Both Ia and Ib exhibit an intense K-band[11] at ~ 305 mμ (ϵ 17,000) corresponding to the long wave length band at 307 mμ (ϵ 24,000) for *trans*-chalcone.[12] This represents unmistakable evidence for the exocyclic unsaturated ketone structure of Ia and Ib and suggests that the latter compounds are in the *trans* configuration. In all *cis*-chalcones reported,[12] a separate band at 250–260 mμ, attributable to independent absorption by the acrylophenone group, can be observed, while the short wave length band at ~ 230 mμ, present in *trans*-chalcones, has disappeared. The less planar *cis* compounds absorb at shorter wave lengths and with lower intensities than their *trans* isomers in the 300 mμ band region.

The band at ~ 305 mμ in chalcones and in the cyclic analogs (I) probably is due to a planar extended cinnamoyl chromophore, since benzalacetone[13] and 2-benzalcyclohexanone[9b] absorb light strongly at 280–290 mμ. In the 2-benzal-1-tetralones (I), an inflection in the acrylophenone absorption region near 275–280 mμ can be observed. Masked absorption in this region was found by Black and Lutz[12] through graphical resolution, even in *trans*-chalcone. A comparison of the longest wave length maxima in *trans*-α-methylchalcone[12] and the *trans*-2-benzal-1-tetralones (I) indicates that in the excited states there is less interference of approach to planarity caused by the α-methylene group in the cyclic compounds (I) (type 1 steric effect[5a]) than by the α-methyl group in *trans*-α-methylchalcone (type 2 steric effect[5a]). The greater resonance stabilization of the excited states of I leads to a bathochromic shift from 290 to 305 mμ. The ultraviolet absorption spectra of Ia and Ib indicate no significant differences between these molecules in the excited states.

In 2-benzal-1-indanone (Ic), the five-membered ring allows greater coplanarity of the system. The more extensive molecular orbital overlap in Ic has a bathochromic and hyperchromic effect on the extended cinnamoyl band (318 mμ, ϵ 22,500) with respect to the less coplanar six-membered ring compound Ia or Ib. Steric inhibition of coplanarity in 2-(*o*-nitrobenzal)-1-tetralone (Xa), λ_{max} 272 mμ (ϵ 20,400), and 2-(*o*-nitrobenzal)-1-indanone (Xc), λ_{max} 278 mμ (ϵ 19,500), as compared to Ia and Ic is indicated by the appearance for the former two compounds of a strong band in the acrylophenone chromophore region and by the transition from the extended cinnamoyl band to an inflection at ~ 305 mμ. Similar shifts are caused by the *o*-nitro group in *o*-nitrochalcone,[14] λ_{max} 262 mμ (ϵ 17,500).

The infrared carbonyl stretching frequencies of the exocyclic unsaturated ketones I in CCl_4 solution indicate that in the ground state the C=O bond has about the same single bond character in these cyclic systems as in the chalcones. Whereas *trans*-chalcone absorbs infrared light strongly at 1667 cm.$^{-1}$, 2-benzal-1-tetralone (Ia) and 2-benzal-4,4-dimethyl-1-tetralone (Ib) have intense bands in CCl_4 at 1666 and 1673 cm.$^{-1}$, respectively. It appears that, although ultraviolet spectra indicate hardly any energy differences between Ia and Ib for the transition to excited states, non-planarity has a small but definite effect on the vibrational spectra for the latter compound. In 2-benzal-4,4-dimethyl-1-tetralone (Ib) the quasi-axial methyl group through non-bonded interactions makes it more difficult for the conjugated system to reach planarity and polarization of the C=O bond is inhibited. 2-(*o*-Nitrobenzal)-1-tetralone (Xa) has a C=O band at 1680 cm.$^{-1}$ while *o*-nitrochalcone[14b] has one at 1671 cm.$^{-1}$. The increase in frequency with respect to 2-benzal-1-tetralone (Ia) is due to steric inhibition of resonance by the *o*-nitro group. The effect of ring strain causes five-membered ring ketones to absorb infrared light at higher frequencies than their six-membered analogs[15,16] and this is reflected in the carbonyl frequency at 1697 cm.$^{-1}$ of 2-benzal-1-indanone (Ic).

The infrared absorption bands associated with the carbonyl group of 1-tetralone (IIa) and 4,4-dimethyl-1-tetralone (IIb) are located at the expected frequencies[16] for aryl ketones (1685 cm.$^{-1}$). The introduction of a benzyl group into the 2-position of the tetralones has no effect on the car-

---

[10] Slight bond twisting probably will be more readily accommodated than bond angle bending and the above conformation should be relatively free of strains caused by bond angle distortions.

[11] The K-band is the one associated with the conjugated carbonyl system; see A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, Ltd., London, 1954, p. 113.

[12] W. B. Black and R. E. Lutz, THIS JOURNAL, **77**, 5134 (1955).

[13] G. Gamboni, *et al.*, *Helv. Chim. Acta*, **38**, 256 (1955).

[14] (a) N. H. Cromwell, *et al.*, THIS JOURNAL, **71**, 711 (1949); (b) **76**, 5752 (1954); (c) H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955).

[15] L. P. Kuhn, *et al.*, *ibid.*, **72**, 5058 (1950).

[16] F. Miller, "Organic Chemistry," Vol. III, H. Gilman, editor, John Wiley and Sons, Inc., New York, N. Y., Chapter 2, 1953.

TABLE I

SUMMARY OF ULTRAVIOLET AND INFRARED ABSORPTION SPECTRA

	Ultraviolet max.[a]		Infrared bands 1700–1600 cm.$^{-1}$			
					CCl$_4$ sol.[b]	
Ketone	λ, mμ	ε × 10^{-3}	Band	Nujol mull	Wave no.	Approx. % abs.
2-Benzal-1-tetralone (Ia)[c]	227	11.7	$C{=}O$	1655	1666	82
	(276)[d]	12.0	$C{=}C$	1635	(1645)	32
	305	17.2	Phenyl	1605	1600	82
2-Benzal-4,4-dimethyl-1-tetralone (Ib)	227	11.4	$C{=}O$	1668	1673	94
	(279)	12.0	$C{=}C$	1612	(1620)	80
	307	16.5			1610	90
			Phenyl	1598	1605	90
2-Benzal-1-indanone (Ic)	227	9.85				
	(277)	8.90	$C{=}O$	1690	1697	100
	318	22.5	$C{=}C$	1620	1630	85
			Phenyl	1605	1608	76
				1580		
trans-Chalcone	227	9.8	$C{=}O$	1650[e]	1667	67[f]
	307	24.3			1648	40
			$C_6H_5C{=}C$	1608	1610	83
cis-Chalcone[e]	250	13.7	$C{=}O$	1655		
	295	8.9	$C_6H_5C{=}C$	1608		
trans-α-Methylchalcone[g]	222	10.5				
	(260)	11.2				
	290	17.4				
4,4-Dimethyl-1-keto-1,4-dihydronaphthalene (VIIIb)	242	10.6	$C{=}O$	1657	1665	81[h]
	(259)	8.6	$C{=}C$	1624	1637	19
	(289)	2.9	Phenyl	1601	1604	39
	(296)	2.5				
2-Benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IXb)	252	11.0	$C{=}O$	1655	1662	100
	(289)	2.5	$C{=}C$	1640	(1650)	90
			Phenyl	1600	1605	75
2-(*o*-Nitrobenzal)-1-tetralone (Xa)	272	20.4	$C{=}O$	1670	1680	98
	(308)	9.9	$C{=}C$	1622	(1625)	78
			Ar	1600	1608	93
2-(*o*-Nitrobenzal)-1-indanone (Xc)	278	19.5				
	(302)	15.5	$C{=}O$	1696	1710	40
			$C{=}C$	1630	(1650–35)	13
			Ar		1608	20
o-Nitrochalcone[j]	262	17.5	$C{=}O$	1669	1671	64
					1650	46
			$ArC{=}C$	1608	1605	15
1-Tetralone						
4,4-Dimethyl- (IIb)	246	10.9	$C{=}O$	1685[k]	1685	95
	289	1.5	Phenyl	1600	1605	60
2-Benzyl-4,4-dimethyl- (IVb)	248	12.6	$C{=}O$	1680	1686	99
	(300)	1.7	Phenyl	1600	1605	65
2-Benzyl-2-bromo-4,4-dimethyl- (Vb)	258	10.6	$C{=}O$		1692	100
	(292)	2.5	Phenyl		1603	70
2-Bromo-4,4-dimethyl- (IIIb)	251	11.2	$C{=}O$		1705	96
	294	1.8	Phenyl		1605	62
2,2-Dibromo-4,4-dimethyl[l]	265	8.75	$C{=}O$		1708	97
	(290-300)	1.80	Phenyl		1605	70
2-Bromo-2-(α-bromobenzyl)-4,4-dimethyl- (VIb)	263	13.1	$C{=}O$		1690	96
	(297)	2.7	Phenyl		1605	61
2-Benzal-4,4-dimethyl- oxide (VIIb)	259	16.6	$C{=}O$	1680	1692	99
	(295)	2.6	Phenyl	1605	1600	73
2-[α-(N-Morpholino)-benzyl]-4,4-dimethyl- (XIII)	248	12.5	$C{=}O$		1678	98
	290	1.9	Phenyl		1600	42
2-Benzal-1-indanone oxide (VIIc)	255	14.1	$C{=}O$		1725	80
	(291)	2.7	Phenyl		1612	30
2-Benzyl-3,4-dimethyl-1-naphthol acetate (XI)	(214)	27.5	Ester $C{=}O$		1770	96
	237	39.3	Aromatic		1630	24
	(269)	4.6	Phenyl		1605	50
	(280)	5.9				
	289	6.2				

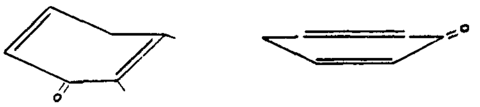
TABLE I (*Continued*)

	(311)	1.6				
	(326)	0.6				
2-Benzyl-3,4-dimethyl-1-naphthol (XII)	213	28.8	OH	3760		
	240	38.0	Aromatic	1628		
	(269)	3.6	Phenyl	1595		
	(290)	4.1				
	(317)	3.1				
	(330)	2.1				
1-Indanone	243[m]	12.3	C=O		1722	80
			Phenyl		1613	20
1-Tetralone (IIa)[n]	248	11.6	C=O	1679[k]	1685	81
	292	1.7	Phenyl		1604	33

[a] Ultraviolet spectra were determined with a Cary model 11-MS recording spectrophotometer using 0.0001 *M* methanol solutions. [b] The infrared measurements were done with a Perkin–Elmer model 21 double-beam instrument using matched 1.0-mm. NaCl cells. [c] See ref. 2. [d] Values in parentheses indicate shoulders or inflections. [e] See ref. 15. [f] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 77 and 119. [g] See ref. 15. [h] See ref. 20. [i] See ref. 14b and N. H. Cromwell and G. D. Mercer, THIS JOURNAL, **79**, 3815 (1957). [k] Pure liquid. [l] M.p. 102–103°, prepared by bromination of IIIb, see ref. 7. [m] See ref. 5b. [n] R. Barkley, M.S. Thesis, 1958, Univ. of Nebr.

bonyl frequency in such compounds, nor does it much change the electronic distribution in the excited state of these molecules. Here the benzyl substituent probably assumes the more stable equatorial position.

The introduction of an endocyclic double bond into the 4,4-dimethyl-1-tetralones did not shift the location of the high intensity maximum (K-band) in the ultraviolet appreciably, but the absorption curves of the resulting 4,4-dimethyl-1-keto-1,4-dihydronaphthalenes (VIIIb) and (IXb) have a characteristic shape, sloping down gradually on the longer wave length side of the K-band. Cross conjugation in cyclic α,β-unsaturated ketones causes no displacement or only a slight shift in the ultraviolet.[17,18] Thus Δ^4-3-ketosteroids absorb at 241 mμ (ϵ 16,000)[19] and $\Delta^{1,4}$-3-ketosteroids show maximum absorption at 244 mμ (ϵ 15,000).[20] In the infrared, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IXb) has a carbonyl band at 1662 cm.$^{-1}$ which indicates that the cross conjugated double bond is included in an extensive molecular orbital overlap contributing greatly to the stabilization of the ground state in this molecule. This seems to be true for most cross conjugated cyclic dienones[18] and may be exemplified by the carbonyl stretching frequencies[21] in carbon disulfide of Δ^4-androstene-3,17-dione (1678 cm.$^{-1}$) and $\Delta^{1,4}$-androstadiene-3,17-dione (1668 cm.$^{-1}$). That the second carbon-to-carbon double bond in 4,4 - dimethyl - 1 - keto - 1,4 - dihydronaphthalene (VIIIb) does extend conjugation in the excited state is suggested in the case of the 2-benzyl derivative IXb of this ketone, which has its K-band at 252 mμ.[22] Introduction of α-substituents on α,β-unsaturated enones should shift the wave length of absorption by 10 mμ.[23] Stereochemical considerations and an examination of models imply that ketones VIIIb and IXb exist in a nearly planar distorted boat conformation, since they contain five trigonal carbon atoms in the cyclohexane ring. Thus the strain arising from an attempt to maintain 120° bond angles will be accommodated mainly by the bonds at carbon-4 and at the carbonyl carbon atom.



Near-planar, distorted-boat conformation for cyclohexadienones.

The spiroepoxyketones 2-benzal-1-tetralone oxide[2] (VIIa), 2-benzal-4,4-dimethyl-1-tetralone oxide (VIIb) and 2-benzal-1-indanone oxide (VIIc) exhibit bathochromic and hyperchromic shifts of absorption maxima with respect to the 2-benzyl-1-tetralones (IVa) and (IVb) and to 1-indanone. *trans*-Chalcone oxide[14c] shows analogous ultraviolet absorption characteristics and this suggests that hyperconjugation through the three-ring is effective also in the spiroepoxyketones. The oxides VIIa, b and c are probably in the *trans* configuration. The infrared studies with these oxides VIIa,[2] VIIb and VIIc in CCl_4 revealed C=O bands at 1690, 1692 and 1725 cm.$^{-1}$, respectively. This represents a small frequency increase with respect to the parent benzyl compounds, IVa and IVb, and indanone. Bond distortion to accommodate the spiroepoxide ring may be responsible for reducing the planarity between the carbonyl and the adjacent aromatic ring.

A displacement of the carbonyl stretching vibration by 20 cm.$^{-1}$ in going from 4,4-dimethyl-1-tetralone (IIb) to its 2-bromo derivative IIIb (see Table II) seems to indicate that the bromine atom in the latter is mainly in the equatorial conformation. This is consistent with ultraviolet spectra

---

(17) R. B. Woodward, THIS JOURNAL, **62**, 1208 (1940).

(18) For an extensive discussion of the ultraviolet and infrared absorption spectra of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene and related compounds see R. D. Campbell and N. H. Cromwell, *ibid.*, **79**, 3456 (1957).

(19) L. Dorfman, *Chem. Revs.*, **53**, 47 (1953).

(20) In the case of extended conjugation the shift is considerable, *e.g.*, $\Delta^{4,6}$-3-ketosteroids absorb at 284 mμ (ϵ 28,000).

(21) K. Dobriner, E. R. Katzenellenbogen and R. N. Jones, "Infrared Absorption Spectra of Steroids," Interscience Publishers, Inc., New York, N. Y., 1953, pp. 112, 114.

(22) The low K-band (242 mμ) of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene with respect to 4,4-dimethyl-1-tetralone (246 mμ) is probably due to the less planar quasi-boat conformation of the former; see also ref. 18.

(23) L. F. Fieser, M. Fieser and S. Rajagopalan, *J. Org. Chem.*, **13**, 800 (1948); L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3d ed., Reinhold Publ. Corp., New York, N. Y., 1949, p. 190.

TABLE II

ABSORPTION SPECTRA AND CONFORMATIONAL ANALYSIS

1-Tetralone	No.	λ, mμ	ε × 10^{-3}	Δmμ[a]	C=O, cm.$^{-1}$	Δcm.$^{-1}$[a]	Predominant conformation of halogen
Parent cpd.	IIa	248	11.6		1685		
2-Chloro[b]					1697	12	a?
2,2-Dichloro[b]					1712	27	a,e
2-Benzyl-	IVa[c]	247	12.6		1686		
2-Benzyl-2-bromo-[c]	Va	259	11.8	12	1689	3	a
2-Bromo-2-(α-bromobenzyl)-	VIa	261	12.5	14	1686	0	a
4,4-Dimethyl-	IIb	246	10.9		1685		
2-Bromo-	IIIb	251	11.2	5	1705	20	e
2,2-Dibromo-		265	8.75	19	1708	23	e,a
2-Benzyl-	IVb	248	12.6		1686		
2-Benzyl-2-bromo-	Vb	258	10.6	10	1692	6	a
2-Bromo-2-(α-bromobenzyl)-	VIb	263	13.1	15	1690	4	a

[a] All increments were calculated by subtracting the value for the parent ketone from that of the halogen derivative. See ref. 27. [c] See ref. 2.

data and with the slow reactivity with amines[3,7] exhibited by IIIb. Jones, *et al.*,[24] have shown that in rigid ring systems an equatorial bromine will cause a shift of +16 to +22 cm.$^{-1}$ in the carbonyl frequency of cyclohexanones, while an axial bromine will effect only slight displacement of that band. This empirical generalization was explained by the reasoning that, with bromine in the equatorial conformation, the coplanar C–Br dipole is more effective in suppressing the polarization of the C=O bond thus raising the carbonyl stretching frequency. Corey[25a] has employed this generalization to assign conformations in various 2-halocyclohexanones, but recently Kumler and Huitric[25b] came to different conclusions from dipole moment studies on such compounds. The latter authors suggested a flexible form for 2-halocyclohexanones. Examination of models indicates that in 6-bromo-Δ^2-cyclohexenones the only quasi-boat form possible is the one which has the carbonyl carbon at the flagpole position. In this conformation, with bromine equatorially disposed, there are more non-bonded interactions than in the equivalent quasi-chair conformation. In both distorted boat and chair conformations there are less non-bonded interactions when the halogen is equatorial than when it is axial. Electronically, however, the axial conformation is generally favored.

In the 2-halo-1-tetralones an equilibrium between the two quasi-chair conformational isomers, with bromine axial and equatorial, respectively, is to be expected, but the presence of other groups could cause one form to predominate. Thus in 2-bromo-4,4-dimethyl-1-tetralone (IIIb) one expects the bromine to take up preferentially the equatorial position in order to minimize 1,3-interactions with the methyl group in the axial conformation. 2,2-Dibromo-4,4-dimethyl-1-tetralone[7] showed ultraviolet and infrared spectra bands to be associated with the carbonyl group which indicates that the second bromine atom enters the 2-position in an axial conformation (and that the bromine atom in IIIb is in the equatorial conformation); see Table II.

The bulky 2-benzyl group in Va and Vb, and certainly the more bulky 2-(α-bromobenzyl) group in VIa and VIb, are expected to be nearly equatorially oriented, which necessitates a predominantly axial conformation for the 2-bromo substituent in these molecules.[26] This is borne out by the infrared spectra of these compounds which exhibit only slight shifts (3–6 cm.$^{-1}$) in the carbonyl frequencies with respect to the corresponding unhalogenated tetralones, the derivatives with the bulkier[27] α-bromobenzyl groups showing the least frequency displacements. It may be observed that the carbonyl bands in the 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (Vb) and 2-bromo-2-(α-bromobenzyl)-4,4-dimethyl-1-tetralone (VIb) appear at slightly higher wave numbers than those of their analogs Va and VIa, which are not *gem*-dimethyl substituted. This may indicate that the presence of an axial methyl group interferes sterically with the preferentially axial bromine in the former compounds.[26] The preferred conformation for the 2-bromoketones Va and Vb seems to be that in which the bromine is nearly axial, and for IIIb that in which the bromine is nearly equatorial. This assumption, which is consistent with spectral data, also may be deduced qualitatively from the respective relative reactivities of the compounds, 2-bromo-4,4-dimethyl-1-tetralone (IIIb) reacting much slower with secondary amines[7] than the 2-benzyl derivatives Va and Vb.

Useful information about the conformation of the bromine in 2-bromo-1-tetralones and probably in 6-halo-Δ^2-cyclohexenones in general may be derived also from the K-band displacement in the ultraviolet spectra. As can be seen in Table II a

---

(24) R. N. Jones, *et al.*, THIS JOURNAL, **74**, 2828 (1952), and earlier papers.

(25) (a) E. J. Corey, *et al.*, *ibid.*, **77**, 5415 (1955), and preceding papers; (b) W. D. Kumler and A. C. Huitric, *ibid.*, **78**, 3369 (1956).

(26) In the 2-bromo-2-(α-bromobenzyl)-4,4-dimethyl-1-tetralone (VIb), the bromine should definitely be axial due to steric as well as electronic reasons and the molecule probably assumes the more staggered quasi-chair conformation. But in 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (Vb), the 1,3-interaction between axial Br and CH_3 seems slightly greater than that between axial $C_6H_5CH_2$ and CH_3, and the structure may be an intermediate type in which the bromine is a bit less axial and benzyl a bit less equatorial than are the corresponding groups in VIb (*cf.* Table II, shifts of absorption maxima).

(27) In the case of less bulky substituents as with 2-methyl- or 2-ethyl-1-tetralone, Stevens, THIS JOURNAL, **77**, 4590 (1955), found frequency shifts of 9–12 cm.$^{-1}$ upon introduction of the 2-chloro substituent. This could indicate either an equilibrium between the conformations with axially and equatorially oriented chlorine atoms or the presence of a more nearly planar boat conformation in these molecules.

bathochromic shift of 10–15 mμ seems to indicate an axially disposed halogen, while equatorial halogens cause much smaller displacements (*e.g.*, 5 mμ). Thus the 2-bromo-2-(α-bromobenzyl)-1-tetralones (VIa) and (VIb), which for steric reasons should have a predominantly axial bromine atom show the most pronounced bathochromic effect (15–16 mμ) in the series. In 2-halocyclohexanones a bathochromic shift by about 25 mμ of the low intensity R-band at 280 mμ has been attributed to the presence of axial bromine.[28] In the 1-tetralones the benzenoid absorption overshadows any R-bands (ε 50) and it appears that the presence of axial bromine causes rather a shift in the high intensity K-band of these conjugated ketones.

All saturated 1-tetralones studied were found to display the characteristic benzenoid band, which appears as a broad hump at about 280–300 mμ with a molar extinction coefficient of less than 3,000. The presence of the conjugated C=O chromophore next to the benzene ring accounts in part for the smoothing out of the benzenoid fine structure bands[11] and for the bathochromic and hyperchromic displacement of these bands. In the 2-bromo-1-tetralones and in the 2-benzal-1-tetralone oxides a hyperchromic effect on the benzenoid absorption is observed. With the introduction of unsaturation into the 1-tetralone ring, the benzenoid absorption band appears masked and reduced to an inflection at 298 mμ (ε 2,500) as found in the 4,4-dimethyl-1-keto-1,4-dihydronaphthalenes (VIIIb)[18] and (IXb).

Acknowledgment.—This investigation was supported in part by a grant from the National Science Foundation, N.S.F. G-1091.

Experimental[29]

4,4-Dimethyl-1-tetralone (IIb).—The directions outlined by Arnold and co-workers[30] were followed, and the fraction boiling at 87–90° and 0.6 mm. pressure was collected, $n^{25}\text{D}$ 1.5448.

2-Benzal-4,4-dimethyl-1-tetralone (Ib).—To a mixture of 3.5 g. (0.02 mole) of 4,4-dimethyl-1-tetralone and 2.0 g. (0.02 mole) of benzaldehyde was added slowly 10 ml. of a 4% ethanolic potassium hydroxide solution. To the dark-green and warm solution an additional 5 ml. of potassium hydroxide solution was added and after three hours the deposited crystals were removed by filtration and washed with dilute ethanol. The product weighed 4.0 g. (76.5% yield) and melted at 107–108°. Recrystallization from alcohol gave pale yellow fluffy needles, m.p. 110°. The yields were only slightly lower when heat was applied to the reaction.

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.87; H, 6.84.

2-Benzyl-4,4-dimethyl-1-tetralone (IVb).—A solution of 8.0 g. (0.03 mole) of 2-benzal-4,4-dimethyl-1-tetralone (Ib) in 180 ml. of absolute ethanol was shaken at 45–50° under 3 atm. pressure of hydrogen and in the presence of 0.25 g. of platinum oxide. Within 15 min. the theoretical amount of hydrogen had been taken up. The residue left upon evaporation was washed with dilute alcohol. The yield of crude 2-benzyl-4,4-dimethyl-1-tetralone (IVb), m.p. 56–58°, was 7.5 g. (93%). It was used unpurified for the bromination reaction described below. Recrystallization from petroleum ether (b.p. 30–40°) raised the m.p. to 61–62°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.51; H, 7.54.

2-Bromo-2-benzyl-4,4-dimethyl-1-tetralone (Vb).—The bromination of 3.7 g. (0.014 mole) of 2-benzyl-4,4-dimethyl-1-tetralone (IVb) in 10 ml. of chloroform was undertaken at room temperature with stirring using 2.2 g. (0.0138 mole) of bromine dissolved in 5 ml. of the same solvent. After the initial bromine color had faded, the remaining solution of bromine was added over a period of 25 minutes. After an additional 30 minutes the solution was evaporated to dryness and the resulting solid washed well with petroleum ether, dilute sodium bisulfite or sodium carbonate solution and finally with water. The dried solid melted at 101–102° (93% yield). It was recrystallized from alcohol or petroleum ether, m.p. 102°.

Anal. Calcd. for $C_{19}H_{19}OBr$: C, 66.47; H, 5.58. Found: C, 66.68; H, 5.90.

This α-bromoketone Vb reacted with warm alcoholic silver nitrate and released iodine from acidified potassium iodide in acetone–alcohol.

2-Benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IXb). **a. Synthesis.**—A mixture of 1.0 g. of α-bromoketone Vb and 1.0 g. (3.45 molar equiv.) of cyclohexylamine was allowed to stand at room temperature, in the dark and under nitrogen for 20 hours. The nearly solidified mixture was digested with isopropyl ether and the theoretical amount of cyclohexylamine hydrobromide was removed by filtration. The filtrate was washed well with water, extracted with 5% hydrochloric acid and rewashed with water. The dried ether solution was evaporated *in vacuo* and the residue purified with charcoal in methanol solution. Partial evaporation and cooling gave 0.59 g. (77%) of white crystals of 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IXb), m.p. 112–113.5°. It slowly decolorized a solution of bromine in carbon tetrachloride. Recrystallized from methanol it melted 113–113.5°.

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.74; H, 6.87.

Mixtures of endocyclic unsaturated compound IXb and exocyclic unsaturated compound Ib melted at 88–105°. The unsaturated ketone IXb was recovered unchanged upon its interaction with excess piperidine at room temperature for 15 days. No amine addition product was found.

b. **Hydrogenation of** (IXb).—A 0.7-g. sample of IXb in 20 ml. of ethanol at 35° was hydrogenated under 3 atm. of hydrogen in the presence of 0.05 g. of platinum oxide. After 10 min. the mixture was filtered and the filtrate evaporated to yield 0.63 g. (90% yield) of 2-benzyl-4,4-dimethyl-1-tetralone (IVb), m.p. 56–59°. Two crystallizations from petroleum ether raised the m.p. to 59.5–61°. A mixed melting point experiment with authentic IVb showed no depression.

c. **Attempted Epoxidation of** (IXb).—The reaction of the endocyclic unsaturated ketone IXb with hydrogen peroxide under conditions employed for the epoxidation of the benzal derivative Ib was unsuccessful. The only solid isolated was starting ketone IXb, with a 30% recovery. An oil, which did not crystallize, was also obtained and was not further characterized.

d. **Rearrangement to 2-Benzyl-3,4-dimethyl-1-naphthol.**—Aromatization of IXb took place readily under conditions known to effect a dienone–phenol rearrangement.[30] A 0.6-g. sample of dienone IXb was dissolved in 15 ml. of acetic anhydride and 0.3 g. of sulfuric acid. The yellow solution stood at room temperature for 40 hours and was then stirred with ice-water for 1.5 hours, so as to hydrolyze the acetic anhydride. A white solid was collected and washed with water. The yield of **2-benzyl-3,4-dimethyl-1-naphthol acetate** (XI) was 0.66 g. (95%), melting partly at 114–116° and at 125–126°, m.p. 116–116.5° after recrystallization from methanol.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.26; H, 6.58.

Hydrolysis of the acetate XI yielded the corresponding naphthol which melted unsharply and gave gummy products on purification attempts from ether or petroleum ether. A solution of 1.0 g. of the naphthol acetate XI in 20 ml. of 10% methanolic potassium hydroxide was heated under reflux for 30 minutes, then diluted with 15 ml. of water and treated with charcoal. Very slowly, with stirring and under cooling, 2.5 ml. of concd. hydrochloric acid was added, so that a white precipitate was formed. The solid was collected by filtration, washed with cold water until free of chloride ions, and dried. Thus a 96% yield of crude 2-

---

[28] R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

[29] Melting points were read on a calibrated thermometer. Analyses are by Micro-tech Anal. Lab., Skokie, Ill.

[30] R. T. Arnold, J. S. Buckley and J. Richter, THIS JOURNAL, **69**, 2324 (1947).

benzyl-3,4-dimethyl-1-naphthol was obtained, m.p. 96–99°. Recrystallization from petroleum ether, b.p. 60–70°, without heating, gave a tan powder, m.p. 106–115°. Further purification was difficult and of no avail. The naphthol, unlike the acetate, slowly gave a brown-red coloration with aqueous ferric chloride in ethanol solution.

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.38; H, 7.02.

2-Bromo-2-(α-bromobenzyl)-4,4-dimethyl-1-tetralone (VIb).—The addition of 1.35 g. (0.0081 mole) of bromine in 3 ml. of carbon tetrachloride to a cooled and stirred solution of 2.1 g. (0.008 mole) of 2-benzal-4,4-dimethyl-1-tetralone (Ib) in 15 ml. of the same solvent was carried out as usual.[2] To initiate the reaction a small amount of the solution was removed and heated to boiling until the color of bromine disappeared. It was then added to the rest of the solution and the bromine addition was continued. Removal of the solvent *in vacuo* left a residue which was digested with petroleum ether, b.p. 60–70°, and collected by filtration. It weighed 3.1 g. (91%) and decomposed at 143° turning into a yellow liquid by 145°. Recrystallization from petroleum ether, b.p. 90–100°, afforded white crystals, m.p. 144° dec. When purified from methanol the dibromoketone melted at 141–141.5° dec. The two solids did not depress each other's melting points and showed identical absorption in ultraviolet light.

Anal. Calcd. for $C_{19}H_{18}OBr_2$: C, 54.05; H, 4.29. Found: C, 54.05, 54.14; H, 4.50, 4.58.

2-Benzal-4,4-dimethyl-1-tetralone Oxide (VIIb). a. **By Epoxidation of 2-Benzal-4,4-dimethyl-1-tetralone (Ib).**—To a solution of 4.0 g. (0.015 mole) of unsaturated ketone Ib in 160 ml. of methanol at 30°, was added 3.5 g. (0.025 mole) of a 30% hydrogen peroxide solution and then slowly 3.5 ml. of 16% sodium hydroxide. After three hours of stirring the mixture was cooled and a white solid, m.p. 138–139°, was collected. More solid was obtained from the filtrate, bringing the total yield of spiroepoxyketone VIIb to 93%. An analytical sample obtained from methanol melted at 138.5–139°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.06; H, 6.63.

b. **By a Darzens Condensation.**—A sample of 1.25 g. (0.005 mole) of 2-bromo-4,4-dimethyl-1-tetralone (IIIb), obtained by direct bromination of 4,4-dimethyl-1-tetralone,[30] was dissolved in 9 ml. of methanol–dioxane (2:1); 0.5 g. (0.005 mole) of benzaldehyde, and then slowly a solution of 0.11 g. (0.005 mole) of sodium in 2.0 ml. of methanol, were added in the cold and with stirring. Within five minutes a white solid appeared. The mixture was neutralized with dilute acetic acid, and 1.3 g. (94% yield) of 2-benzal-4,4-dimethyl-1-tetralone oxide (VIIb), m.p. 137–138°, was collected by filtration. It was identical in melting and mixed melting point with VIIb as described in a.

Chemical Stability of 2-Benzal-4,4-dimethyl-1-tetralone (Ib). a. **With Sulfuric Acid.**—The results were similar to those observed with 2-benzal-1-tetralone.[2] The exocyclic unsaturated ketone Ib was recovered unchanged in nearly quantitative yields when allowed to stand for 8 days in a solution of acetic anhydride and sulfuric acid, or for one day in concd. sulfuric acid. Melting and mixed melting points of recovered and starting ketone were identical.

b. **With Amines.**—A mixture of 0.77 g. of Ib and an equal amount of morpholine stood at room temperature for 19 hours. Isopropyl ether was added and the water-washed ether solution was extracted with cold dilute hydrochloric acid. Basification of the acid extract with sodium carbonate in the cold yielded 0.11 g. (10% of theoretical) of **2-[α-(N-morpholino)-benzyl]-4,4-dimethyl-1-tetralone (XIII).** Recrystallized from ethanol–water, it melted at 149–150°.

Anal. Calcd. for $C_{23}H_{27}O_2N$: C, 79.05; H, 7.79; N, 4.01. Found: C, 79.31; H, 7.91; N, 3.97.

When only one molar equivalent of amine was employed or the reaction mixture was heated on a steam-bath for two hours, the amount of amine addition product formed was negligible. That the addition of morpholine to Ib is reversible is shown in the following experiment.

A solution of 0.14 g. of 2-[α-(N-morpholino)-benzyl]-4,4-dimethyl-1-tetralone (XIII) in 0.4 g. (11 molar equiv.) of morpholine and 0.2 g. of benzene was allowed to stand for 2.5 days in a dark place. It was diluted with isopropyl ether, washed with water, and extracted with a 5% hydrochloric acid solution. From the latter by neutralization with sodium carbonate, 14% of XIII was recovered. Evaporation of the ether solution left 0.04 g. (40%) of 2-benzal-4,4-dimethyl-1-tetralone (Ib), identified by its ultraviolet spectrum and its mixed melting point with authentic Ib.

2-Benzal-1-indanone (Ic).[31]—In order to avoid the formation of appreciable amounts of a dimeric condensation product, m.p. 242°, the reaction of 20 g. (0.151 mole) of 1-indanone with 16 g. (0.151 mole) of benzaldehyde was carried out with only 20 ml. of 4% ethanolic potassium hydroxide under ice-bath cooling. The crude product (95% yield) melted at 103–106° and was purified by extraction with hot dilute methanol. Pure Ic melted at 109–111° (lit.[31] 109–110°, 113–114°).

The epoxidation of 2-benzal-1-indanone (Ic) with alkaline hydrogen peroxide was carried out as described for VIIb. **2-Benzal-1-indanone oxide (VIIc)**, m.p. 121–122° from alcohol, was obtained in 90% yield.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.26; H, 5.29.

2-(*o*-Nitrobenzal)-1-tetralone (Xa).—To a solution of 1.0 g. of 1-tetralone in 1.0 g. of *o*-nitrobenzaldehyde the specified catalysts were added. Upon standing for one to five days no products other than dark oils could be isolated. Catalysts tried were: a 4% alcoholic potassium hydroxide solution, a few drops of a 1% alcoholic potassium hydroxide solution using ether as the solvent, 5 drops of piperidine in 3.0 ml. of ethanol and heating on the steam-bath, 3 g. of acetic anhydride and heating to 140° for two hours. With 0.4 g. of sodium amide in ether solution a 12% yield of 2-(*o*-nitrobenzal)-1-tetralone (Xa) was secured. It was crystallized from dilute acetic acid, m.p. 120–122°.

Best results were obtained when 80% (by weight) sulfuric acid was used. One gram of *o*-nitrobenzaldehyde was dissolved in 12 ml. of cold 80% sulfuric acid and 1.0 g. of 1-tetralone was added with stirring. The following day the mixture was poured into ice-water and 1.55 g. (85%) of a dark yellow solid was collected. It was purified with charcoal in ethanol or glacial acetic acid. Pure 2-(*o*-nitrobenzal)-1-tetralone (Xa) melted at 121.5–122°.

Anal. Calcd. for $C_{17}H_{13}O_3N$: C, 73.11; H, 4.70; N, 5.02. Found: C, 73.16; H, 5.16; N, 5.37.

2-(*o*-Nitrobenzal)-1-indanone (Xc).—The condensation of 1-indanone with *o*-nitrobenzaldehyde in refluxing acetic anhydride was accomplished as described by Singh and Ray.[6] The yield of crude product was 69%. Recrystallization from glacial acetic acid after treatment with charcoal gave a 36% yield of yellow crystals of Xc, m.p. 167–167.5° (lit.[6] 167°). When 80% sulfuric acid was employed under conditions described for 2-(*o*-nitrobenzal)-1-tetralone (Ia), a 90% yield of condensation product, m.p. 165–166° resulted. Recrystallization from glacial acetic acid and treatment with charcoal gave a 75% yield of pure 2-(*o*-nitrobenzal)-1-indanone (Ic), m.p. 167°.

LINCOLN, NEBRASKA

---

(31) (a) F. S. Kipping, *J. Chem. Soc.*, **65**, 480 (1894); (b) B. Schmid, *J. prakt. Chem.*, **62**, 552 (1900).