recrystallization from benzene-heptane weighed 150 mg., m.p. 146-147.5°. (The reaction product obtained in A, above, was treated with a seed obtained by this procedure and the solid diol precipitated as described.) The infrared spectra of the products obtained by both method A and method B are superimposable and a mixed melting point determination of the two solids showed no depression (145-147°). Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.27; H, 9.70.

 $\label{eq:rans-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol.--trans-1-Phenyl-6-methyl-6-(α- hydroxyisopropyl)-cyclohexene oxide (1 g., 5 mmoles) was reduced with LiAlH_4 (1 g., 25 mmoles) using exactly the same procedure as that used for the cis isomer described in the previous experiment (method B). Again it was necessary to obtain seed crystals by vapor phase chromatography. Seeding the oily product yielded trans-1-phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol, 150 mg. on recrystallization from heptane, m.p. 118-119.5°. Anal. Caled. for C18H24O2: C, 77.37; H, 9.74. Found: C, 77.30; H, 9.75.$

Cleavage Study: cis-1-Phenyl-2-methyl-2-(α -hydroxyisopropyl)-cyclopentanol.—The cis isomer (100 mg., 0.427 mmole) placed in a 5-ml. semi-micro distilling apparatus; 3 ml. of 10% sulfuric acid in ethanol was added to the flask, the flask was then warmed in an oil-bath and 2 ml. of ethanol was distilled through a water condenser into a receiver which was surrounded by a brine-ice mixture. Heating was discontinued and the still-pot was allowed to cool to room temperature. The contents of the receiver were transferred to a test-tube and 0.4 mmole of dinitrophenylhydrazine was added. The mixture was acidified with several hours during which time a precipitate of acetone 2,4-dinitrophenylhydrazone formed. After drying *in vacuo* the hydrazone melted at 125–126° (rept. 126°) and weighed 7.5 mg. (.0293 mmole) corresponding to 6.9% cleavage to give acetone.

The still-pot residue was diluted with 2 ml. of ethanol, and transferred to a test-tube containing 0.4 mmole of 2,4dinitrophenylhydrazine. After warming on a steam-bath to effect solution, a fluffy yellow precipitate formed in the test-tube and the hot mixture was allowed to cool to room temperature. After drying *in vacuo*, the precipitate weighed 143.5 mg. (0.347 mmole) and melted over a wide range, 138-148°. On recrystallization, the hydrazone weighed 129 mg. (90% recovered) and melted sharply at 147-148°. This corresponds to 81.4% cleavage to 2,3-dimethyl-6-benzoylhexene-2.

A sample of the 2,3-dimethyl-6-benzoylhexene-2 obtained in a larger run was purified by v.p.c. on a $\frac{1}{2}$ detergent column sent for analysis. *Anal.* Calcd. for C₁₈H₂₀O: C, 83.28; H, 9.32. Found: C, 83.61; H, 9.34. The 2,4-dinitrophenylhydrazone melted at 149–150°

The 2,4-dinitrophenylhydrazone melted at $149-150^{\circ}$ and its m.p. was not depressed when mixed with the $147-148^{\circ}$ melting compound obtained above. *Anal.* Calcd. for C₂₁H₂₄N₄O₄: C, 63.63; H, 6.06. Found: C, 63.51; H, 5.81.

Cleavage Study: trans-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol.—The trans isomer (100 mg., 0.427 mmole) was treated exactly as the corresponding cis isomer; 36.5 mg. (0.143 mmole) of acetone 2,4-dinitrophenylhydrazone was isolated, m.p. 126°. This corresponds to 33.5% cleavage to yield acetone. 2,3-Dimethyl-6-benzoylhexene-2 2,4-dinitrophenylhydrazone (76.8 mg., 0.186 mmole) was isolated, m.p. 146-148°. This corresponds to 43.5% cleavage to yield the benzoyl compound. Cleavage Study: cis-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol.—Using the same procedure as with the cyclopentane analog there was obtained from 100 mg.

Cleavage Study: *cis*-1-Phenyl-2-methyl-2-(α -hydroxyisopropyl)-cyclohexanol.—Using the same procedure as with the cyclopentane analog there was obtained from 100 mg. of diol 5.2 mg. of acetone 2,4-dinitrophenylhydrazone, m.p. 118-123°. The yield of once-recrystallized material, m.p. 126°, corresponds to less than 5% of theory. From the non-volatile portion there was isolated 90 mg. of the 2,4dinitrophenylhydrazone of 2,3-dimethyl-7-benzoyl-2-heptene, m.p. 158° dec. Anal. Calcd. for C₂₂H₂₈O₄N₄: C, 64.37; H, 6.39. Found: C, 64.08; H, 6.07. Cleavage Study: *trans*-1-Phenyl-2-methyl-2-(α -hydroxyisopropyl)-cyclohexanol.—The *trans* isomer (100 mg., 0.404 mmole) was treated exactly as the corresponding *cis* isomer: 41.5 mg (0.173 mmole) of acetone 2,4-dinitro-

Cleavage Study: trans-1-Phenyl-2-methyl-2-(α -hydroxyisopropyl)-cyclohexanol.—The trans isomer (100 mg., 0.404 mmole) was treated exactly as the corresponding cis isomer; 41.5 mg. (0.173 mmole) of acetone 2,4-dinitrophenylhydrazone was isolated m.p. 125-126°. This corresponds to 42.8% cleavage to yield acetone. 2,3-Dimethyl-7-benzoylheptene-2,2,4-dinitrophenylhydrazone (71.0 mg., 0.174 mmole) was isolated, m.p. 155°. This corresponds to 43% cleavage to yield the benzoyl compound.

Cleavage Study: 2-Phenyl-4-methyl-2,4-pentanediol.— A sample (100 mg.) of this diol prepared by Brutcher⁵ was cleaved exactly as described above for the cyclic analog. There was isolated 05.9 mg. (49%) of acetone-2,4-dinitrophenylhydrazone, m.p. 125°, and 76.1 mg. (46%) of acetophenone 2,4-dinitrophenylhydrazone, m.p. 242°. No depression was observed on mixed m.p. with authentic acetophenone 2,4-dinitrophenylhydrazone.

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA, LINCOLN 8, NEBR.]

Epoxyketones. IV.¹ Stereostructure, Absorption Spectra and Three-ring Carbonyl Hyperconjugation

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trans-4'-Phenylchalcone oxide and 4-phenylacrylophenone oxide were each made by two different methods. The epoxide ring in several arylaroylethylene oxides was found to be resistant to cleavage by an amine and a stereochemical interpretation of the results from this type of reaction with trans-chalcone oxide is given to help in assigning configurations to amine addition products of α -bromochalcone. A detailed examination of spectroscopic data previously gathered and of new measurements indicates: (1) in the solid ground state aroylethylene oxides and cis- and trans-aryl aroyl ethylene oxides have a non-conjugated gauche conformation; (2) in CCl, solution the aroyl and trans-aryl aroyl ethylene oxides exist as mixtures of gauche and cisoid (conjugated) conformers; (3) the ethylene oxide ring transmits an electrical effect of a β -phenyl group, but p-substituents in the β -phenyl group do not extend the conjugation; (4) α -methoxy-4-phenylacetophenone shows conformational isomerism in CCl, solution which is similar to that which has been demonstrated for α -halo- and α -aminoketones.

Ultraviolet absorption spectra studies with cis and trans pairs of aryl aroyl ethylene oxides¹⁻³ have given results which have been discussed^{1,4} in terms of three-ring carbonyl hyperconjugation. Because it was thought that the ethylene oxide ring

(1) For paper III see, N. H. Cromwell and R. A. Setterquist, THIS JOURNAL, 76, 5752 (1954).

- (3) C. L. Stevens, et al., J. Org. Chem., 19, 522, 533 (1954).
- (4) N. H. Cromwell, Rec. Chem. Prog., 19, 214 (1958).

would not be able to support a partial positive charge as effectively as the ethylenimine ring, it was suggested^{1,5} that the infrared spectra of epoxy ketones might fail to show significant electrical interaction between the three-ring and the carbonyl group in the ground state as had been found to be the case for the ethylenimine ring.⁶

(5) N. H. Cromwell and M. A. Graff, J. Org. Chem., 17, 414 (1952). (6) See N. H. Cromwell, R. E. Bambury and J. L. Adelfang, THIS JOURNAL, 82, 4241 (1960), and previous papers in the series.

⁽²⁾ H. H. Wasserman and N. E. Aubrey, ibid., 77, 590 (1955).

With the hope of obtaining epoxyketones for spectral comparison with the previously studied 2-phenyl-3-*p*-phenylbenzoylethylenimines,^{5,7} two methods of synthesis of 4'-phenylchalcone oxide (I) were investigated. Bergmann and Wolff⁸ had claimed that they obtained two isomers of this material on alkaline hydrogen peroxide oxidation of 4'-phenylchalcone, while Bachmann and Wiselogle⁹ reported a single product melting at 136-137°.

An improved procedure of epoxidation of 4'phenylchalcone produced only the single product, previously reported,⁴ which would be expected to have the *trans* configuration.^{1,10} A Darzens-type condensation of benzaldehyde with α -bromo-4phenylacetophenone produced the same *trans* isomer, m.p. 136–137°, which is also to be expected as the favored configuration from this type of reaction.^{1,11} After allowing the *trans* isomer to stand in methanolic sodium methoxide, no indication was found of the presence of a second product which could be assigned a *cis* configuration. It seems probable that the *trans* form (I) is both the kinetically and thermodynamically favored isomer in these reactions.

It has been pointed out previously^{1,11} that *cis*-2nitrochalcone oxide is obtained from the *trans* form under conditions of relative insolubility of the *cis* isomer compared to the *trans* form. In the present study *cis*-2-nitrochalcone oxide was rearranged with sodium methoxide to the thermodynamically more stable *trans* form by dissolving the former in a sufficient amount of methanol and isopropyl alcohol. The result of this experiment further confirms the earlier conclusion¹ that the *trans*-2-nitrochalcone oxide is the thermodynamically favored isomer in solution.

Attempts to cleave the epoxide ring in *cis*and *trans*-2-nitrochalcone oxide, ¹ α -methylchalcone oxide, ¹² and *trans*-4'-phenylchalcone oxide with amines returned most of the starting material, indicating considerable resistance to ring cleavage in these structures.

Earlier studies¹³ with *trans*-chalcone oxide showed that the epoxide ring in this structure is readily cleaved with amines of low steric demand^{13a} by an SN2 attack (first order with respect to amine and first order with respect to epoxide)^{13b} at the β -carbon atom. The products of these reactions were found to be α -hydroxy- β -amino- β -phenylpropiophenones,^{13a,14} but configurations were not assigned to these racemic compounds in the earlier communications. It is now possible to assign these configurations with certainty and relate them to the structures tentatively assigned to the analogous *erythro*- and *threo*- α -bromo- β -morpho-

(7) N. H. Cromwell and R. J. Mohrbacher, THIS JOURNAL, 75, 6252 (1953).

(8) E. Bergmann and H. A. Wolff, ibid., 54, 1644 (1932).

(9) W. E. Bachmann and F. Y. Wiselogle, ibid., 56, 1559 (1934).

(10) H. O. House and R. S. Po, ibid., 80, 2428 (1958).

(11) H. Kwart and L. G. Kirk, J. Org. Chem., 22, 116 (1957).

(12) H. O. House and D. J. Reif, THIS JOURNAL, 77, 6525 (1955);

79, 6491 (1957).
(13) (a) N. H. Cromwell and N. G. Barker, *ibid.*, 72, 4110 (1950);
(b) 73, 1051 (1951).

(14) (a) N. H. Cromwell and F. W. Starks, *ibid.*, **72**, 4108 (1950);
(b) K. C. Tsou and N. H. Cromwell, J. Org. Chem., **15**, 1293 (1950).

lino- β -phenylpropiophenones by Southwick and Shozda.¹⁵

Reaction 1 in the series^{18a} outlined in Chart I produces the *dl-erythro-* α -hydroxy- β -amino- β -phenylpropiophenones A and B. Reaction of A^{14b} and B^{18a} with phenylmagnesium bromide pro-1,1,3-triphenyl-3-morpholinopropan-1,2duced diol and the piperidino analog identical with the products obtained from the reactions of morpholine and piperidine, respectively, with trans-1,1,3-triphenyl-2,3-epoxypropanol-1.¹⁶ In general, a Walden inversion is involved when an ethylene oxide ring is opened by an amine.¹⁷ The results of these experiments are in agreement with the conclusion that A and B have erythro configurations. Acetylation^{13a} of A and B with acetic anhydride (reaction 2) gives the α -acetoxy- β -amino- β -phenylpropiophenones C and D, respectively, which also would have dl-erythro configurations (no inversion).^{13,14} The same products, C and D, also result^{14a} from the treatment with triethylammonium acetate in dry benzene (reaction 3) of the α -bromo- β -amino- β -phenylpropiophenones E and F, respectively, obtained from the addition of the amines to the cis and/or trans forms of α -bromochalcone (reaction 4). Since reaction 3 is carried out under conditions expected^{14a} to favor an SN2 attack at the α -carbon without the participation of an ethylenimmonium ion intermediate, the formation of the *dl-erythro* products C and D indicate that E and F have *dl*-threo configurations. Southwick and Shozda¹⁵ used other evidence and rationalizations in assigning the *dl-threo* configuration to the addition product of α -bromochalcone and morpholine. These considerations are important in connection with current investigations of steric controls in conjugate additions.15,18

4-Phenylacrylophenone oxide (II) was prepared for the absorption spectra studies by two methods. Direct epoxidation of 4-phenylacrylophenone¹⁹ gave a good yield of the desired product II. Using a method similar to one described by House and co-workers²⁰ for the preparation of acrylophenone oxide, the oxidation of β -N,N-dimethylamino-4phenylpropiophenone methiodide (IV) gave a good yield of the epoxyketone II. The methiodide IV was prepared from β -dimethylamino-4-phenylpropiophenone (III) which was made in two ways. A Mannich reaction starting with 4-phenylacetophenone produced the hydrochloride of III in 75% yield while the reaction of β -chloro-4-phenylpropiophenone¹⁹ with dimethylamine gave a 60% yield of the same product.

 α -Methoxy-4-phenylacetophenone was made for the absorption spectra studies from α -diazo-4-

(15) P. L. Southwick and R. J. Shozda, THIS JOURNAL, 81, 5435 (1959).

(16) 1,1,3-Triphenyl-2,3-epoxypropanol-1, m.p. 130°, obtained from *trans*-chalcone oxide, m.p. 89-90°, was first described by E. P. Kohler, N. K. Richtmyer and W. F. Hester, *ibid.*, **53**, 205 (1931), and later by C. L. Bickel, *ibid.*, **59**, 325 (1939), and undoubtedly has a *trans* configuration.

(17) E. L. Eliel in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 111.

(18) N. H. Cromwell, THIS JOURNAL, 81, 4702 (1959).

(19) R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957).
(20) H. O. House, D. J. Reif and R. L. Wasson, *ibid.*, **79**, 2490 (1957).



phenylacetophenone¹⁹ following the procedure of

Newman and Beal²¹ for a similar material. Discussion of the Infrared Absorption Spectra.—A close inspection of well resolved infrared absorption spectra curves obtained from measurements in carbon tetrachloride solution shows two carbonyl bands each for acrylophenone oxide,20,22 4-phenylacrylophenone oxide, trans-chalcone oxide, trans-4-methoxychalcone oxide²³ and trans-4'-phenylchalcone oxide; see Table I. The stronger and higher frequency bands were located between 1687 and 1697 cm. -1 with the weaker bands at a 10-20 cm.-1 lower frequency. cis- and trans-2-Nitrochalcone oxide,¹ acetophenone,⁶ 4-phenylacetophenone,⁶ propiophenone,⁶ β -phenylpropiophenone, $^{6}\beta$ -(2-nitrophenyl)-propiophenone, $^{6}\beta$ -(4methoxyphenyl)-propiophenone and β ,4-diphe-nylpropiophenone⁷ all show single symmetrical carbonyl bands between 1687 and 1695 cm.-1. House and Blaker²⁴ have reported split carbonyl bands for several other aroyl ethylene oxides and for some glycidic esters.

The aroyl ethylene oxides described above which show two carbonyl frequencies in carbon tetrachloride solution exist as two molecular species in this solvent. A conjugated *cisoid* conformation⁶ is assigned to the species responsible for the lower frequency bands (1670–1683 cm.⁻¹) while a nonconjugated *gauche*⁶ structure is assigned to the

(21) M. S. Newman and P. F. Beal, III, This JOURNAL, 72, 516 (1950).

(22) A complete curve, generously supplied by Dr. H. O. House, shows two carbonyl bands for this epoxyketone as determined in CC14 solution: a strong one at 1693 cm.⁻¹ and a weaker one as a shoulder at 1683 cm.⁻¹.

(23) E. Weitz and A. Scheffer, Ber., 54B, 2327 (1921).

(24) H. O. House and J. W. Blaker, THIS JOURNAL, 80, 6389 (1958).

higher frequency bands (1687–1697 cm.⁻¹). Careful inspection of the total infrared spectra of these compounds indicates that carbonyl band bifurcation in these cases is probably not due to Fermi resonance as has been found for certain cyclic α,β -unsaturated ketones.²⁵ The epoxyketones reported here as showing split carbonyl bands in carbon tetrachloride solution show only a single carbonyl band in the solid phase. Moreover, in more polar solvents these split bands tend to coalesce, with the lower frequency band disappearing.²⁶ Models clearly indicate the improbability of the very sterically crowded *transoid* arrangement for the *cis*-aryl aroyl ethylene oxides. A *cisoid* conformation of the *trans* configuration also shows less crowding than the *transoid* conformation.



It seems unlikely that a combination of only inductive and coulombic field effects (dipoledipole interactions) are sufficient²⁴ to explain the two carbonyl bands observed with some of these epoxyketones. Just as with the ethylenimine ketones,6 both inductive and coulombic field effects of the three-ring oxygen atom would be expected to increase the frequency of the carbonyl band in comparison with that of the parent propiophenones. However, as the data indicate, the lower frequency band for these ethylene oxides is 10-20 cm.-1 below that of the corresponding parent propiophenone. This low band belongs to the cisoid conformer in which the steric requirements²⁷ for three-ring carbonyl hyperconjugation are met, while the higher band belongs to a gauche conformation in which these requirements are not met, and in some instances there may be a small dipoledipole interaction²⁴ which would account for the small elevation in frequency of the high band.

 α -Methoxy-4-phenylacetophenone shows two well defined carbonyl bands of nearly equal strength. The frequency of the lower band (1686 cm.⁻¹) is only a bit less than those found for 4-phenylacetophenone⁶ (1690 cm.⁻¹) and 4-phenylbutyrophenone⁷ (1687 cm.⁻¹) while the high band is found at 1707 cm.⁻¹. It seems likely that rotational isomerism, similar to that which has been reported for α -halogenated ketones²⁸ and α -aminoketones,⁶ is responsible for the splitting of the carbonyl band in α -methoxymethyl aryl ketones. The higher frequency band is assigned to a *cis*

(25) P. Yates and L. L. Williams, ibid., 80, 5896 (1958).

(26) For example, compare the values given in Table I for *irans*-epoxy-chalcone in CCl₄ with, $\gamma_{\rm C=0}$, 1687 (Nujol), 1694/80 and 1673/38 (CS₂) 1690/90 and shoulder at 1675/30 (CHCl₃), 1691 (CH₃CN). Polar solvents tend to increase the population of the form with the less polar carbonyl group; see ref. 28.

(27) N. H. Cromwell and G. V. Hudson, THIS JOURNAL, 75, 872 (1953).

(28) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 2nd ed., 1958, pp. 139, 140 and 401;
(b) L. J. Bellamy, L. C. Thomas and R. L. Williams, J. Chem. Soc., 3704 (1956); (c) L. J. Bellamy and R. L. Williams, *ibid.*, 4294 (1957);
(d) R. N. Jones and E. Spinner, Can. J. Chem., 35, 504 (1957).

				aviolet ^a	Infrared b
R_1	R:	Sol. ¢	λ, mμ	€ X 10 ⁻	$\gamma_{\rm C=0}, {\rm cm}, -1/\%$ abs.
н	CH-CHC ₆ H ₅ trans	E	250	16.8	$1697/84^{d}$
	\searrow	M	250	16.4	$1680/64^{d}$
	cis ^d	E	248	12.9	1694
н	CH-CHC6H4OCH3-p transe	М	230	14.9	1696/72
			250	15.9	1680/67
	0		(285)	7.0	
Н	CH ₂ CH ₂ C ₈ H ₄ OCH ₂ -p	\mathbf{M}	228	13.9	1687
	- · · · -		242	13.8	
			278	2.93	
C ₆ H ₅	CH ₂ OCH ₃	h.c. ^f	281	24.5	1707/86°
		м	286	24.8	$1686/85^{a}$
C_6H_5	$CH_2CH_2N(CH_3)_2$	h.c.	276	28.4	1683
C ₆ H ₅	CH-CH ₂	h.c.	282	25.5	1687/83
	\mathbf{h}				1672/75
C_6H_5	CH-CHC ₆ H ₅ trans	h.c.	286	31.3	1690/77
		м	294	26.0	1670/56

TABLE I

^a Ultraviolet spectra were measured with a Cary instrument, model 11MS. ^b Infrared spectra were determined with a Perkin-Elmer instrument model 21 employing sodium chloride optics and measured over the range of 700-4000 cm. using CCl₄ solutions in matched cells. • Ultraviolet solvents: h.c., 2,2,4-trimethylpentane; M, methanol; E, 95% ethanol. • See ref. 2. • See ref. 23. • 1.0-cm. cell, 6.95×10^{-6} mole/liter (5.0-cm. cell, 5.52×10^{-6} mole/liter, λ 280 ϵ 2.59 \times 10⁴). 9 11.88 mg/ml. in 1.0-mm. cell (1.20 mg/ml. in 5.0-mm. cell, 1706/76, 1686/75).

conformation in which the C==O and C-O bonds are nearly eclipsed (E), while the lower frequency band is assigned to a *gauche* conformation P which may receive some slight polarization from an intramolecular three-ring electrostatic interaction as indicated.⁶ The relative band strengths (ratio



 a_2/a_1) were not changed significantly on a tenfold dilution of the solutions. Coulombic field effects (dipole-dipole interactions)^{6,28} in the cis conformer E are undoubtedly responsible for the elevated frequency band. The effect of solvent variation and steric hindrance factors on this type of conformational isomerism will be reported in a later paper. For steric reasons similar interactions are expected to be less important with the epoxyketones.

Both β -alkoxy¹⁹ and β -amino-4-phenylpropiophenones show only single symmetrical carbonyl bands and thus give no evidence of conformational isomerism in carbon tetrachloride solution for such structures.

Discussion of the Ultraviolet Absorption Spectra.—The ultraviolet maxima comparison for acrylophenone oxide²⁰ (in ethanol, λ 246 m μ , ϵ 11,600), *cis*-chalcone oxide² (in ethanol, λ 248 m μ , ϵ 12,900) and 4-phenylacrylophenone oxide (see Table I), with the corresponding propio-phenones, propiophenone²⁹ (in ethanol, λ 242 m μ , ϵ 13,500), β -phenylpropiophenone⁶ (in methanol, λ 243 m μ , ϵ 13,300), $\bar{4}$ -phenylpropiophenone¹⁹ (in isoöctane, λ 276 m μ , ϵ 23,400) and β ,4-diphenylpropiophenone⁷ (in isoöctane, λ 276 m μ , ϵ 25,200) clearly implies an electrical interaction between the

(29) E. A. Braude and F. Sondheimer, J. Chem. Soc., 3764 (1955).

three-ring and the carbonyl group in the excited state, with a small effect of phenyl transmitted by the three-ring. The maxima for trans-chalcone oxide and trans-4'-phenylchalcone oxide (see Table I) are found at still longer wave lengths with increased extinction coefficients, and here the effect of the β -phenyl group is quite pronounced.

trans-4-Methoxychalcone oxide and trans-chalcone oxide have aroyl associated maxima at identical wave lengths with the former compound showing a lower extinction coefficient (see Table I). Thus, just as in the case of the analogous ethylenimine ketones,⁶ the p-substituent on the β -phenyl group has not extended the three-ring carbonyl conjugation in this cross-conjugated system. Both trans-4-methoxychalcone oxide and trans-1-cyclohexyl - 2 - (ϕ - methoxyphenyl) - 3 - benzoylethylenimine⁶ show a strong band at 230 mµ which is probably an enhanced anisole E band,³⁰ caused by interaction of the anisole group with the threering. Black and Lutz have given evidence for

$$CH_3 \overleftarrow{O} - \underbrace{CH}_X \xrightarrow{CH} - CH - \longleftrightarrow CH_3 \overleftarrow{O} = \underbrace{CH}_X \xrightarrow{O} CH - \underbrace{CH}_X \xrightarrow{O} CH -$$

the partial independence of the *p*-methoxystyrene chromophore in the chalcone series.⁸¹ Introduction of an additional chromophoric or auxochromic group in one arm of a cross-conjugated system may have a hypsochromic effect on the ultraviolet absorption maximum of an aryl ketone.³²

A comparison of the ultraviolet maximum for α methoxy-4-phenylacetophenone (Table I) with that for 4-phenylacetophenone⁶ shows an increase in λ of 3–6 m μ , depending on the solvents used,

(30) A. Gillam and E. Stern, "Electronic Absorption Spectroscopy," Edward Arnold, Ltd., London, 1957; p. 141.

 (31) W. Black and R. Lutz, THIS JOURNAL, 77, 5134 (1955).
 (32) See, for example, N. H. Cromwell and P. H. Hess, *ibid.*, 82, 136 (1960), who report that introduction of a double bond in the cyclohexyl ring of 4-biphenyl cyclohexyl ketone to produce 4-biphenylyl-4-biphenylyl-1-cyclohexenyl ketone changes λ_{max} from 283 mµ (e 24,200) to 281 mµ (e 20,800).

and dilution of the isoöctane solution had no appreciable effect on λ or ϵ . This may be taken as further evidence for the three-ring electrostatic polarization in these α -methoxymethyl aryl ketones described in the infrared section of this paper. The effect is less in the more polarizing solvent methanol, being somewhat swamped out.⁶ Such effects are not observed with either the β -alkoxy-¹⁹ or β -dimethylamino-4-phenylpropiophenones (see Table I).

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Experimental³³

trans-4'-Phenylchalcone Oxide (I). (a) Epoxidation of trans-4'-Phenylchalcone.—A 1.0 g. (0.0035 mole) sample of trans-4'-phenylchalcone³⁴ dissolved in a solution of 60 ml. of dioxane containing 1% by volume of sec-amyl alcohol was mixed with 5 ml. (0.049 mole) of 30% hydrogen peroxide and 0.67 g. (0.012 mole) of potassium hydroxide in 10 ml. of methanol. The temperature of the reaction mixture was maintained at 20° for 6.5 hr. and then diluted with 75 ml. of water and allowed to stand at room temperature for 12 hr. A 1.04 g. yield (98.1%) of a colorless solid, m.p. 135-137.5°, was isolated; recrystallized from benzene and petroleum ether, m.p. 137-138°.⁹ (b) Darzens Condensation.—A mixture of 2.65 g. (0.025 mole) of benzaldehyde, 6.90 g. (0.025 mole) of α bromo-4-phenylacetophenone and 2.00 g. (0.037 mole) of sodium methoxide in a solution of 150 ml. of dioxane and 75 ml. of mathenol was held at 18° for 30 minutes. Acidi

(b) Darzens Condensation.—A mixture of 2.65 g. (0.025 mole) of benzaldehyde, 6.90 g. (0.025 mole) of α -bromo-4-phenylacetophenone and 2.00 g. (0.037 mole) of sodium methoxide in a solution of 150 ml. of dioxane and 75 ml. of methanol was held at 18° for 30 minutes. Acidification of the reaction mixture with glacial acetic acid t ρ H 6 and flash evaporation at 50° produced a sticky, brown residue which was washed with water and recrystallized from chloroform and methanol to give 3.71 g. (49.5% yield) of I, m.p. 137-138.5°.

4-Phenylacrylophenone Oxide (II). (a) Epoxidation of 4-Phenylacrylophenone.—A 0.500 g. (0.0024 mole) sample of 4-phenylacrylophenone¹⁹ dissolved in 6 ml. of dioxane and cooled to 9-10° was mixed with 2.5 ml. (0.025 mole) of 30% hydrogen peroxide and 1.0 ml. (0.0003 mole) of 15% aqueous sodium hydroxide. After 30 minutes the reaction mixture was diluted with three times its own volume of water to produce 0.485 g. (89% yield) of colorless product, m.p. 121-122.5°, recrystallized from petroleum ether.

(b) Oxidation of β -N,N-Dimethylamino-4-phenylpropiophenone Methiodide.—A suspension of 2.0 g. (0.0051 mole) of the methiodide IV in 250 ml. of acetone was mixed with 25 ml. (0.25 mole) of 30% hydrogen peroxide and 25 ml. of aqueous sodium hydroxide (0.031 mole) and allowed to stand at 25° for 30 minutes. Isolation of the product produced 0.92 g. (82% yield) of II.

Anal. Caled. for C15H12O2: C, 80.33; H, 5.39. Found: C, 80.03; H, 5.19.

 β -N,N-Dimethylamino-4-phenylpropiophenone (III). (a) Mannich Reaction.—A mixture of 6.0 g. (0.031 mole) of 4-phenylacetophenone, 1.86 g. of paraformaldehyde and 3.23 g. (0.040 mole) of dimethylamine hydrochloride, three drops of coned. hydrochloric acid, and 35 ml. of 95% ethanol was refluxed for 8 hr. After standing at room temperature for 12 hr. an additional amount of paraformaldehyde (0.47 g.) and of dimethylamine hydrochloride (0.81 g.) and 10 ml. of 95% ethanol were added to the reaction mixture. This was refluxed an additional 8 hr. and then allowed to stand 12 hr. at room temperature. A colorless crystalline solid (the hydrochloride of III) was isolated; 6.74 g. (75% yield), m.p. 182–187°, recrystallized from abs.

Anal. Calcd. for C₁₇H₂₀NOCI: C, 70.45; H, 6.60; Cl, 12.23, Found: C, 70.54; H, 6.86; Cl, 12.48.

Treatment of 2.0 g. of the hydrochloride of III with aqueous sodium carbonate produced 1.52 g. of the free base III, m.p. 80-81°.

Anal. Caled. for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53. Found: C, 80.76; H, 7.44; N, 5.48.

(b) From β -Chloro-4-phenylpropiophenone.—A 2.45 g. (0.010 mole) sample of the chloroketone¹⁹ and 10 ml. of anhydr. dimethylamine were sealed in a thick walled Pyrex tube and allowed to stand at 25° for 58 hr. The tube was opened and the excess dimethylamine evaporated. The residue was recrystallized from abs. ethanol to give a 60% yield of the hydrochloride of III, m.p. 186–187°, which was shown to have a chlorine content of 12.47% (calcd. 12.23%). Methiodide of III.—A solution of 0.30 g. (0.0012 mole) of III in 50 ml. of anhydr. ether and 5 ml. of methyl iodide stood in the refrigerator for 15 minutes to precipitate 0.413 g. (87% yield) of the methiodide IV, m.p. 234–236°; λ (methanol) 222, 298 m μ ($\epsilon \times 10^{-3}$, 26.4, 18.9); γ_{c-0} 1678 (Nujol).

Anal. Calcd. for C₁₈H₂₂NOI: C, 54.69; H, 5.61. Found: C, 54.12; H, 5.63.

Isomerization of Aryl Aroyl Ethylene Oxides. $cis \rightleftharpoons trans$ Isomerism of 2-Nitrochalcone Oxide.—A 0.50 g. (0.0019 mole) sample of cis-2-nitrochalcone oxide¹ was dissolved in a mixture of 134 ml. of methanol and 175 ml. of isopropyl alcohol containing 0.38 g. (0.0071 mole) of sodium methoxide and allowed to stand at room temperature for 70 hr. Neutralization with acetic acid and concentration of the reaction mixture gave a mixed product which was chromatographed on an activated alumina column to give 0.175 g. of the *trans*-epoxyketone, m.p. 112-114°, ¹ and 0.062 g. of the *cis* isomer, m.p. 174-176°.¹ The infrared spectra of the *cis* and *trans* forms were identical with those previously reported for these isomers.¹

trans-4'-Phenylchalcone oxide (0.10 g., 0.00035 mole) was dissolved in 25 ml. of methanol containing 0.055 g. (0.001 mole) of sodium methoxide and allowed to stand at room temperature for 19 hr. Isolation of the epoxyketone returned only the *trans* isomer, m.p. 136-138°.

Attempted Reaction of Epoxyketones with Morpholine.---When 0.20-g. samples of the *cis*- and *trans*-2-nitrochalcone oxides were each dissolved in 5 ml. of morpholine and allowed to stand at room temperature for several days only the starting materials were recovered (75-90%).

A similar experiment with $trans - \alpha$ -methylchalcone oxide¹² returned 90% of the starting material after a reaction time of seven days. trans-4'-Phenylchalcone oxide returned 68% of the starting material after 3 days reaction time. A 0.60-g. (0.002 mole) sample of this latter oxide returned 79% of the starting material after standing at room temperature for 2 days with 0.35 g. (0.004 mole) of morpholine in 100 ml. of methanol.

 α -Methoxy-4-phenylacetophenone.—Following the procedure of Newman and Beal,²¹ purified α -diazo-4-phenylacetophenone¹⁹ (0.50 g., 0.00225 mole) dissolved in 25 ml. of methanol was treated with 2 ml. of boron trifluoride etherate and the mixture was allowed to stand at 5-15° until nitrogen evolution was complete (1 hour). The reaction mixture was added to an excess of dilute hydrochloric acid and the solid that formed immediately was collected and washed with water. Treatment with Norite followed by crystallization from aqueous methanol provided 0.29 g. (57%) of α -methoxy-4-phenylacetophenone, m.p. 87-89°. An analytical sample, m.p. 89-89.5°, was prepared by recrystallization from aqueous methanol followed by sublimation under reduced pressure.

Anal. Caled. for C₁₆H₁₄O₂: C, 79.62; H, 6.24. Found: C, 79.86; H, 6.24.

In another experiment the reaction mixture was poured on aqueous sodium carbonate solution and a dried benzene solution of the crude product was chromatographed on slightly basic alumina. Concentration of the benzene eluates and crystallization of the residue from a small amount of petroleum ether afforded a 13% yield of α -methoxy-4phenylacetophenone dimethyl ketal, m.p. 52-53°. An analytical sample, m.p. 52-53°, was obtained by distillation under reduced pressure; $\lambda 252 \text{ m}\mu (\epsilon 18,800)$.

Anal. Caled. for C₁₇H₂₀O₄: C, 74.97; H, 7.40. Found: C, 74.84; H, 7.47.

⁽³³⁾ All m.p.'s are corrected.

⁽³⁴⁾ N. H. Cromwell, R. P. Cahoy, W. E. Franklin and G. D. Mercer, THIS JOURNAL, 79, 922 (1957).