mixed melting point with an authentic sample of alcohol were determined. Butyl 3,5-dinitrobenzoate, m.p. 60°, mixed melt 61°.

A second 5-gram sample of the unknown was added dropwise to 10 cc. of hot 50% H_2SO_4, the volatile materials distilled into ethyl alcohol and the 2,4-dinitrophenylhydrazone of formaldehyde was obtained. After recrystallizing from ethyl alcohol the melting and mixed melting points were taken: formaldehyde 2,4-dinitrophenylhydrazone, m.p. 164°, mixed melt, 164°.

Identification of Benzyl Alkyl Ether.—The product, a sample of which gave a negative test for halogen (alcoholic $AgNO_3$) when oxidized with basic $KMnO_4$, gave benzoic acid, which proved the presence of the benzyl radical.

The presence of oxygen was determined by the method of Davidson.[8] The benzyl ether was then cleaved at the oxygen bond by refluxing 5 cc. with a mixture of 5 cc. of acetic anhydride, 5 cc. of acetic acid and 1 cc. of concentrated H_2SO_4 for four hours. The reaction mixture was then cooled and dissolved in 50 cc. of ether, washed with 10% $NaHCO_3$ until the washings were basic, twice with water, the ethereal solution fractionated and the two acetate esters collected. Boiling points, densities, and refractive indices were determined on the esters after which they were treated with 3,5-dinitrobenzoic acid to give the solid benzoates: Benzyl 3,5-dinitrobenzoate, m.p. 110°, mixed melt 111°; butyl m.p. 60°, mixed melt 61°; propyl m.p. 73°, mixed melt 74°; ethyl m.p. 93°, mixed melt 93°.

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TUSKEGEE INSTITUTE, ALA. RECEIVED FEBRUARY 12, 1951

(8) David Davidson, *Ind. Eng. Chem., Anal. Ed.*, **12**, 40 (1940).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Stereoisomeric Dibromides and α-Bromo Derivatives of Benzalacetophenone and the Mechanism of Dehydrohalogenation

BY ROBERT E. LUTZ, DAVID F. HINKLEY[1a] AND ROBERT H. JORDAN[1b]

A second and non-crystalline (*cis*) α-bromobenzalacetophenone has been obtained by sunlight inversion of the known (*trans*) crystalline form. It is formed in small amounts in the potassium acetate dehydrohalogenation of the high-melting benzalacetophenone dibromide but it is not obtained in the similar dehydrohalogenation of the low-melting dibromide. The ultraviolet absorption characteristics and interconversions of the isomers are discussed in relation to configuration. The assignment of configurations to the benzalacetophenone dibromides is made on the basis of differing behaviors on dehydrohalogenation where two competing mechanisms are suggested.

This investigation stemmed from a study of the possibility of stereochemical guidance in the reactions involved in the preparation of the diastereoisomeric α,β-dimorpholinylbenzylacetophenones,[2] and from the recent study of *cis*-benzalacetophenone.[3]

The higher-melting benzalacetophenone dibromide (m.p. 159–160°) (II) is the chief product in bromination of *trans*-benzalacetophenone.[4] The lower-melting isomer (m.p. 123–124°) (I) is formed at the same time in very small amounts but is difficult to isolate in pure condition from the mixture; it can be obtained in quantity from the much more favorable mixture of stereoisomers produced by the addition of hydrogen bromide under controlled conditions to the crystalline α-bromobenzalacetophenone (III)[4b,c] which is now shown to be *trans*.

The elimination of hydrogen bromide from the high-melting dibromide (II) by means of potassium acetate[4c] gives a mixture from which has been isolated the crystalline α-bromobenzalacetophenone, m.p. 41–42°, here to be designated as the *trans*-isomer (III). In a repetition of the experiment under controlled conditions this mixture was obtained in a yield of 95% and it was found to consist of about 66% of the *trans*-isomer and 34% of an oil which has now been characterized and is here designated as the *cis*-isomer. Benzoylphenylacetylene[5a] apparently was not formed to any significant extent. When the lower-melting dibromide was dehydrohalogenated similarly by the action of potassium acetate, reaction occurred much more rapidly and an 87% yield of product was obtained which proved to be nearly pure crystalline *trans*-isomer. Both *cis*- and *trans*-α-bromobenzalacetophenones were shown in separate experiments to be stable under these reaction conditions and therefore were independent products. Although the dehydrohalogenations had not followed fully consistent stereochemical courses, there was exhibited significantly different behaviors of the two dibromides.

The new (*cis*) isomer has been obtained directly by sunlight inversion of an isoöctane solution of the crystalline (*trans*) isomer. It is a yellow oil which in spite of its lability and the difficulty of purification by ordinary techniques has been obtained in a relatively high state of purity (*ca.* 96–97%). The sunlight inversion from *trans* to *cis* was practically complete, and the position of the photoequilibrium appeared to lie far over on the side of the *cis* isomer. The conversion of the new (*cis*) isomer back into the solid (*trans*) isomer was brought about (a) by heating at 160°, (b) by the action of iodine under heating at 100°, and (c) by the action of sunlight on a chloroform solution containing iodine. These reactions show that the solid (*trans*) isomer actually is the stable form and that the new (*cis*) isomer is the labile form. Since steric interference between spatially adjacent

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(1) (a) du Pont Company Fellow in Chemistry, 1950–1951; (b) at University of Virginia Medical School.

(2) *Cf.* (a) N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946); (b) R. E. Lutz and W. R. Smithey, *J. Org. Chem.*, **16**, 51 (1951); (c) R. H. Jordan, R. E. Lutz and D. F. Hinkley, *ibid.*, in press.

(3) (a) R. E. Lutz and R. H. Jordan, THIS JOURAL, **72**, 4090 (1950). *Cf.* also the *cis*- and *trans*-benzalacetophenone semicarbazones [I. M. Heilbron and F. J. Wilson, *J. Chem. Soc.*, **101**, 1482 (1912); **103**, 1504 (1913)] and the β-methoxybenzalacetophenone derivatives [C. Dufraisse and R. Netter, *Compt. rend.*, **189**, 299 (1929)].

(4) (a) A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 205; (b) F. J. Pond, H. J. York and B. L. Moore, THIS JOURNAL, **23**, 790 (1901); (c) R. D. Abell, *J. Chem. Soc.*, **101**, 1000 (1912).

(5a) *Cf.* C. L. Bickel, THIS JOURNAL, **69**, 2134 (1947); **72**, 349 (1950).

phenyl and benzoyl groups would be much greater than between adjacent phenyl and bromo, the above transformations constitute adequate evidence for the assignment (already indicated above) of the *trans* configuration to the stable crystalline isomer and the *cis* configuration to the labile non-crystalline isomer.

The ultraviolet absorption curve of *trans* α-bromobenzalacetophenone (Fig. 1) is consistent with expectation based on the assignment of this configuration. The dominant peak falls at 297.5 mμ (see Table I) which is in the range expected of a *trans*-benzalacetophenone structure,[3a] and there is also a strong band at 252.5 mμ which corresponds to that of a benzoyl group. However, the extinction coefficient of the 297.5 mμ band (15.7 × 10^3) is significantly lower than that of the corresponding band of the parent *trans* benzalacetophenone itself (which is 23.6 × 10^3), and this difference may be interpreted as evidence of appreciable steric interference by the bromine atom with the conjugation involved.[5b]

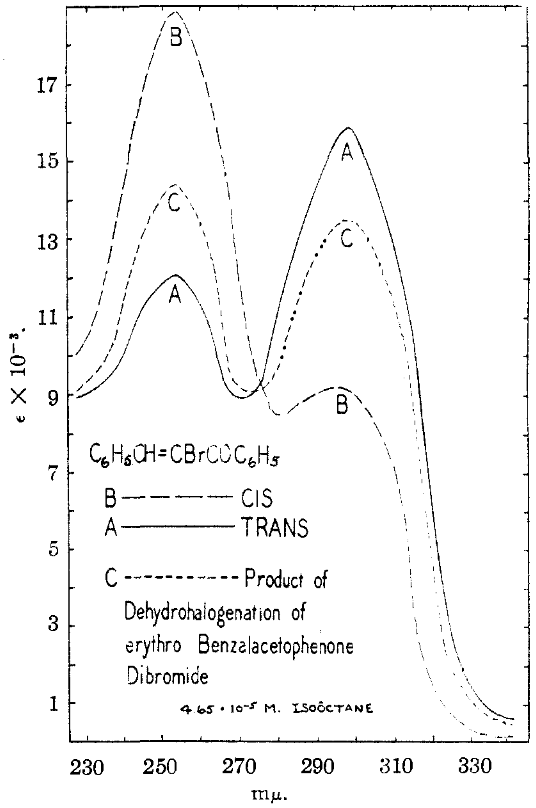

Fig. 1.

TABLE I

ULTRAVIOLET ABSORPTIONS[a,b]

Compound	Isomer	M.p., °C.	λmax, mμ	ε × 10^{-3}
Benzalacetophenone	A, *erythro*	160	253	14.8
dibromides	B, *threo*	124	253	13.7
α,β-Dimorpholinylbenzyl-	A	184	240	12.2
acetophenones	B	179	237	14.6
Dibenzoylethylene	*meso*	178	261	23.6
dibromides[b]	*dl*	108	261	23.6
α-Bromobenzalaceto-	*trans*	42	252.5	12.1
phenones			297.5	15.7
	cis	oil	252.5	18.8
			297.5	9.1

[a] These ultraviolet absorptions were measured by means of a Beckman DU quartz spectrophotometer at dilutions of about 0.00005 molal. [b] The solvent was absolute ethanol except in the case of the benzalacetophenone dibromides and the α-bromobenzalacetophenones where isoöctane was used.

It would be expected that in *cis*-α-bromobenzalacetophenone there would exist a considerable amount of interference with the planarity of the system just as in the case of the parent *cis* benzalacetophenone itself. In fact the new (*cis*) isomer shows a greatly suppressed *trans*-benzalacetophenone type peak at 297.5 mμ (see Fig. 1 and Table I) (ε = about 9.3 × 10^3) and a strong benzoyl type band at 252.5 mμ (ε = 19 × 10^3).

The difference in exaltation of molecular refractions should serve in some degree as a measure of the difference in interferences with planarity in this and other *cis–trans* pairs because of the dependence on polarizability of the conjugated system involved. The higher exaltation of the supercooled liquid

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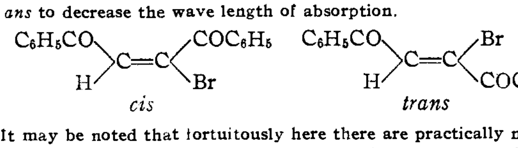
(5b) In a recent article [A. L. Nussbaum, O. Mancera, R. Daniels, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3263 (1951)] which appeared while the present paper was in press, the bathochromic effects of bromine on α,β-unsaturated ketone systems were explained in terms of the relative contributions of bromonium resonance structures. The different types of compounds in order of magnitude of the effect are as follows: $RCBr{=}CHCOR > RCH{=}CBrCOR > RCH{=}CBrCOC_6H_5 > C_6H_5CH{=}CBrCOR$ (R = H or alkyl). From these findings, disregarding steric factors which were not considered, it would be predicted that in the case of the α-bromobenzalacetophenones where there are phenyls at both ends of the system, the relative positive polarization of the bromine would be further diminished and that the bathochromic effect would be very small or negligible. The situation is complicated however by the fact that there is a difference of 8 mμ in the λ_{max} of the parent *cis* and *trans* benzalacetophenones.[8] The data show that within the *trans* type actually there is no bathochromic effect of substitution of α-bromine, but that within the *cis* type there is a significant shift toward the longer wave length.

In the case of the *cis* and *trans* dibenzoylethylenes and their monobromo derivatives there is a similarly interesting relationship [L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950)]. The substitution of bromine gives rise to a shift of λ_{max} of 8 mμ (ethanol) both within the *cis* and within the *trans* types, but in opposite directions in the two types; in the *cis* compounds it is to increase and in the *trans* to decrease the wave length of absorption.



$$\underset{cis}{(C_6H_5CO)(H)C{=}C(COC_6H_5)(Br)} \qquad \underset{trans}{(C_6H_5CO)(H)C{=}C(Br)(COC_6H_5)}$$

[It may be noted that fortuitously here there are practically no shifts of the λ_{max} upon substitution of bromine with respect to relative stability rather than configurational similarities of the compounds being compared; *i.e.*, the *labile* dibenzoylethylene (which is *cis*) and the labile (but *trans*) bromo derivative have practically the same λ_{max} in ethanol, and similarly the stable (*trans*) dibenzoylethylene and the stable (*cis*) bromo derivative have nearly identical λ_{max}.]

These results are understandable in terms of the following. Steric interference by the bromine in the *cis* compounds in which the α(*gem*)-benzoyl is sandwiched between the bromine and the β-phenyl or benzoyl tends to diminish significantly the effectiveness of the conjugation of the unsaturated ketone or diketone system, but it would not seriously affect the ability of the bromine to accommodate a positive charge. Increases in the wave length of absorption, though not quantitatively predictable, are thus not unexpected. In the case of the *trans* compounds the configuration of the unsaturated ketone or diketone system is impeded although perhaps to a lesser degree, but now the bromine is under serious steric pressure, an effect which should operate to stretch or to distort the angle of the C–Br bond and to diminish significantly the effectiveness of positive bromine resonance forms. The absence of change or actual decrease in wave length of absorption in this type is thus consistent with theory.

It is to be concluded from these data that in the types of phenomena under discussion steric factors may be important, especially when highly conjugated systems are involved.

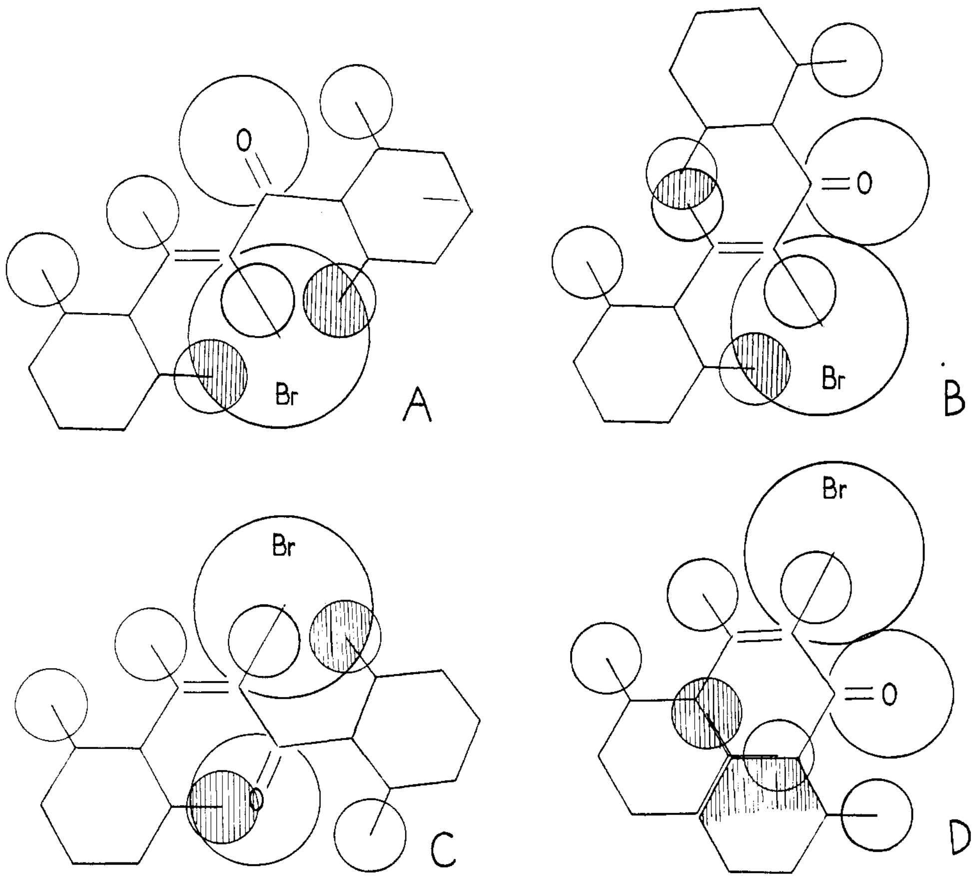


Fig. 2.—Scale drawing of *cis*- and *trans*-α-bromobenzalacetophenones, based on the following dimensions[6]: C–C, 1.54; C=C, 1.33; C–H, 1.08; C=O, 1.22; atomic radii; H, 0.75; O, 1.4; Br, 1.95; bond angles; C—C=O, 122°; C=C—C, 124.

isomer (*trans*) (M_D 3.84) as compared with that of the new *cis*-isomer (M_D 3.37) indicates a higher degree of conjugation in this form and is consistent with the ultraviolet absorption characteristics described above.

In connection with the problem of fine structure of the *cis*- and *trans*-benzalacetophenones and also the *cis*-α-bromo derivative, it is obvious from planar scale drawings (Fig. 2) based on van der Waals radii[6] and commonly accepted bond angles[6] that in this state which would be required for fully effective resonance to exist, the carbonyl oxygen would face inward toward the central ethylene double bond rather than outward or away from it, and that the interference between groups in the *cis*-isomers is much greater than in the *trans*. In the case of *trans*-α-bromobenzalacetophenone the situation is not as obvious, however, because there is less total overlapping of groups in either of the two planar forms (Fig. 2A, B), and because the difference in the two cases is relatively small. In favor of the form involving the carbonyl oxygen facing inward (Fig. 2A) it may be said that the overlap of the benzoyl group occurs only in one direction, between the α-bromine and ortho-hydrogen; whereas the other form involves not only overlap in two directions, between the beta and ortho hydrogens and between oxygen and bromine, but also much greater electrostatic repulsions between the groups.

The higher-melting and less-soluble benzalacetophenone dibromide (II) has the higher extinction coefficient at the λ_{max} of its characteristic benzoyl-type ultraviolet absorption band, and the lower-melting and more-soluble isomer has the lower extinction coefficient. It was found that the ultraviolet absorption curves of the two isomeric dimorpholinylbenzylacetophenones, $C_6H_5CH(NC_6H_8O)CH(NC_4H_8O)COC_6H_5$, show a similar difference in extinction coefficients of the main ultraviolet bands,[7] but in this case it is the lower-melting more-soluble isomer which has the higher extinction coefficient of the pair. Incidentally, it has been found that *dl*- and *meso*-dibenzoylethylene dibromides, $C_6H_5COCHBrCHBrCOC_6H_5$, which are lower-melting-more-soluble and higher-melting-less-soluble, respectively, show almost identical ultraviolet absorptions and practically no difference in extinction coefficients.

On theoretical grounds one might argue that in a pair of similarly substituted diastereoisomers, particularly in a symmetrical pair such as the *dl*- and *meso*-dibenzoylethylene dibromides, the higher-melting less-soluble *meso*-isomer would normally involve the nearer approach to a *trans* relationship of the various like groups with respect to the central

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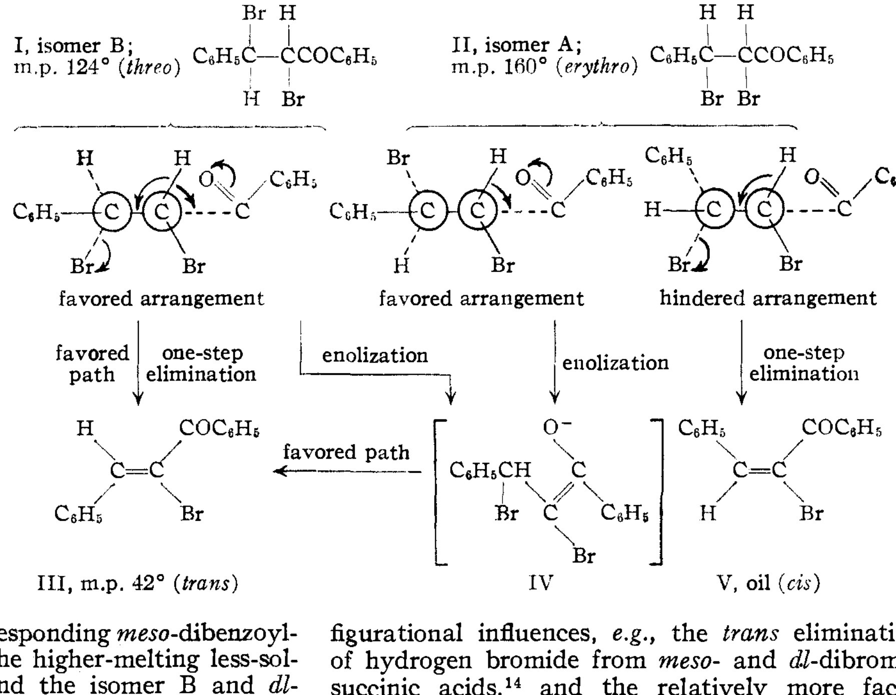
[6] L. C. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940.

[7] The work on the isomeric α,β-dimorpholinylbenzylacetophenones will be described in a subsequent paper (*cf.* ref. 2c).

bond connecting the two asymmetric centers, and that this would have a consistent effect on physical properties including the extinction coefficient of the principal ultraviolet absorption band of the benzoyl group. The absence of such a difference in the case of the symmetrically substituted dibenzoylethylene dibromides, although doubtless fortuitous, indicates that the extinction coefficient is not in any simple fashion related to diastereoconfiguration, and consequently is of no use in distinguishing between the compounds under consideration here.

It seems possible to make a tentative assignment of the *erythro* configuration to the higher-melting benzalacetophenone dibromide and *threo* to the lower-melting isomer on the basis of the fact that the higher-melting isomer on dehydrohalogenation gives a significant amount of *cis* α-bromobenzalacetophenone in contrast with the lower-melting isomer which does not, and on the basis of the relatively much greater facility of dehydrohalogenation of the latter. The greater rate of dehydrohalogenation of the lower-melting isomer already noted above was found to hold in controlled experiments designed to demonstrate rigorously the close analogy with the *dl*- and *meso*-dibenzoylethylene dibromides where the configurations are known[8]; in benzene with excess triethylamine at room temperature the lower-melting isomer reacted approximately 100 times as fast as the higher-melting isomer, and *dl*-dibenzoylethylene dibromide reacted 7 times as fast as the *meso* isomer. It is assumed that the more sterically favorable mode of elimination of hydrogen bromide is *trans*, although the steric influence might well be considerably overshadowed by the tendency of the reaction to produce in both cases the more stable *trans* product. Assignment of configurations on this basis is consistent with the fact that the isomer A and the corresponding *meso*-dibenzoylethylene dibromide are the higher-melting less-soluble diastereoisomers, and the isomer B and *dl*-dibenzoylethylene dibromide are the lower-melting more-soluble isomers.



III, m.p. 42° (*trans*)

IV

V, oil (*cis*)

It is necessary for clarification of the above conclusion to comment on the nature and significance of *trans* elimination as applied to the present case and others which are analogous. In this type of dehydrohalogenation at least two mechanisms may be postulated, one involving enolization-ionization such as was suggested long ago by Thiele,[9] and the other an inversion type reaction in which the molecule at the time of removal of the α-hydrogen but before the development of an actually-free enolate ion, undergoes simultaneous rearward loss of a bromide ion (see IIc).[10] A true enolization mechanism would undoubtedly involve the disappearance of distinctive epimeric configurations since the formation of the enolate (IV) would presumably involve only one, and that the more favored, of the two possible configurations, and therefore would not be likely to permit any configurational guidance in the regeneration of diastereoconfiguration through the asymmetric α-carbon.

The stereochemistry involved here is illustrated in formulas I-V. In so far as the dehydrohalogenation is a direct abstraction of hydrogen bromide without actual enolization, it is analogous to debromination of *meso*- and *dl*-2,3-dibromobutanes[11] where the postulate is made on the basis of evidence that the molecules assume a preferred orientation with respect to the angle of rotation of the central bond between the two asymmetric centers[12] and where consistent *trans* elimination of bromine is favored and is especially facilitated in the *meso*-isomer.[10,13] In the removal of vicinal hydrogen and bromine there have already been observed examples of the operation of strong configurational influences, *e.g.*, the *trans* elimination of hydrogen bromide from *meso*- and *dl*-dibromosuccinic acids,[14] and the relatively more facile elimination of hydrogen bromide from the *dl*-isomer as compared with the *meso*-[12] and from

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[8] R. E. Lutz, THIS JOURNAL, **49**, 1106 (1927).

[9] J. Thiele, *Ann.*, **306**, 92 (1899); **308**, 333 (1899).

[10] *Cf.* (a) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 118; (b) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941); (c) P. S. Skell and C. R. Hauser, THIS JOURNAL, **67**, 1661 (1945).

[11] S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939).

[12] W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, **61**, 1640 (1939); J. D. McCullough, *ibid.*, **62**, 480 (1940).

[13] W. G. Young, Abstr. of Papers, Eighth Org. Symp., A. C. S., St. Louis, Mo., December, 1939, p. 92.

[14] R. Fittig and C. Petri, *Ann.*, **195**, 61 (1879).

bromofumaric acid as compared with bromomaleic acid.[15] In the case of the benzalacetophenone dibromides the favored steric arrangements of the two isomers are illustrated. It is obvious that the favored arrangement of the *erythro*-isomer (II) is not ideal for *trans* elimination, and it is here that one would expect to find the greater resistance toward 1,2-dehydrohalogenation and the proportionally greater reaction albeit a slower one through the indicated hindered form *via* configuration-destroying enolization.

If the above postulates are correct the enolization or ionization mechanism involving the active hydrogen would appear to be dominant here in the case of the dibromide A (*erythro*) to the extent of the 66% yield of the *trans* product obtained, but it would be negligible in the consistently *trans* dehydrohalogenations of the presumably less easily enolizable *dl*- and *meso*-dibromosuccinic acids, and (as has actually been shown[10c]) in the case of β-phenylethyl bromide.

Acknowledgment.—The ultraviolet absorptions of the benzalacetophenone and dibenzoylethylene dibromides were carried out by Haywood G. France in a program of study designed to determine the influence of diastereoconfiguration of α,β-asymmetric carbons on the ultraviolet absorption characteristics of a benzoyl group. In view of the preliminary results it would seem that these effects are very small and unpredictable. The problem will be continued only incidentally in connection with other work in this and related fields.

Experimental Part

The Preparation of the Lower-melting Benzalacetophenone Dibromide B (I).[4b,c]—A solution of 5.92 g. of *trans*-α-bromobenzalacetophenone, m.p. 41–42°, in 100 ml. of carbon disulfide at 0° was treated with an excess of dry hydrogen bromide for 30 minutes. The solvent was evaporated under reduced pressure and the dry residue, 7.4 g. (97%), was crystallized from 50 ml. of hot absolute ethanol (room temperature), 7.3 g., m.p. 111–120°; recrystallization from 75 ml. gave 5.0 g., needles, m.p. 123–124° (66%). In view of the solubility ratio of the two isomers, these data indicate a 93% production of the isomer-B.[*Cf.* 2c]

The higher-melting dibromide[4a] was recrystallized from benzene to ensure a product free from the lower-melting isomer; m.p. 159–160° (ref. 2a, 156–157°).

The Preparation of *trans*-α-**Bromobenzalacetophenone** (III). **A. The Action of Potassium Acetate on the Higher-melting Benzalacetophenone Dibromide A.**—This and the experiments B and C below follow essentially the method of Abell.[4c] The reaction with the lower-melting dibromide B (I) proceeds much more rapidly than that with the dibromide A (II) as shown by the immediate development of potassium bromide precipitate in this case and the very slow development in the case of the dibromide A. The time of heating in experiment B (below) was chosen so that the approximate average time of exposure of the more quickly formed products under the reaction conditions would be comparable with that in this experiment.

A solution of 5.00 g. of the dibromide A (m.p. 159–160°) and 2.67 g. (two equivalents) of fused potassium acetate in 55 ml. of 95% ethanol was refluxed for 4 hours; yield of salt 1.38 g. (85%). Two-thirds of the solvent was distilled, 100 ml. of ether was added, and this solution was extracted five times with 50-ml. portions of distilled water. After drying (drierite) and evaporating under a water-pump vacuum, the residual yellow oil (3.7 g., 95%) was dried *in vacuo* for one hour. A portion (0.566 g.) was dissolved in 30 ml. of hot *n*-pentane; cooling to −20°, seeding and refrigeration at −20° overnight gave 0.132 g.; concentrating to 5 ml. and cooling gave an additional 0.155 g., m.p. (both fractions) 40–42°; evaporation gave 0.249 g. of yellow oil. The total yield of solid (III), identified by mixture m.p., represented 51% of the main product (or 48% actual yield). The residual oil (*cis*-isomer) (V) represented 44% of the main product or 42% actual yield.

Ultraviolet absorption curves of the original product before crystallization showed, respectively, at λ_{max} 252.5 and 297.5 mμ, ϵ = 14.39 and 13.45 × 10^3 (Fig. 1). Linear interpolation of these values between the corresponding extinction coefficients of the pure isomers (Fig. 1) gave identical values for the composition of the main product of 66% of *trans*-α-bromobenzalacetophenone (III) and 34% of the *cis*-isomer (V) (representing actual productions of 62.5 and 32%, respectively). Sunlight irradiation of a very dilute isoöctane solution of the original product caused practically complete isomerization to the *cis*-isomer; this was demonstrated by the change in ϵ at λ_{max} 252.5 and 297.5 mμ to 18.45 and 9.20 × 10^3, respectively. These results also indicated the absence of a significant amount of a third component.

B. The Action of Potassium Acetate on the Lower-melting Dibromide B.—Similar treatment of 5.00 g. of the dibromide-B (m.p. 123–124°) caused a much more rapid precipitation of potassium bromide. After 2 hours of refluxing, 1.4 g. (87%) of salt had precipitated. A similar work-up of the filtrate gave a clear yellow oil; 3.37 g. (87%). Crystallization of 0.500 g. from 30 ml. of *n*-pentane gave three fractions of III totalling 0.440 g., m.p. 40–41°, and a fourth of 0.023 g., m.p. 38–40°; this represents 93% content of the main product and an actual yield of 81%.

The original main product in dilute isoöctane solution at λ_{max} 252.5 and 297.5 mμ showed ϵ = 12.17 and 15.52 × 10^3, respectively. Linear interpolations of these values between the corresponding values for the pure isomers indicated that the composition of the main product was 99 and 97.5% of III, respectively. Extinction coefficients at λ_{max} 252.5 and 297.5 mμ of the original product after irradiation in dilute isoöctane solution were 18.40 and 9.25 × 10^3, respectively, and they indicated practically complete conversion to the *cis*-isomer (V).

C.—In a repetition of the above (B) on a larger scale using 36.8 g. (0.1 mole) of benzalacetophenone dibromide A of m.p. 158–160°, but with distillation of most of the solvent during the second and final hour of boiling, a 70% yield of clear yellow oil was obtained which showed n^{20}_D 1.6534 and ϵ at 252.5 mμ = 14.0 × 10^3 and at 297.5 mμ, 13.1 × 10^3. From the refractive index by linear interpolation between the values for the pure isomers, this oil appeared to contain 72% of the *trans*-isomer. On similar interpolation based on λ_{max} 252.5 mμ and λ_{max} 287.5 mμ the content of *trans*-isomer appeared to be 71 and 61%, respectively. This close agreement established the validity of the assumption that the oils obtained by the above procedure actually consist in the main of the two geometric isomers only. Calculations from the above data indicate that the actual yield of the *trans*-isomer was close to 46% and the yield of *cis*, 24%.

The oil thus obtained was used successfully without further purification in many of the following experiments. It distilled at 160–165° under 0.5 mm. pressure; yield 20.1 g., pale yellow. Recrystallization from 20 times its volume of *n*-pentane gave 12.0 g. of *trans*-isomer of m.p. 41–42° (42%).

D, E.—The above experiment (C) was repeated at room temperature (D) and at 5° (E) with qualitatively similar results, but the reaction times required were much greater, namely, five days and two months, respectively.

F.—The *action* of 2.1 g. *of triethylamine* in 50 ml. of acetone on 5 g. of the low-melting benzalacetophenone dibromide at 20–25° and storage at 8° for 4 hr. and then overnight at −10°, filtering, evaporating, treatment with ether and water, drying the ether layer and evaporating, gave an oil which solidified on seeding; 3.5 g. (90%), m.p. 40–42°.

trans-α-**Bromobenzalacetophenone** (III) has been adequately described in the literature. It is crystallized from isoöctane, *n*-pentane or 95% ethanol, and best at low temperature (−20°) with careful seeding, m.p. of 42° (Abell,[4c] 43°). The $n^{24.4}_D$ of melted and supercooled material was 1.6638; $d^{24.4}$ 1.4119; M_D 75.42, calcd. 71.58; (exaltation 3.84).

cis-α-**Bromobenzalacetophenone** (V).—Sunlight irradiation of an isoöctane solution 0.0000465 molal in *trans*-α-bromobenzalacetophenone lowered the extinction coefficient of the 297.5 mμ ultraviolet absorption band, and at the same rate raised the extinction of the 252.5 mμ band, to points

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[15] A. Michael, *J. prakt. Chem.*, **52**, 308 (1895).

close to those finally arrived at as approximately correct for the pure *cis*-isomer. The inversion proceeded rapidly and was practically complete in 24 min.

For preparation at higher concentrations, 25 g. of the *trans*-isomer in 2 l. of *n*-pentane required exposure to bright sunlight for 10 days. The course of the isomerization was followed by spectroscopic examination of portions of the product at intervals of 6, 10 and 11 days; the $\epsilon_{252.5\ m\mu}$ were 18.2, 18.8 and 18.8 × 10^3, respectively, and the $\epsilon_{297.5\ m\mu}$ were 9.45, 9.1 and 9.1 × 10^3. The *cis*-isomer (V), isolated by evaporation of the solvent, was a yellow oil which could not be induced to crystallize from a variety of solvents at temperatures ranging down to −60°. It could not be safely distilled because of slow isomerization to the *trans*-isomer at the temperature involved.

The best sample of the oil, of $\epsilon_{252.5\ m\mu}$ 18.8 × 10^3, was shown to be nearly pure by analysis, molecular weight, ultraviolet absorption characteristics, subsequent isomerizations to the *trans*-isomer, reactions parallel with those of the *trans*-isomer, including conversion into α-bromo-β-morpholinylbenzylacetophenone[7] in good yield, and by practically complete solubility in a saturated solution of the *trans*-isomer in 40% aqueous methanol at 25.0°. The solubility of the *trans*-isomer (37.7 mg. per 25.0 ml.) was determined by evaporating a measured volume under a stream of nitrogen and drying *in vacuo* at 0.5 mm. pressure (the reliability of this measurement was shown by resubjection of the residue to the evaporation procedure for 10 hr. and the loss of only 1.0 mg. in that time). The complete solubility of a sizable amount of the *cis*-isomer in this solution was shown by dissolving 52.3 mg. in 50 ml. of the saturated *trans* solution at 25.0°, thermostating in the presence of added 10 mg. of the *trans*-isomer as a seed, and evaporation of a 25.0-ml. aliquot of the solution; residue 64.2 mg. (this is exactly the amount calcd. on the basis of complete solubility of the added *cis*-isomer). This result shows that the product of irradiation contained practically none of the *trans*-isomer, but it must be emphasized that the possibility of the presence of small amounts of other impurities has not been excluded. There is evident here an almost quantitative conversion at photoequilibrium to the *cis*-isomer, and little if any resinification or formation of other by-products, and the physical constants determined appear to be close to correct: $n^{24.4}{}_{D}$ 1.6334; $d^{24.4}$ 1.3691; M_D 74.95 (calcd. 71.58, exaltation 3.37).

Anal. Calcd. for $C_{15}H_{11}BrO$: mol. wt., 387.2; C, 62.74; H, 3.86. Found: mol. wt., 286.2; C, 62.99; H, 4.33.

It was evident from consistently high analyses for hydrogen that an appreciable though small amount of impurity was present. This impurity has been shown to be a hydrocarbon residue (2.2 mg. per 100 ml.) left upon evaporation of the *n*-pentane used, and also formed upon irradiation of the solvent for 10 days (4.4 mg. per 100 ml.). (Unfortunately this exposure was not nearly as effective as in the experiment above, because of weather.) On this basis the analytical sample contained at least 2.6% of impurity of composition presumably $(CH_2)_n$, and the above analysis corrected for the contribution of this impurity is C, 62.78; H, 4.13, with the hydrogen value within the acceptable range. This amount of impurity would have had a small but appreciable effect on the physical constants and would involve a correction on the order of $n^{24.4}{}_{D}$ +0.0055; $d^{24.4}$ +0.0054; exaltation M_D +0.21; $\epsilon \times 10^3$ at λ_{max} 252.5 mμ, +0.49, and at λ_{max} 297.5, +0.24.

Inversion of *cis*-α-Bromobenzalacetophenone.—Solutions of 2.5 g. of the *cis*-isomer (V) in 25 ml. of chloroform, one containing a quantity of iodine sufficient to lend a persistent and distinct color, were exposed to bright sunlight for 90 min. The products were recovered by evaporating the solvent, dissolving in 10 ml. of ethanol and refrigerating at −20° for 24 hr. Only the product from the iodine-catalyzed reaction crystallized; yield 1.0 g., m.p. 40–42°; second crop, 0.8 g., m.p. 39–42° (total yield 72%, identified as *trans*-isomer by mixture m.p.). The residue from the portion irradiated in the absence of iodine could not be induced to crystallize despite seeding with the *trans*-isomer, and here, as in the case of the *n*-pentane solution, the photoequilibrium evidently lies well over on the side of the *cis*-isomer.

The *cis*-isomer was isomerized also (a) by heating at 160° for one hour under an atmosphere of nitrogen, and (b) by catalytic action of iodine and heating at 100° under nitrogen; the yields of *trans*-isomer of correct m.p. were 67 and 60%, respectively.

The *cis*-isomer was recovered unchanged after treatment with 0.5 equivalent of potassium acetate in ethanol under refluxing for 2 and for 9 hours; the recovered oils which resisted efforts to crystallize them, were identified by extinction coefficients at the two λ_{max}.

CHARLOTTESVILLE, VA. RECEIVED APRIL 16, 1951

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

The Structure of Humulone and Lupulone as Revealed by Ozonization[1a]

BY J. F. CARSON

This paper reports the ozonization of the two important constituents of hops, humulone and lupulone, the results of which require a modification in the currently accepted structures of these compounds. The ozonization of humulone I and of lupulone III yielded acetone isolated as the 2,4-dinitrophenylhydrazone in yields, respectively, of 1.26 and 2.09 moles per mole of compound. In neither case could isobutyraldehyde be detected. These results prove that the side chain attached to C_4 of humulone and the two side chains attached to C_4 of lupulone should be represented as $(CH_3)_2C{=}CH{-}CH_2{-}$. The data confirm the accepted structure of the side chain attached to C_6 of humulone and lupulone.

The structure of the side chain attached to C_4 of humulone I was considered by Wieland[2] to be $(CH_3)_2CH{-}CH{=}CH{-}$ because in the alkaline degradation of humulone I to humulinic acid II, isobutyraldehyde and isohex-2-enoic acid were isolated. The position of the double bond in the side chain attached to C_5 in humulinic acid was established by Wieland and Martz.[3] Ozonization of humulinic acid yielded acetone, which revealed the position of this double bond and also, assuming no rearrangement, the position of the double bond in the chain attached to the C_6 of humulone I. In the case of lupulone III, no similar alkaline degradation was possible and the two side chains attached to C_4 were assumed by Wöllmer[4] to be $(CH_3)_2CH{-}CH{=}CH_2{-}$ by analogy with humulone I. Similarly the position of the double bond in the side chain on C_6 of lupulone was assumed as shown in III without proof.

Recently, Cook and Harris[5] have reported that in their hands, the alkaline degradation of humulone yielded isohex-3-enoic acid instead of the

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[1a] NOTE ADDED IN PROOF.—Full priority for the revised structure of lupulone is due to the work of M. Verzele and F. Govaert (*Bull. soc. chim. Belg.*, **58**, 432 (1949)) which escaped our notice. These investigators, on the basis of alkaline degradation and ozonization, have arrived at the same structure for lupulone as advanced here.

[2] H. Wieland, *Ber.*, **58**, 102 (1925).

[3] H. Wieland and E. Martz, *ibid.*, **59**, 2352 (1926).

[4] W. Wöllmer, *ibid.*, **58**, 672 (1925).

[5] A. H. Cook and G. Harris, *J. Chem. Soc.*, 1873 (1950).