[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

THE HALODIPHENACYLS.[1] I

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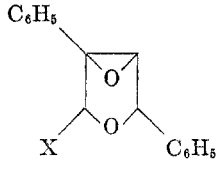
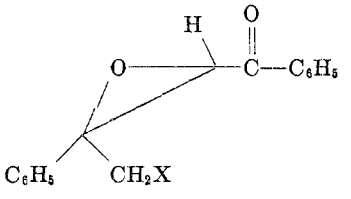
Recently two independent groups of workers (1, 2) have reinvestigated the structure of the bromodiphenacyls. The appearance of these papers has prompted the present report of a similar investigation initiated in 1950. This work presents a correlation of the structures of the α-chloro-, α-bromo-, and α-iododiphenacyls by chemical and physical means. The structures of β-halodiphenacyls were similarly correlated and a new conversion of β-bromodiphenacyl to the α-isomer is reported. The α-chloro-, α-bromo-, and α-iododiphenacyls have been synthesized by an independent route that has lead to the simultaneous formation of the β-isomer in small yields.

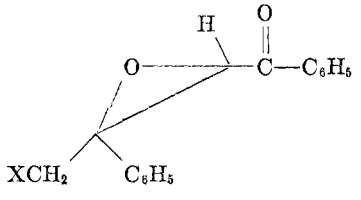
Until the recent work, the reaction products from phenacyl halides with base were considered to be diastereoisomers represented by formula I (3). The recent articles (1, 2) cite the literature of the problem. Both reject I and propose that the two isomers from each phenacyl halide are epimers having the structures II and IIa. From the work reported here the α-isomers are considered to have the *trans*- structure (II).



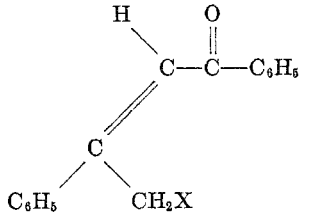
I



II



IIa



III

The reaction of phenacyl chloride with potassium hydroxide in alcohol gave 95 % of crude diphenacyls which were separated by fractional crystallization into

[1] Abstracted from the thesis submitted by Mr. Robert J. Church in October 1951 to the Graduate School of Wayne University in partial fulfillment of the requirements for a degree of Master of Science and from the thesis of Mr. Vincent J. Traynelis submitted in April 1953 to the Graduate School in partial fulfillment of the requirements for a degree of Doctor of Philosophy.

[2] Wyandotte Chemical Corporation Fellow, 1952–1953.

20% of pure α-chlorodiphenacyl, m.p. 116–117° (4) and 47% of pure β-chlorodiphenacyl, m.p. 147–148° (4).

Under the same conditions, phenacyl bromide gave 66% of the crude diphenacyls. Fractional crystallization afforded separation into 16% of pure α-bromodiphenacyl, m.p. 135–136° and 34% of β-bromodiphenacyl, m.p. 160–161°. The bromodiphenacyl has been reported by various workers as melting sharply at some temperature between 124° and 136°. Ajello (5) reported an isomer melting at 136° but Campbell and Khanna (6) claimed to have separated this material into isomers melting at 129° and 161°. In this work the 136°-isomer was isolated from three different chemical reactions and was recrystallized to constant melting point.

β-Bromodiphenacyl reacted readily with sodium iodide in acetone to give an 80% yield of β-iododiphenacyl. The β-chlorodiphenacyl, under more vigorous conditions, gave a 22% yield of the same β-iodo isomer. The α-bromodiphenacyl and the α-chloro isomer could both be converted to the same α-iododiphenacyl.

The iododiphenacyls were unstable at room temperature and in a melting point determination decomposed before they melted. Determination of the identity of different samples by mixture melting point data was unreliable with these iodo isomers. The identity of the iodo isomers could best be determined by comparison of the infrared spectra (Figs. 1 and 2), and the ultraviolet spectra (Figs. 4 and 5).

The fact that the β-chloro- and β-bromo-diphenacyls gave the same β-iodo isomer indicated that they have the same skeletal structure. The fact that the α-chloro- and α-bromo-diphenacyls gave the same α-iodo isomer, which was different from the β-iodo isomer, indicated that they are structurally related. The spectral data (Figs. 1, 2, 4, and 5) also indicated that the isomers in the α-series and the β-series respectively are structurally related and that the re-

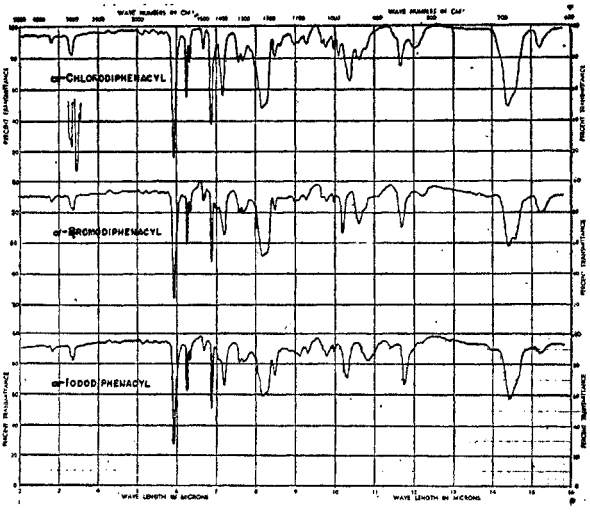


FIG. 1. INFRARED SPECTRA OF THE α-HALODIPHENACYLS

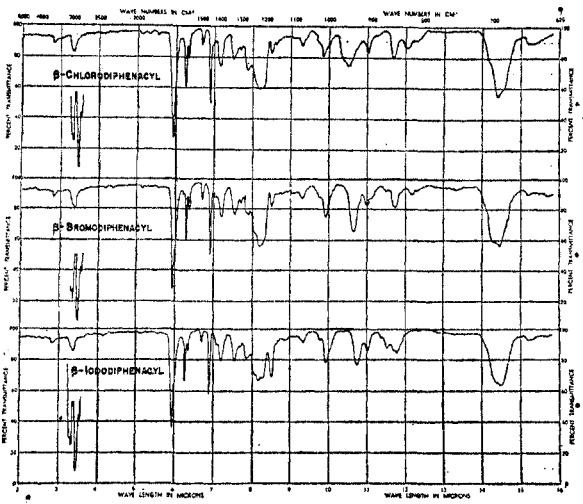


FIG. 2. INFRARED SPECTRA OF THE β-HALODIPHENACYLS

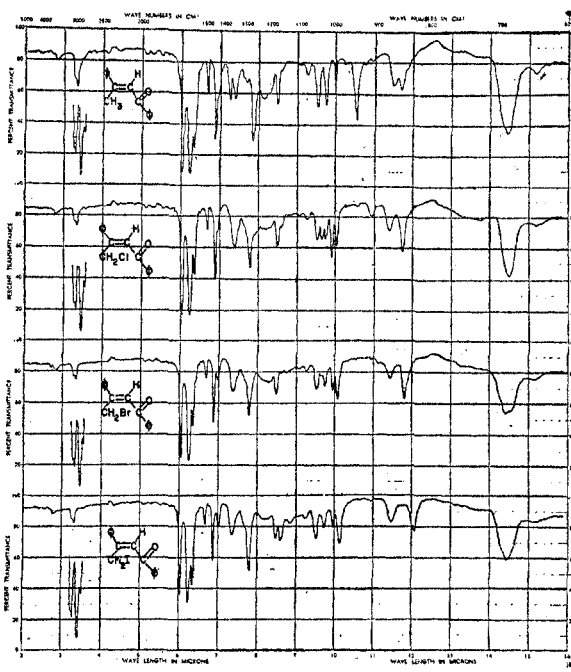


FIG. 3. THE INFRARED SPECTRA OF THE HALODYPNONES

action with sodium iodide has not caused a conversion from one series to the other.

The α-chloro-, α-bromo-, and α-iododiphenacyls were synthesized by epoxidation of the corresponding α,β-unsaturated ketones (III). Dypnone was used as

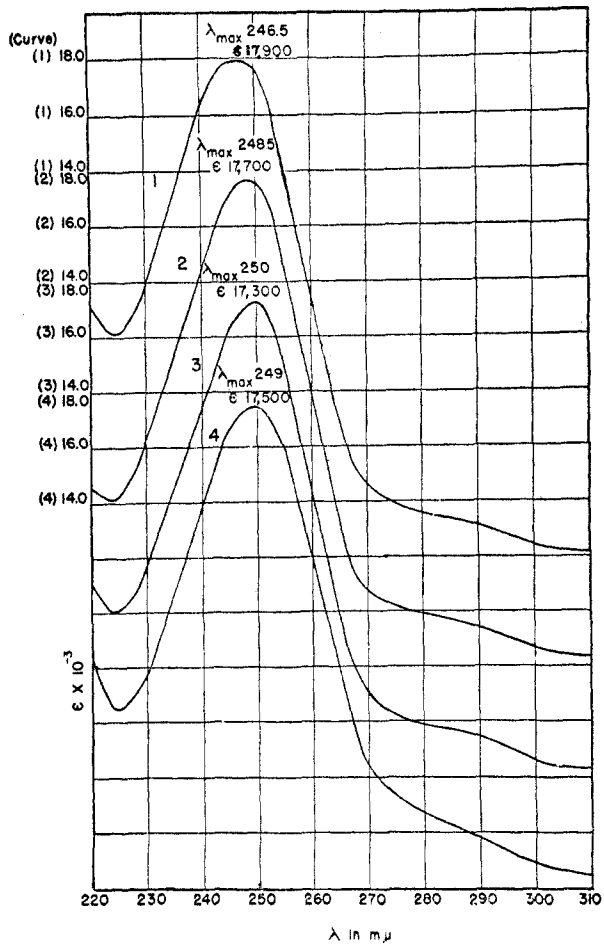


FIG. 4. ULTRAVIOLET SPECTRA OF THE α-HALODIPHENACYLS. Curve 1, Benzalacetophenone Oxide; Curve 2, α-Chlorodiphenacyl; Curve 3, α-Bromodiphenacyl; Curve 4, α-Iododiphenacyl.

the starting material for the preparation of the halogen-substituted ketones. The reaction of dypnone with sulfuryl chloride gave III (X = Cl) in 15% yield. N-Bromosuccinimide reacted with dypnone to give III (X = Br) in 51% yield. The bromo ketone (III, X = Br) and the chloro ketone (III, X = Cl) when treated with sodium iodide in acetone gave the iodo ketone (III, X = I) in 90% and 71% yield respectively.

The three halodypnones (III) were epoxidized with hydrogen peroxide in a basic alcohol solution (7). The reaction with chlorodypnone was rapid at 0–5° with the formation of 91% of crude product along with 3.5% of chloride ion. The crude product was separated by fractional crystallization to give 51% α-chlorodiphenacyl, m.p. 116–117° and 16.5% β-chlorodiphenacyl, m.p. 146–147°. The isomers were shown to be identical with the products from the phenacyl

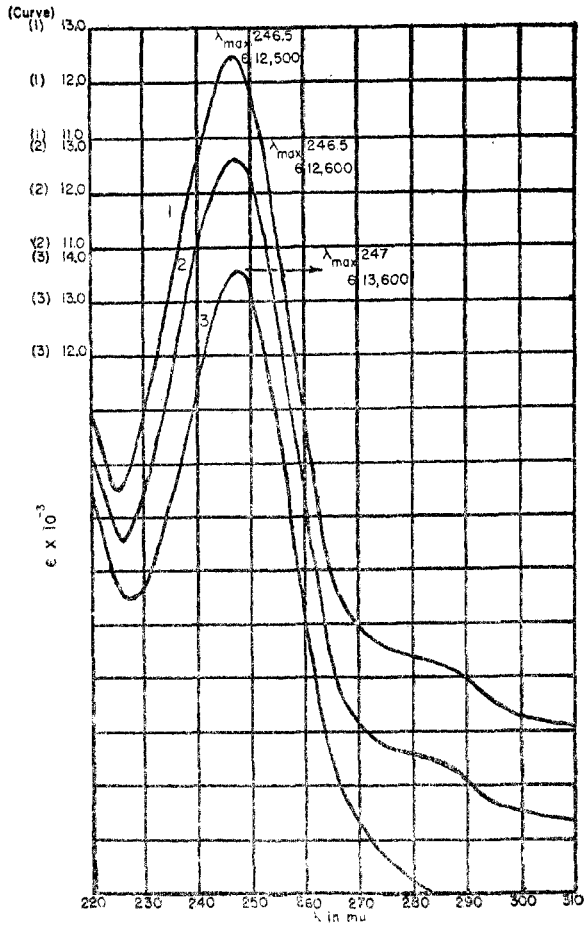


FIG. 5. ULTRAVIOLET SPECTRA OF THE β-HALODIPHENACYLS. Curve 1, β-Chlorodiphenacyl; Curve 2, β-Bromodiphenacyl; Curve 3, β-Iododiphenacyl.

halide reaction with base by mixture melting point determinations and comparison of ultraviolet and infrared spectra.

Epoxidation of bromodypnone (III, X = Br) gave 83% of crude isomers and 16% of bromide ion was formed. The isomers were separated to give 49% of α-bromodiphenacyl, m.p. 135–136°, and 12% of β-bromodiphenacyl. Both isomers were identical with the products of the initial base condensation of phenacyl bromide as proved by mixture melting point determination and comparison of infrared and ultraviolet spectra. In the previous work (2) this reaction was used with bromodypnone but only the α-isomer was reported.

Epoxidation of iododypnone (III, X = I) gave 70% of crude isomers and 25% of liberated iodide ion. Fractional crystallization separated the isomers into 39% of α-iododiphenacyl and 8% of β-iododiphenacyl, identical with the compounds prepared above as shown by infrared and ultraviolet spectra.

Dypnone and benzalacetophenone were epoxidized as model compounds.

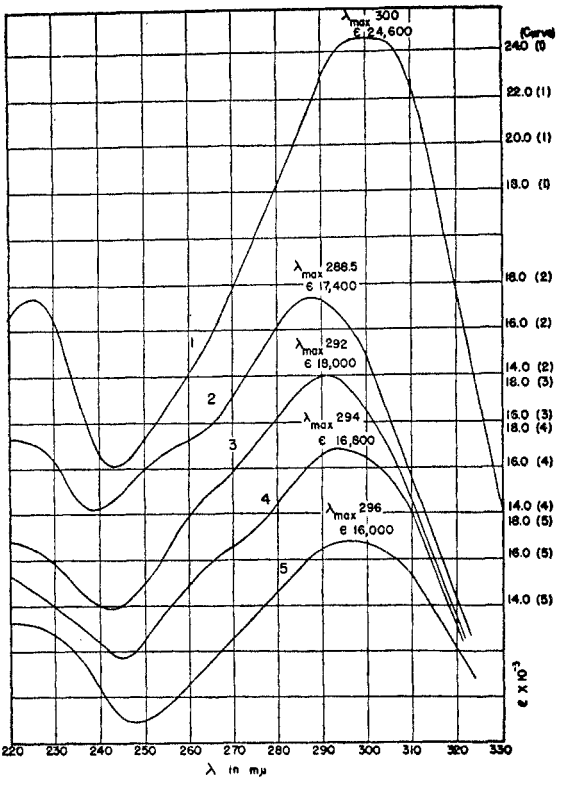


FIG. 6. ULTRAVIOLET SPECTRA OF THE HALODYPNONES. Curve 1, Benzalacetophenone; Curve 2, Dypnone; Curve 3, Chlorodypnone; Curve 4, Bromodypnone; Curve 5, Iododypnone.

Dypnone gave two epoxides under the conditions of the reaction but benzalacetophenone gave only one.

The assignment of structure of the bromodypnone (III, X = Br) is based on the known property of N-bromosuccinimide to brominate in the allyl position and on the ultraviolet spectrum (Fig. 6) which indicates that the double bond is in conjugation with the phenyl as well as the carbonyl group. A further comparison of the ultraviolet spectra of the known *cis*- and *trans*-benzalacetophenones (8) with the spectrum of the pure crystalline III (X = Br) indicates that III (X = Br) is the *trans*-isomer. The fact that the iododypnone (III, X = I) was prepared from bromodypnone by treatment with sodium iodide in acetone and that by this reaction the chlorodypnone (III, X = Cl) was converted to the same iododypnone indicated that all the halodypnones had the same carbon skeleton. All three of these compounds were sharp melting crystalline solids and a comparison of the infrared and ultraviolet spectra (Figs. 3 and 6) indicated that no allylic rearrangement had occurred during the displacement reaction and that each had the phenyl group *trans*- to the benzoyl group.

Pure *trans*-benzalacetophenone was converted in solution by direct sunlight

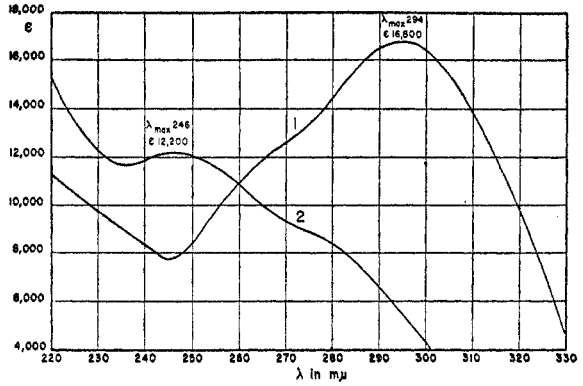


FIG. 7. ULTRAVIOLET SPECTRA SHOWING EFFECT OF SUNLIGHT ON *trans*-BROMODYPNONE. Curve 1, original solution; Curve 2, solution after 32 minutes exposure to sunlight.

into a mixture of *cis*- and *trans*-isomers (8). Fig. 7 shows that pure *trans*-bromodypnone behaved in a similar manner and was converted in direct sunlight into a mixture of compounds (Fig. 7, Curve 2). However, in alcoholic solution containing alkali the maximum value of ϵ at 299 mμ was decreased only from 16,800 to 14,600 in four hours in diffused laboratory light indicating that no appreciable amount of the *cis*-compound was present in the above epoxidations. The chlorodypnone exhibited the same general behavior toward light as the bromo analog.

The conversion of the α-isomer to the β-isomer in a basic solution containing halide ion is a common transformation (3) and provides one explanation for the formation of small amounts of the β-isomer in the epoxidation reactions. A new conversion of β- to an α-isomer is reported here. β-Bromodiphenacyl was treated with an ether solution of dry hydrogen bromide to give an addition product containing the elements of the hydrogen bromide in 69% yield. The infrared spectra of the addition product contained an absorption band associated with a hydroxyl group and the ultraviolet spectrum showed the carbonyl group still in conjugation with the phenyl group indicating that the hydrogen bromide had opened the oxide ring. When the addition product was dissolved in liquid ammonia, hydrogen bromide was eliminated with the formation of the α-isomer, m.p. 135–136°, in 69% yield.

Recently Cromwell (9) considered that epoxybenzalacetophenone, in view of its synthesis from *trans*-chalcone and hydrogen peroxide was probably the *trans*-form. This keto epoxide exhibited abnormally high ultraviolet absorption intensities which were attributed to three-ring hyperconjugation of the *trans*-form. This high intensity was analogous to the high intensity of the *trans*-form compared to the *cis*-form in the ethylene imine series. The high intensities in the ethylene imines were also attributed to hyperconjugation of the three-membered ring in the *trans*-form.

All the α-halodiphenacyl isomers have abnormally high absorption intensities almost exactly equal to epoxybenzalacetophenone (Fig. 4 and *cf.* Fig. 5). In view of the absorption spectra and the synthesis from pure *trans*-halodypnones

by epoxidation the compounds of the low-melting α-series are considered to have the *trans*-form as indicated by Formula II.

EXPERIMENTAL

Preparation of the bromodiphenacyls. A solution of 19.9 g. (0.1 mole) of phenacyl bromide in 200 ml. of methanol was cooled to 0–5°. At this temperature, a solution of 6.2 g. (0.11 mole) of potassium hydroxide in 75 ml. of methanol was added with stirring over a period of 20 minutes. After an additional 45 minutes at 5°, the solid was filtered, washed, and dried. The yield amounted to 9.5 g. An additional 1.0 g. was obtained by dilution with water.

The filtrate and the methanol washings were acidified and extracted with ether. After drying the extract over sodium sulfate, the ether was removed and the residue was crystallized from ethanol to give 0.8 g. (6%) of phenacyl alcohol, m.p. 85–87°. The mixture melting point with an authentic sample was not depressed.

The 10.5 g. (66%) of crude diphenacyls was fractionally recrystallized from ethanol to give 2.5 g. (16%) of α-bromodiphenacyl, m.p. 135–136° and 5.4 g. (34%) of β-bromodiphenacyl, m.p. 160–161°.

Anal. Calc'd for $C_{16}H_{13}BrO_2$: C, 60.58; H, 4.13; Br, 25.2; Mol. wt., 317.

Found (β-isomer): C, 60.40; H, 4.37; Br, 24.9; Mol. wt. (Rast micro method) 324.

Found (α-isomer): C, 60.30; H, 4.40; Br, 25.5.

Preparation of the chlorodiphenacyls. Using 15.5 g. (0.1 mole) of the phenacyl chloride dissolved in 150 ml. of methanol and following the same procedure as for the phenacyl bromide, 12.9 g. (95%) of crude chlorodiphenacyls was obtained. Fractional recrystallization using ethanol gave 2.8 g. (20%) of α-chlorodiphenacyl, m.p. 116–117°, and 6.4 g. (47%) of β-chlorodiphenacyl, m.p. 147–148°.

Anal. Calc'd for $C_{16}H_{13}ClO_2$: C, 70.45; H, 4.80.

Found (α-isomer): C, 70.78; H, 5.00.

Found (β-isomer): C, 70.55; H, 5.18.

Reaction of sodium iodide with α-bromodiphenacyl. An acetone solution of 320 mg. (1.0 millimole) of α-bromodiphenacyl and 300 mg. (2.0 millimoles) of sodium iodide was heated at gentle reflux for 95 minutes. The sodium bromide was filtered and gave 95 mg. (92%). The filtrate was diluted with water and the resulting solid weighed 365 mg. (100%). Recrystallization from ethanol gave 310 mg. (86%) of α-iododiphenacyl. When the rate of heating of a melting-point bath was approximately 2° per minute and the sample was inserted at 70°, the compound decomposed at 71–72°. The α-iododiphenacyl has previously been reported to decompose between 70° and 90° (10).

Anal. Calc'd for $C_{16}H_{13}IO_2$: C, 52.79; H, 3.60.

Found: C, 53.17; H, 4.06.

The α-iododiphenacyl was unstable and turned to a black mass after two days at room temperature. In a similar reaction of sodium iodide with α-chlorodiphenacyl, the displacement proceeded so slowly that the α-iododiphenacyl decomposed almost as fast as it formed. From 550 mg. of α-chloro compound there was obtained only 20 mg. of α-iododiphenacyl, the infrared spectrum of which was identical with the sample prepared above.

Reaction of sodium iodide with β-bromodiphenacyl. After 18 hours at room temperature, 86% sodium bromide had precipitated from an acetone solution of 950 mg. (3.0 millimoles) of β-bromodiphenacyl and 680 mg. (4.5 millimoles) of sodium iodide. The solution was then heated between 45–55° for two hours to complete the reaction and was diluted with water. The yield of crude product was 1.05 mg. (97%). Recrystallization from ethanol gave 870 mg. (80%) of colorless needles. When the rate of heating was approximately 2° per minute and the sample was inserted at 109°, the compound decomposed at 110–110.5°. A β-iodo isomer has been reported to melt with decomposition at 150–153° (10).

Anal. Calc'd for $C_{16}H_{13}IO_2$: C, 52.79; H, 3.60.

Found: C, 52.35; H, 3.46.

When stored in the cold, the β-iododiphenacyl remained unchanged after one month,

while at room temperature it decomposed to a black mass in two weeks. In an experiment with 550 mg. of β-chlorodiphenacyl, 150 mg. (22%) of material was isolated after 24 hours of reflux. The infrared and ultraviolet spectra were identical with β-iododiphenacyl.

Reaction of β-bromodiphenacyl with hydrogen bromide. To a solution of 500 mg. (1.58 millimoles) of β-bromodiphenacyl in a 50% ether-benzene mixture was added 25 ml. of ether containing 500 mg. of dry hydrogen bromide. After 24 hours in the cold, the solution was concentrated and diluted with petroleum ether. The yield of solid was 370 mg. An additional 65 mg. was obtained on further concentration of the mother liquor. The total yield was 69% and the compound had m.p. 144–145° (dec.). Recrystallization from benzene-petroleum ether including one treatment with charcoal gave 350 mg. (56%) of a β-bromodiphenacyl-hydrogen bromide adduct, m.p. 144–145° (dec.).

Anal. Calc'd for $C_{16}H_{14}BrO_2$: C, 48.29; H, 3.54; Br, 40.17.
Found: C, 48.08; H, 3.69; Br, 40.2.

Reaction of β-bromodiphenacyl-hydrogen bromide adduct with liquid ammonia. One gram (2.51 millimoles) of this hydroxy dibromide was dissolved in 100 ml. of liquid ammonia and allowed to react for one hour. After evaporation of the liquid ammonia, the residue was washed with water and dried to give 0.78 g. (98%) of II. The material was dissolved in cyclohexane at room temperature, filtered, and cooled to give 0.55 g. (69%) of pure α-bromodiphenacyl, m.p. 135–136°. A mixture melting point with II from the phenacyl bromide reaction was not depressed, m.p. 135–136°.

Bromodypnone (III, X = Br). Dypnone, b.p. 120–131° (0.1 mm.), was prepared in 60% yield according to the directions in *Organic Syntheses* (11). A mixture of 11.1 g. (0.05 mole) of dypnone, 8.9 g. (0.05 mole) of N-bromosuccinimide, 0.3 g. (0.0012 mole) of benzoyl peroxide, and 60 ml. of anhydrous carbon tetrachloride was heated at gentle reflux for 30 minutes, after which time another 0.3 g. of benzoyl peroxide was added. After an additional hour at reflux, 4.9 g. (98%) of succinimide, m.p. 123–125°, was separated by filtration. The solvent was removed by evaporation and the resulting viscous pale yellow oil was caused to crystallize by trituration with methanol. Recrystallization from methanol gave 7.7 g. of β-bromomethylchalcone (bromodypnone), m.p. 66–67°. The yield of light yellow needles was 51%.

Anal. Calc'd for $C_{16}H_{13}BrO$: C, 63.78; H, 4.35; Br, 26.55.
Found: C, 63.80; H, 4.54; Br, 26.47.

Chlorodypnone. A solution of 4.4 g. (0.02 mole) of dypnone in 25 ml. of carbon tetrachloride was cooled in an ice-bath and 2.7 g. (0.02 mole) of sulfuryl chloride was added. The mixture was then refluxed gently for 23 hours. After this period of time the solvent was removed and the resulting oil was dissolved in methanol. This solution was cooled and seeded to effect crystallization. (The initial seeds were obtained by crystallization of a drop of the above oil on a watch glass.) The first four crops of crude solid amounted to 2.2 g. (42%). After two further crystallizations from methanol, 0.8 g. (15%) of pure β-chloromethylchalcone (chlorodypnone) was obtained as pale yellow needles, m.p. 74–75°.

Anal. Calc'd for $C_{16}H_{13}ClO$: C, 74.84; H, 5.07.
Found: C, 75.13; H, 5.26.

Iododypnone. Solutions of 3.0 g. (0.01 mole) of bromodypnone in 25 ml. of anhydrous acetone and 1.5 g. (0.01 mole) of sodium iodide in 10 ml. of anhydrous acetone were mixed and allowed to stand at room temperature for one hour. The resulting sodium bromide was filtered and washed with acetone and the filtrate was poured into 50 ml. of ice-water. The solid was filtered, washed with water, and recrystallized from methanol. The yield of β-iodomethylchalcone (iododypnone) was 3.1 g. (90%). The pale yellow platelets melted at 74–75° (dec.).

Anal. Calc'd for $C_{16}H_{13}IO$: C, 55.20; H, 3.76.
Found: C, 55.37; H, 3.65.

Chlorodypnone (0.80 g., 0.003 mole) was dissolved in 5 ml. of acetone and added to 10 ml. of a saturated solution of sodium iodide in acetone. After 1½ hours at room temperature, 0.18 g. (100%) of sodium chloride was separated. From the reaction 0.74 g. (71%) of β-iodomethylchalcone was isolated, m.p. 75–76° (dec.). The mixture melting point with a sample

prepared above was not depressed and the ultraviolet and infrared spectra of the two samples were identical.

Epoxidation of bromodypnone. A solution of 1.20 g. (0.004 mole) of bromodypnone in 90 ml. of methanol was cooled in an ice-bath. To this was added simultaneously 1 ml. of 2 *N* (0.002 mole) sodium hydroxide and 5 ml. of 15% hydrogen peroxide. After about five minutes, a precipitate began to form. The mixture was allowed to stand in an ice-bath for 30 minutes, after which the solid was filtered and washed with methanol. To the filtrate was added 5 ml. of 15% hydrogen peroxide. The mixture was placed in the refrigerator for 1½ hours, after which the solid was filtered off and washed with methanol. To the filtrate was added 100 ml. of water and after crystallization was complete, the solid was filtered, washed with water, and dried *in vacuo*. The crude yield of the combined solids was 1.05 g. (83%).

After the excess hydrogen peroxide was destroyed, the filtrate was acidified with a solution of nitric acid. Bromide ion was determined *via* the Volhard method and amounted to 16%.

The crude solid was fractionally crystallized from absolute ethanol and gave 0.62 g. (49%) of α-bromodiphenacyl, m.p. 133–134°; and 0.15 g. (12%) of β-bromodiphenacyl, m.p. 155–157°.

Final recrystallization from absolute ethanol gave 0.48 g. (38%) of pure α-bromodiphenacyl, m.p. 135–136° and 0.12 g. (10%) of pure β-bromodiphenacyl, m.p. 159–160°. The mixture melting points of these bromodiphenacyls with the corresponding compounds from phenacyl bromide were not depressed.

Anal. Calc'd for $C_{16}H_{13}BrO_2$: C, 60.46; H, 4.31.
Found (α-isomer): C, 60.58; H, 4.13.
Found (β-isomer): C, 60.77; H, 4.40.

Epoxidation of chlorodypnone. The epoxidation procedure was the same as for bromodypnone. From 0.51 g. (0.002 mole) of chlorodypnone, 2 ml. of 0.5 *N* (0.001 mole) of sodium hydroxide, and 2 ml. of 30% hydrogen peroxide, after 21 hours in the refrigerator, was isolated 0.50 g. (91%) of crude product, m.p. 102–107°. Chloride ion was determined using Volhard's procedure and amounted to 3.5%.

The crude solid was fractionally crystallized from absolute ethanol and gave 0.28 g. (51%) of α-chlorodiphenacyl, m.p. 116–117° and 0.09 g. (16.5%) of β-chlorodiphenacyl, m.p. 146–147°. The mixture melting points of the above samples with the corresponding isomers obtained from the action of base on phenacyl chloride were not depressed.

Anal. Calc'd for $C_{16}H_{13}ClO_2$: C, 70.45; H, 4.80.
Found (α-isomer): C, 70.81; H, 4.92.
Found (β-isomer): C, 70.31; H, 4.83.

Epoxidation of iododypnone. After a total of four days in the refrigerator, a solution of 0.35 g. (0.001 mole) of iododypnone, 2 ml. of 0.5 *N* (0.0005 mole) sodium hydroxide, and 5 ml. of 30% hydrogen peroxide gave 0.250 g. (70%) of crude product. Iodide ion was determined *via* Volhard's method and amounted to 25%.

The crude product was recrystallized from absolute ethanol and gave 0.210 g. (58%) of pure isomers. Fractional crystallization of 0.20 g. gave 0.14 g. (39%) of α-iododiphenacyl and 0.03 g. (8%) of β-iododiphenacyl. The identity was established by comparison of the infrared and ultraviolet spectra with spectra of the iododiphenacyls obtained from the sodium iodide reactions.

Anal. Calc'd for $C_{16}H_{13}IO_2$: C, 52.79; H, 3.60.
Found (α-isomer): C, 53.33; H, 4.11.
Found (β-isomer): C, 52.99; H, 3.57.

Epoxidation of dypnone. Using the procedure described for the epoxidation of chlorodypnone, 4.4 g. (0.020 mole) of dypnone, 5 ml. of 2 *N* (0.010 mole), and 20 ml. of 15% hydrogen peroxide gave 4.3 g. (90%) of crude product. Fractional crystallization from methanol afforded separation into two isomers. The low-melting dypnone oxide crystallized in colorless plates and amounted to 3.0 g. (64%), m.p. 93–94°. The high-melting dypnone oxide formed colorless needles and amounted to 0.34 g. (7%), m.p. 160–161°.

Anal. Calc'd for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88.

Found (low-melting isomer): C, 80.40; H, 6.00.
Found (high-melting isomer): C, 80.48; H, 6.23.

Benzalacetophenone oxide. This oxide, m.p. 88–89°, was prepared in 86% yield using the procedure of Weitz and Scheffer (7).

Spectra. The infrared spectra were determined with a Baird Associates double beam infrared recording spectrophotometer in chloroform solution (cell width, 0.1 mm.). The isolated absorption band at 3.42 microns was the absorption of a polystryrene film used to calibrate the machine.

The ultraviolet spectra were determined with a Beckman D. U. spectrophotometer in cyclohexane solution.

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SUMMARY

The structures of the α- and β-chloro-, -bromo-, and -iodo-diphenacyls, respectively, have been correlated by physical and chemical means. The α-halodiphenacyls were synthesized from halodypnones (III) by a reaction that led to small amounts of the β-halodiphenacyls as by-products. The structures of the halodypnones were proven by spectral studies. From these data the low-melting α-halodiphenacyls are considered to have the *trans* structure II.

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