2-Aminofluoranthene (IV, R = H) was best obtained by rapid hydrogenation of 2-nitrofluoranthene (2 g.) in absolute ethanol (75 ml.), in the presence of decolorizing charcoal (1 g.) and platinum oxide (350 mg.), at a pressure of 45 lb./sq. in. Precipitation with water yielded 1.45 g. (82%) of amine, which separated from a mixture of benzene and petroleum ether in yellow needles, m.p. 128–129°. Solutions of the amine are sensitive to light and darken rapidly upon standing.

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.18; H, 5.16; N, 6.64.

2-Acetylaminofluoranthene (IV, R = $COCH_3$) was obtained when 2-nitrofluoranthene (1 g.) suspended in 50 ml. of benzene was hydrogenated as before and the resulting solution was filtered directly into a solution of acetic anhydride (10 ml.) in benzene (50 ml.). When the solution was boiled for several minutes and then cooled, 400 mg. (38%) of the amide separated in orange–yellow microcrystals; m.p. 225–226° after recrystallization from glacial acetic acid.

Anal. Calcd. for $C_{18}H_{13}NO$: N, 5.40. Found: N, 5.65.

Ethyl N-2-fluoranthylcarbamate (IV, R = $COOC_2H_5$) was formed when a mixture of 2-aminofluoranthene (600 mg.), ethyl chloroformate (0.6 ml.), pyridine (0.6 ml.), benzene (30 ml.) and decolorizing charcoal (1 g.) was heated for 10 minutes at 50° and then allowed to stand in the dark for 12 hours. The precipitated urethan was separated from charcoal by solution in warm benzene from which it separated in yellow plates, m.p. 135–136°; yield 500 mg. (63%).

Anal. Calcd. for $C_{19}H_{15}NO_2$: N, 4.84. Found: N, 5.12.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of the Ketonization Reaction of Enols.[1] II[2]

BY HOWARD E. ZIMMERMAN

RECEIVED SEPTEMBER 15, 1955

The study of the stereochemistry of ketonization has been extended to include the 2-methyl-3-phenylindanone system. The enol of 2-methyl-3-phenylindanone was found to lead preferentially to the less stable stereoisomeric product, *cis*-2-methyl-3-phenylindanone (IIa). Furthermore, enolization of IIa proved to be more facile than that of the *trans*-isomer IIb. These results are discussed in light of our previous findings which led to the conclusion that ketonization proceeds by protopic attack on the less hindered side of the enolic double bond.

Previously we have discussed[2] the kinetically controlled ketonization reaction of enols, which very frequently leads to the formation of the thermodynamically less stable of two possible stereoisomers. It was proposed that the reaction geometry results from a preferential attack of the proton donor on the less hindered side of the enolic double bond. This hypothesis was supported by experimental evidence in the 1-phenyl-2-benzoylcyclohexane series and also by six examples cited from the literature. It was therefore of interest to devise further tests of this hypothesis not only to strengthen its validity but also to further define the limits of its generality. The present study was concerned with the enol (I) of 2-methyl-3-phenylindanone (II).

2-Methyl-3-phenylindanone has been described in the literature by several researchers. Bergmann reported[3] the reduction of 2-methyl-3-phenylindone (III) with phosphorus and hydriodic acid to yield 2-methyl-3-phenylindanone (II), m.p. 64–65°. Somewhat later Ingold by catalytic hydrogenation of III obtained an oil which was considered[4] to be II. Finally, Shoppee[5] reported the formation of 2-methyl-3-phenylindanone (II) by reaction of 2-methyl-3-phenylind-2-en-1-yl acetate with aqueous base; again II was obtained as an oil. Both this oil and that of Ingold yielded 2,4-dinitrophenylhydrazones, m.p. 179° and 176–177°, respectively, the latter in unstated yield.

For the present study it was necessary first to prepare *cis*- and *trans*-2-methyl-3-phenylindanone (IIa and IIb) in reasonable quantities and to establish their configurations before proceeding with a consideration of the ketonization of I to yield these products. It was found that catalytic hydrogenation of 2-methyl-3-phenylindone (III) with PtO_2 in either benzene or ethyl acetate yielded *cis*-2-methyl-3-phenylindanone (IIa), m.p. 60.0–60.5°, while hydrogenation with the same catalyst in an ethanol–ethyl acetate mixture containing sodium hydroxide led to *trans*-2-methyl-3-phenylindanone, m.p. 61.0–62.0°. These stereoisomers exhibited a large mixed melting point depression and possessed similar solution infrared spectra which however differed markedly at several wave lengths in the 8–15 μ region. Both isomers yielded the same 2,4-dinitrophenylhydrazone, isomerization having occurred under the strongly acidic reaction conditions. Also, the same products of *alpha* bromination were obtained from IIa and IIb. The assignment of the *cis*-configuration to the isomer obtained by hydrogenation under non-alkaline conditions[6] was supported by equilibration experiments. Treatment of *cis*-2-methyl-3-phenylindanone (IIa) with 0.8 *N* methanolic sodium methoxide at room temperature for 2.5 hours yielded a mixture of IIa and IIb shown by infrared analysis[8] to consist

(1) Presented at the Organic Division, Minneapolis A.C.S. Meeting, Sept., 1955.

(2) Paper I of this series: *J. Org. Chem.*, **20**, 549 (1955). Literature examples of this phenomenon are cited in this paper.

(3) E. Bergmann and H. Taubadel, *Ber.*, **65**, 467 (1932).

(4) C. Ingold and C. Wilson, *J. Chem. Soc.*, 1498 (1933).

(5) H. Burton and C. Shoppee, *ibid.*, 1156 (1935).

(6) Hydrogenation under neutral or acidic conditions generally proceeds by *cis*-addition to the olefinic double bond. Note ref. 7 for a discussion of the effect of basicity on the hydrogenation of α,β-unsaturated ketones. Alkaline conditions allow epimerization at the α-carbon atom; and regardless of mechanism the more stable isomer (IIb) should result.

(7) H. Weidlich and M. Meyer-Delius, *Ber.*, **74**, 1195 (1941).

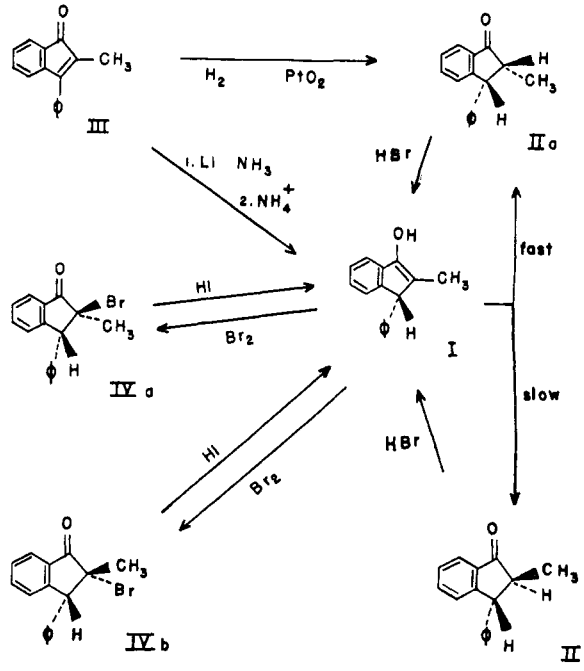
(8) The method of quantitative estimation of relative amounts of IIa and IIb in various mixtures is described in the experimental section.

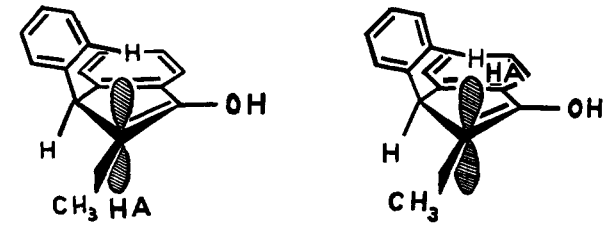
of 79% *trans*-2-methyl-3-phenylindanone (IIb).[9]

The two possible ketonization products thus having been prepared and assigned configurations, it remained to consider the stereochemistry of the ketonization process itself. One mode of generating an unstable enol is the dehalogenation of the corresponding α-bromoketone using a dilute acetone solution of hydriodic acid.[2] In order to obtain the required bromoindanones both IIa and IIb were subjected to bromination in acetic acid. In each case a mixture of the two stereoisomeric 2-bromo-2-methyl-3-phenylindanones (IVa and IVb) was obtained. By crystallization from ligroin these were readily separated to yield α-2-bromo-2-methyl-3-phenylindanone, rectangular plates m.p. 106°, and β-2-bromo-2-methyl-3-phenylindanone, clusters m.p. 135°.[10] Interesting is the marked difference in ease of bromination of the two stereoisomeric 2-methyl-3-phenylindanones. The *cis*-isomer IIa was brominated instantly at room temperature with or without an added hydrobromic acid catalyst while the *trans*-isomer IIb required heating even with an added catalyst. A similar reluctance of one stereoisomer to brominate was noted in our earlier work[2] where it was found that while *cis*-1-phenyl-2-benzoylcyclohexane reacted with bromine under mild conditions, *trans*-1-phenyl-2-benzoylcyclohexane was virtually completely unreactive.[11]

The hydriodic acid debromination of each of the stereoisomeric 2-bromo-2-methyl-3-phenylindanones (IVa and IVb) proceeded smoothly to yield a product from which only *cis*-2-methyl-3-phenylindanone (IIa) could be isolated and this in greater than 50% yield. Infrared analysis of the crude reaction product indicated that of the 2-methyl-3-phenylindanone product 76 (±3)% was the *cis*-isomer IIa (note Table I). The formation of the same percentage of IIa from each of the stereoisomeric bromoketones (IVa and IVb) is expected on the basis of the common enol intermediate I.

The preferred formation of *cis*-2-methyl-3-phenylindanone (IIa) is thus a further case of the kinetically controlled ketonization of an enol to yield the less stable of two possible stereoisomeric products. The transition state (Va) which exercises the observed kinetic control is pictured as closely resembling the original enol in geometry; that is, the enolic system is still sp^2 hybridized in the transition state and the proton donor, which attacks the trigonal α-carbon atom from a perpendicular approach, prefers the less hindered side of the enolic system[2,12,13] with consequent formation of IIa.





Va Vb

The alternative is the transition state Vb leading to product IIb; this is of higher energy than Va, however, due to steric interaction between the attacking proton donor (HA) and the phenyl group at carbon 3. A similar argument accounts for the more facile enolization of the *cis*-ketone IIa noted in the bromination experiments,[14] since due to microscopic reversibility the same favored transition state (Va) is available to the *cis*-ketone IIa. In addition, the increased free energy content of IIa observed in the equilibration experiments enhances the reactivity of this isomer.

As a second mode of generating the enol I the lithium liquid ammonia reduction of 2-methyl-3-phenylindone (III) was considered to be of particu-

(9) Our 60° and 62° ketones having thus been shown to be *cis*- and *trans*-2-methyl-3-phenylidanone, respectively, there still remains a question regarding the earlier preparations. The 64° compound of Bergmann[3] is almost certainly identical with our 62° *trans*-ketone since under the drastic conditions employed by this author the *trans*-product would be anticipated. The oils of Ingold[4] and of Shoppee[5] probably represent mixtures; in our experience hydrogenation produced large quantities of hydroxylic by-products which were removed only by crystallization or chromatography. Since we obtained only the same 2,4-dinitrophenylhydrazone, m.p. 197°, from both IIa and IIb, the 179° 2,4-dinitrophenylhydrazone reported by these workers may be the *cis*-derivative which we failed to obtain.

(10) The α isomer, m.p. 106°, was kinetically favored, since it predominated even when the bromination was run in the presence of sodium acetate to prevent equilibration by HBr. It is a likely but not necessary conclusion that in this isomer the bromine atom is *trans* to the phenyl group in analogy to the geometry of protonation.

(11) That the situation of IIa *versus* IIb is less extreme is seen from the fact that IIb could be induced to brominate by an increment in the severity of the reaction conditions.

(12) Only if the proton donor is assumed to be effectively extremely large due either to very extensive solvation or to an extreme sensitivity of the molecular free energy to hindrance at the site of bond formation can one avoid the conclusion that the lower energy tetrahedral transition state would be the one leading to the more stable product. However, such possibilities are seen not to prevail for the protonation of a non-resonance stabilized carbanion which must have a tetrahedral transition state and which is known to yield the more stable product.[15]

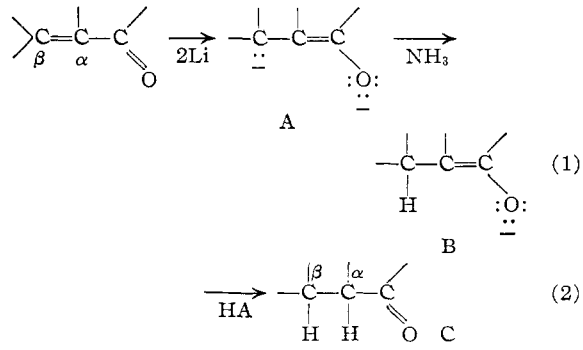
(13) Note an interesting recent discussion of the question of extent of a reaction at the transition state: G. Hammond, THIS JOURNAL, **77**, 334 (1955).

(14) Since enols are brominated extremely rapidly, a difference in the rates of bromination of stereoisomeric ketones can be attributed to a corresponding difference in ease of enolization.[2]

lar interest. Barton[15] has recently considered the stereochemistry of the lithium liquid ammonia reduction of α,β-unsaturated ketones and has concluded that in general the more stable stereoisomer results. However, Barton's attention was focused on the configuration at the β-carbon atom; and, while examples were included in which the more stable α-configuration is obtained, there was no discussion of this point. Now it is known that the primary product of the lithium liquid ammonia reduction of α,β-unsaturated ketones is the lithium enolate (B) formed by ammonia protonation of a dianion intermediate (A). In a subsequent operation the enolate is ketonized by treatment with a proton donor (HA) stronger than ammonia, thus yielding product (C).

TABLE I

Analyzed	*cis*-isomer, %
Crude Li–NH_3 red. prod., inverse dec. with satd. NH_4Cl; run no. 1	69
Crude Li–NH_3 red. prod., inverse dec. with satd. NH_4Cl; run no. 2	68
Crude Li–NH_3 red. prod., inverse dec. with satd. NH_4Cl; run no. 3	80
Crude Li–NH_3 red. prod., inverse dec. with satd. NH_4Cl; run no. 4	73
Crude Li–NH_3 red. prod., inverse dec. with satd. NH_4Cl; run no. 5	67
First indanone chromatographic fraction from Li–NH_3 red., inverse dec. with satd. NH_4Cl; run no. 6	82
Second indanone chromatographic fraction from Li–NH_3 red., inverse dec. with satd. NH_4Cl; run no. 6	80
Crude product of neutral hydrogenation	93
Hydriodic acid debromination of α-2-bromo-2-methyl-3-phenylindanone	76
Hydriodic acid debromination of β-2-bromo-2-methyl-3-phenylindanone	76
Crude Li–NH_3 red. prod., normal dec. with solid NH_4Cl; run no. 1	32
Crude Li–NH_3 red. prod., normal dec. with solid NH_4Cl; run no. 2	28
Sodium ethoxide isomerization of *cis*-2-methyl-3-phenylindanone	21



Clearly, the configuration at the α-carbon atom is determined in the ketonization step,[16] the stereochemistry of which reaction has been shown by us frequently to yield the less stable of two stereoisomers.[2] Therefore, it seemed to us that, despite the impression created in the literature,[15,17] the reaction should follow the usual stereochemical course of ketonization[2,18] and the product with the less stable α-configuration should often result.

In support of this reasoning it was found that the lithium liquid ammonia reduction of 2-methyl 3-phenylindone (III) led predominately to *cis*-2-methyl-3-phenylindanone (IIa) when the lithium salt[19] was decomposed by its addition to saturated aqueous ammonium chloride. Although the infrared spectrum of the crude reduction product closely resembled that of *cis*-2-methyl-3-phenylindanone (IIa), a hydroxylic impurity was seen to be present and the crude oil refused to crystallize even after seeding with either pure IIa or IIb. Chromatography on silicic acid allowed isolation of solid IIa and a considerable amount of an oily hydroxylic by-product was obtained. Infrared analysis of the indanone chromatographic fraction showed the presence of 80 ($\pm 3\%$) *cis*-2-methyl-3-phenylindanone (IIa) and 20 ($\pm 3\%$) *trans*-isomer IIb. Since the hydroxylic impurity did not absorb strongly or selectively in the analytical region of the infrared, the crude reduction products were also analyzed by the infrared technique. The greatest specificity observed was again 80 ($\pm 3\%$)

(15) D. Barton and C. Robinson, *J. Chem. Soc.*, 3045 (1954).

(16) Attack by the proton donor on the oxygen atom must be rapid with respect to attack on the α-carbon; therefore, ketonization of an enolate by reaction with a reasonably strong proton donor should proceed by the way of the rapidly formed enol.

(17) Note also the discussion by L. Sarett and co-workers, THIS JOURNAL, **76**, 1715 (1954).

(18) Literature examples in which the more stable α-configuration is obtained fall into two categories, those in which this more stable α-configuration is actually kinetically preferred and those in which the less stable configuration is kinetically preferred but equilibration under the reaction conditions yields the observed configuration. The most common example of the former situation, in which prototropic attack from the less hindered side of the α-carbon of the enolic system leads to the more stable product, is the reduction of 8(9)-en-11-one steroids and triterpenoids (see ref. 15 for a literature survey). Models indicate a preferred rearward attack on carbon 9 of the 9(11)-en-11-ol (enolic) system.

On the other hand, a study of a model of steroids containing the 7(8)-en-7-ol(enolic) system suggests preferential rearward attack at carbon-7 to give the *cis*-B:C ring fusion. However, the Li–NH_3 reduction of 8-en-7-one steroids and triterpenoids has invariably been reported to yield the stable isomer possessing the *trans* B:C ring fusion (see ref. 15 as well as D. Barton and co-workers, *J. Chem. Soc.*, 876 (1955), for a more recent example). The formation of these stable isomers may indeed be due to equilibration, for in every case cited the lithium enolate was decomposed by the addition of an alcohol thus generating a strongly basic lithium alkoxide which would be anticipated to effect epimerization *via* the enolate. Also pertinent here is the reduction of 8(9)-en-7,11-diones by zinc and methanol in ether to yield the labile saturated 7,11-diones with the *cis* B:C ring junction and the unstable configuration at carbon-8; R. Budziarek and F. Spring, *ibid.*, 956 (1953), have suggested that this proceeds by *cis*-addition of hydrogen. More likely is the usual course of metal reduction of unsaturated ketones, in this case to yield a twofold zinc enolate which on ketonization yields the less stable configuration at carbon-8.

(19) In the present case the dianion (A) may not be protonated at the β-carbon atom by ammonia. This dianion, being stabilized at the β-position by two aromatic rings, should approximate the conjugate base of diphenylmethane in basicity; C. Wooster and N. Mitchell, THIS JOURNAL, **52**, 688 (1930), have reported the stability of the colored diphenylmethide anion in liquid ammonia. Nevertheless, this does not alter the argument, since the stereochemistry of the product would still be determined in a relatively slow protonation of the neutral enol (I) obtained by a rapid protonation of the negative β-carbon atom and the negative enolate oxygen atom by the aqueous ammonium chloride. That these considerations are indeed valid is suggested by the occurrence here of the same stereochemical course as found for the debromination reactions.

IIa.[20] The degree of specificity is then the same within experimental error as obtained in the debromination experiments; this is of course expected on the basis of a common enolic intermediate (I).

The lability of *cis*-2-methyl-3-phenylindanone (IIa), already indicated by the extreme facility of its bromination, was encountered again during attempted alumina chromatography. Using either basic or acid washed alumina only the *trans*-indanone (IIb) could be isolated. Also, whereas the rapid addition of solid ammonium chloride ordinarily would appear to be a reasonable way to convert irreversibly the liquid ammonia solution of a lithium enolate to the corresponding ketone, in the present case this method led predominantly to *trans*-2-methyl-3-phenylindanone (IIb) (see Table I).

Finally meriting attention is the decreased stereoselectivity of ketonization and enolization in the 2-methyl-3-phenylindanone system as compared with the 1-phenyl-2-benzoylcyclohexane situation discussed earlier.[2] Such an experimental finding is consonant with a prediction based on a consideration of models, for carbon 2 of the enol I is seen to be only partially shielded by the phenyl group at carbon 3 from a perpendicular prototropic attack *cis* to this blocking group.

Experimental[21]

Ethyl β,β-Diphenyl-β-hydroxy-α-methylpropionate.—This was prepared essentially by the method of Bergmann and Weiss[22] from 80.0 g. of zinc (20 mesh), 217 g. of ethyl α-bromopropionate, 180 g. of benzophenone and 600 ml. of dry benzene as solvent; the yield of purified product, m.p. 101–102°, was 163 g. (reported[22] m.p. 102–103°).

2-Methyl-3-phenylindone (III).—This was prepared essentially by the method of Bergmann and Weiss[22] from 60 g. of ethyl β,β-diphenyl-β-hydroxy-α-methylpropionate and 300 ml. of concd. sulfuric acid, except that stirring was continued for 4.5 hours. The crude product, obtained by pouring onto 800 g. of ice and chloroform extracting followed by concentrating *in vacuo* on the steam-bath, was dissolved in 60 ml. of boiling ethanol. Large orange crystals separated on cooling, yielding 43.8 g., m.p. 83.5–85.0°. The melting point was not altered by recrystallization or vacuum sublimation (reported m.p. 83–84°,[22] 85°[4]).

Hydrogenation of 2-Methyl-3-phenylindone in Neutral Solution.—Nine grams of 2-methyl-3-phenylindone in 60 ml. of ethyl acetate was hydrogenated at atmospheric pressure in the presence of 500 mg. of platinum oxide catalyst until 1350 cc. of hydrogen had been absorbed. At this point the rate of uptake dropped abruptly to one-half and the formerly deep orange solution had become almost colorless. Filtration and concentration *in vacuo* on the steam-bath yielded an oil. The infrared spectrum indicated that the *cis*-product predominated (note Table I). The oil was taken up in 35 ml. of warm methanol and treated with water almost to cloudiness. Having been seeded with *cis*-2-methyl-3-phenylindanone, the solution slowly separated large rectangular crystals, 4.70 g., m.p. 56–58°. Recrystallization from aqueous methanol brought the melting point to 59–60°.

Hydrogenation of 11.0 g. 2-methyl-3-phenylindone in 100 ml. of thiophene-free benzene with 120 mg. of platinum oxide catalyst using a Parr apparatus resulted in a slightly improved yield. When the rate of hydrogenation was negligible and the hydrogen uptake was 1.35 times theory, the solution was filtered and concentrated to leave a pale yellow oil which solidified. Several crystallizations from aqueous methanol yielded 6.84 g., m.p. 60.0–60.5°. *cis*-2-Methyl-3-phenylindanone exhibited a sharp band at 11.19 μ in the infrared and carbonyl absorption at 5.85 μ.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.42; H, 6.48.

Hydrogenation of 2-Methyl-3-phenylindone in Basic Solution.—To a mixture of 50 ml. of ethyl acetate and 100 ml. of ethanol there was added 10.0 g. of 2-methyl-3-phenylindone, 1.0 g. of solid sodium hydroxide pellets and 150 mg. of platinum oxide catalyst. Hydrogenation in a Parr apparatus was continued until the rate was negligible, at which point 1.2 times the theoretical amount of hydrogen had been absorbed. The solid sodium hydroxide pellets were largely undissolved. These and the catalyst were removed by filtration and the filtrate was concentrated *in vacuo* on the steam-bath to leave a yellow oil which was difficult to crystallize and from which only *trans*-2-methyl-3-phenylindanone could be isolated and this in low yield. This oil was chromatographed on an alumina column (Chicago Apparatus Co. Alumina) 3.5 × 13.0 cm. using 4:1 hexane–ether. After 100 ml. had been eluted the eluent became yellow and a 600-ml. fraction was collected. Concentration gave an oil which crystallized. Recrystallization from aqueous methanol yielded 5.4 g. of *trans*-2-methyl-3-phenylindanone, m.p. 61.0–62.0°.

The Reaction of *cis*-2-Methyl-3-phenylindanone with 2,4-Dinitrophenylhydrazine.—To a hot solution of 198 mg. of 2,4-dinitrophenylhydrazine in 3.0 ml. of ethanol containing 0.40 ml. of concd. hydrochloric acid was added 111 mg. of *cis*-2-methyl-3-phenylindanone. Almost immediately a precipitate separated. The reaction mixture was heated on the steam-bath for a total of three minutes and filtered hot. The crude product was boiled with 5 ml. of ethanol and filtered hot in order to remove troublesome ethanol soluble impurities. One crystallization from ligroin (b.p. 86–100°) containing a minimum of chloroform yielded 153 mg. of red plates, m.p. 196–197°. The melting point was not changed by recrystallization.

Anal. Calcd. for $C_{22}H_{18}O_4N_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.33; H, 4.54; N, 14.34.

Isomerization of *cis*-2-Methyl-3-phenylindanone.—A solution of 120 mg. of *cis*-methyl-3-phenylindanone in 3.0 ml. of methanol and 0.5 ml. of water was treated with 10 mg. of anhydrous potassium carbonate and refluxed on the steam-bath for 50 minutes. At the end of this time the hot reaction mixture was treated with water almost to the saturation point; the crystalline product then slowly separated. Filtration yielded 92 mg. solid, m.p. 56–58°. Recrystallization from methanol and water brought the melting point to 61–62°. This product, which represented pure *trans*-2-methyl-3-phenylindanone, depressed the melting point of the *cis*-isomer to 45°. The infrared spectrum of *trans*-2-methyl-3-phenylindanone had a well defined band at 11.02 μ and carbonyl absorption at 5.85 μ.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.49; H, 6.67.

Treatment of *trans*-2-methyl-3-phenylindanone with 2,4-dinitrophenylhydrazine exactly as described for the *cis*-isomer led to a red crystalline product, m.p. 196–197°, shown by mixed melting point to be identical with the 2,4-dinitrophenylhydrazone obtained from *cis*-2-methyl-3-phenylindanone.

Isomerization of *cis*-2-Methyl-3-phenylindanone with Sodium Ethoxide.—To a sodium ethoxide solution prepared from 46 mg. of sodium and 2.50 ml. of ethanol there was added 222 mg. of *cis*-2-methyl-3-phenylindanone. The resulting yellow solution was allowed to stand at room temperature for 2.5 hours and was then poured into water and ether extracted. The extract was washed with water, dried over sodium sulfate and concentrated under vacuum below room temperature. The residual oil crystallized. Infrared analysis indicated that of the 2-methyl-3-phenylindanone product 79% was *trans*.

Lithium–Liquid Ammonia Reduction of 2-Methyl-3-phenylindone.—To a 500-ml. flask equipped with a Teflon magnetic stirring bar, a Dry Ice condenser connected to a drying tube filled with sodium hydroxide pellets, and an inlet connected to an anhydrous ammonia tank was added 250 ml. of liquid ammonia. Through a small inlet 310 mg. (0.045

(20) The lower specificity noted in some runs is attributed to equilibration during isolation or to increased hydroxylic impurities which would cause low values for per cent. *cis*-indanone to result by leveling absorption in the eleven micron region. The most reliable results are therefore for the chromatographed product.

(21) All melting points were taken on a Fisher–Johns block which had been checked with compounds of known melting point. The microanalyses were performed by Miss H. Beck. Infrared analyses were carried out using a Baird double beam recording instrument.

(22) E. Bergmann and H. Weiss, *Ann.*, **480**, 73 (1930).

mole) of lithium cut into small pieces was introduced during a few minutes. The mixture was stirred for 40 minutes. Then a solution of 2.20 g. (0.010 mole) of 2-methyl-3-phenylindone in 30 ml. of anhydrous ether was added over five minutes with stirring. An additional 50 ml. of ether was added to rinse out the dropping funnel used. After the mixture had been stirred for 15 minutes, it was poured in a thin stream into 600 ml. of a stirred saturated aqueous solution of ammonium chloride containing additional suspended ammonium chloride. The mixture was ether extracted; the extract was washed with water until neutral and then dried over sodium sulfate. Concentration of the ether solution *in vacuo* below room temperature left a yellow oil. Although the infrared spectrum closely resembled that of *cis*-2-methyl-3-phenylindanone, it also contained hydroxylic absorption bands. The oil refused to crystallize, even when seeded with *cis*- and *trans*-2-methyl-3-phenylindanones. This product was chromatographed on a 3.5 × 11.0 cm. column of precipitated silicic acid using 5% ether by volume in hexane; positive pressure proved necessary to obtain a reasonable elution rate. Nine fractions were collected as follows: (1) 50 ml. containing 0.04 g. of oily hydrocarbon; (2) 50 ml. containing 0.13 g. of solid shown to be largely 2-methyl-3-phenylindone by infrared analysis; ((3) 100 ml.) containing 0.60 g. of solid shown by infrared analysis to be 82% *cis*-2-methyl-3-phenylindanone (see Table I); (4) 100 ml. containing 0.24 g. of solid shown by infrared analysis to be 80% *cis*-2-methyl-3-phenylindanone (see Table I); (5) 100 ml. containing 0.07 g. of oil seen to be a mixture of *cis*-indanone and a carbonyl impurity absorbing at 5.92 μ; (6) 200 ml. containing 0.05 g. of oil absorbing at 5.92 μ plus an indanone impurity. Elution with 1:1 ether–hexane was begun. (7) 100 ml. containing 0.62 g. of oily solid showing hydroxylic absorption; (8) 100 ml. containing 0.17 g. of oil showing hydroxylic absorption. Fractions 3 and 4 were combined and subjected to several crystallizations from aqueous methanol to yield 0.35 g. of pure *cis*-2-methyl-3-phenylindanone. No *trans*-isomer could be isolated from the filtrates.

Infrared analysis of the crude lithium–liquid ammonia reduction products from various runs indicated that of the 2-methyl-3-phenylindanone product the per cent. of *cis*-isomer varied from 67 to 80%. There was no consistent correlation with small changes in times of addition of the reactants or in stirring times between different operations.

When the crude reduction product was chromatographed on alumina (Chicago Apparatus Co., 80–200 mesh) in the same manner only *trans*-2-methyl-3-phenylindanone could be isolated.

Bromination of *cis*-2-Methyl-3-phenylindanone.—To a solution of 1.20 g. of *cis*-2-methyl-3-phenylindanone (0.0054 mole) in 5.0 ml. of acetic acid was added a solution of 0.91 g. of bromine (0.0057 mole) in 10.0 ml. of acetic acid. The bromine was instantly decolorized with evolution of hydrogen bromide. After ten minutes at room temperature the yellow solution was poured into 60 ml. of water and extracted with 1:1 ether–hexane. The extract was dried over sodium sulfate and was concentrated *in vacuo* leaving an oil which crystallized. Several crystallizations from ligroin yielded 0.50 g. of rectangular rods of α-2-bromo-2-methyl-3-phenylindanone, m.p. 105–106°.

Anal. Calcd. for $C_{16}H_{13}OBr$: C, 63.80; H, 4.35. Found: C, 64.37; H, 4.06.

In the filtrates, in addition to more rectangular rods, a second crystalline type could be discerned. These crystals, which formed in star-like clusters, were separated and crystallized several times from ligroin to yield 36 mg. of β-2-bromo-2-methyl-3-phenylindanone, m.p. 133.0–134.5°.

Anal. Calcd. for $C_{16}H_{13}OBr$: C, 63.80; H, 4.35. Found: C, 63.55; H, 4.16.

Bromination of 1.00 g. (0.0045 mole) of *cis*-2-methyl-3-phenylindanone in 15 ml. of acetic acid with 0.80 g. of bromine (0.0050 mole) in the presence of 0.80 g. of anhydrous sodium acetate (0.010 mole) proceeded by heating on the steam-bath. At the end of 45 minutes the mixture was poured into water and isolated by benzene extraction and concentration. From the residue a total of 0.61 g. of α-2-bromo-2-methyl-3-phenylindanone could be isolated after crystallization from ligroin containing a small amount of ethyl acetate.

Bromination of *trans*-2-Methyl-3-phenylindanone.—To 276 mg. of *trans*-2-methyl-3-phenylindanone in 2.0 ml. of acetic acid was added to a solution of 208 mg. of bromine in 1.0 ml. of acetic acid. The bromine color persisted, and the reaction mixture was brought to 70°. At the end of five minutes the pale yellow solution was poured into 50 ml. of water, ether extracted, washed with water, dried over sodium sulfate and concentrated under vacuum. The residual oil was subjected to chromatography on silicic acid (Mallinckrodt 100 mesh) using 5% ether in hexane by volume. The first fractions crystallized. Crystallization from ligroin yielded 320 mg. of α-2-bromo-2-methyl-3-phenylindanone, m.p. 104–105°.

A mixture of 7.0 g. of *trans*-2-methyl-3-phenylindanone, 5.6 g. of bromine, 90 ml. of acetic acid and three drops of 48% hydrobromic acid did not react at room temperature. The mixture was heated to 55° for one hour, poured into 300 ml. of water, benzene extracted, dried over sodium sulfate and concentrated *in vacuo*. The residual crystallizing oil, 7.7 g., was taken up in hot ligroin and the two isomeric bromoketones were separated by seeding first with one isomer and decanting the mother liquor and then seeding the decantate with the other isomer. After recrystallization of each isomer so obtained there was isolated 2.09 g. of α-2-bromo-2-methyl-3-phenylindanone, m.p. 105°, and 0.62 g. of β-2-bromo-2-methyl-3-phenylindanone, m.p. 135°. More material could be obtained from the mother liquors.

The Relative Ease of Bromination of the *cis*- and *trans*-2-Methyl-3-phenylindanones.—A solution of 64.5 mg. of bromine (0.40 mmole) and 0.01 ml. of 48% hydrobromic acid (J. T. Baker) in enough acetic acid to bring the volume to 10.0 ml. was prepared. In two separate experiments 9.0 mg. (0.045 mmole) of each of the stereoisomeric 2-methyl-3-phenylindanones in 0.02 ml. of acetic acid was treated at room temperature with 1.00 ml. of the above bromine solution. While the *cis*-indanone decolorized the bromine solution instantly, the *trans*-indanone mixture was only partially decolorized at the end of five minutes and required a total of *ca.* 20 minutes for complete reaction.

The Hydriodic Acid Reduction of α-2-Bromo-2-methyl-3-phenylindanone.—To a solution of 301 mg. of α-2-bromo-2-methyl-3-phenylindanone (1.0 mmole) in 10 ml. of acetone there was added 1.0 ml. of hydriodic acid (Baker, 47%). There was an instantaneous dark coloration of iodine. At the end of three minutes 60 ml. of water and enough sodium thiosulfate to decolorize the iodine were added. The oil which separated was removed by extraction with ether–pentane (1:1). The solution was dried over sodium sulfate and concentrated under vacuum to leave a solid. Infrared analysis indicated 76% *cis*-2-methyl-3-phenylindanone. Crystallization of the solid from aqueous methanol yielded 121.4 mg. of crystals, m.p. 54–55°. This material depressed the melting point of *trans*-2-methyl-3-phenylindanone to 42–44° but did not depress the melting point of pure *cis*-2-methyl-3-phenylindanone. Recrystallization from aqueous methanol brought the melting point to 59–60°.

The Hydriodic Acid Reduction of β-2-Bromo-2-methyl-3-phenylindanone.—This experiment was run precisely as described above for the reduction of the α-bromoindanone except that here the β-2-bromo-2-methyl-3-phenylindanone, m.p. 135°, was used. The crude solid product was shown by the usual infrared analysis to consist of 76% *cis*-2-methyl-3-phenylindanone.

Method of Infrared Analysis for Determining Isomer Ratio.—The analytical method was based on absorption differences in the eleven micron region of the infrared spectrum. *cis*-2-Methyl-3-phenylindanone gave a sharp absorption band at 11.18 μ in the infrared (density = 0.229 at 11.0 mg./0.06 ml. $CHCl_3$) while the *trans*-isomer had a density of 0.046 at this point at the same concentration. The infrared spectrum of *trans*-2-methyl-3-phenylindanone had a sharp band at 11.07 μ (density = 0.200 for 11.0 mg./0.06 ml. $CHCl_3$) while the *cis*-isomer had a density of only 0.046 at this point for the same concentration.

By assuming Beer's law one can derive the relationship

$$R_{c/t} = \frac{C_{cm}}{C_{tm}} = \frac{\dfrac{D''_m}{D''_t} - \dfrac{D'_m}{D'_t}}{\dfrac{D'_m}{D'_c} - \dfrac{D''_m}{D''_c}} \times \frac{D'_t\,D''_t}{D'_c\,D''_c} \times \frac{C_c}{C_t}$$

$R_{c/t}$ = ratio of *cis*- to *trans*-isomer in a mixture
C_{cm} and C_{tm} = concn. of *cis*- and *trans*-isomers in the mixture, resp.

D'_c and D''_c = optical densities at the 2 respective wave lengths for pure *cis*-isomer
D'_t and D''_t = optical densities at the 2 respective wave lengths for pure *trans*-isomer
C_c and C_t = respective concn. at which the two spectra of the pure *cis*- and *trans*-isomers were run
D'_m and D''_m = optical densities at the two critical wave lengths for the mixture.

The densities used were obtained by assuming that the transmittance for all the compounds concerned was 100% at two microns and using the transmittances obtained directly without any consideration of background absorption. The method described was tested on six different mixtures of known composition ranging from all *trans* to all *cis;* in every case the analytical method proved to be accurate within 2%. The method described has the advantage of not requiring that the concentration of the mixtures analyzed be known; however, best results were obtained when absorption in the analytical regions was reasonably intense (*i.e.*, total concn. between 180 and 360 mg./ml.).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE NAVAL STORES STATION][1]

Autoxidation of α-Pinene[2]

BY R. N. MOORE, C. GOLUMBIC AND G. S. FISHER

RECEIVED SEPTEMBER 1, 1955

Although the autoxidation of α-pinene has been studied intermittently for over 100 years, few data are available on the products obtained by non-catalytic, liquid-phase autoxidation at elevated temperatures. In the present investigation, α-pinene was autoxidized in the dark at 100° and the α-pinene hydroperoxides in the resulting oxidate were reduced. The product was fractionated and the volatile fractions analyzed. In addition to unreacted α-pinene (45% of the volatile material) and verbenone (9%), verbenol (16%) and verbenene (trace) which have long been recognized as products of the reaction, α-pinene epoxide (13%), *trans*-pinocarveol (8%), *trans*-carveol (2%) and myrtenal (1%) were obtained. It is suggested that, except for the epoxide, these products result from free radical attack on the α-methyl group of α-pinene to give the myrtenyl free radical and its resonance hybrid the pinocarvyl free radical and the corresponding hydroperoxides. The epoxide is considered to be a secondary oxidation product resulting from the action of a peroxide on the double bond of α-pinene.

Esters of pinic acid and pinonic acid derived from α-pinene, the major constituent of turpentine, are potentially useful as synthetic lubricants and plasticizers.[3,4] Attempts to produce these or similar acids by the autoxidation of α-pinene have led in every case to very complex mixtures of resinous products. These mixtures did contain terpene-acids, but separation and identification of the mixtures of acids was not practical. In order to clarify the reactions involved, a detailed study of the volatile autoxidation products was initiated.

The nature of the oxidation of turpentine by air has been the subject of intermittent investigation and controversy for well over a century. The products isolated from oxidized turpentine and α-pinene include sobrerol,[5] formic and acetic acids,[6] verbenol, verbenone[7] and verbenyl hydroperoxide.[8] The possible presence of myrtenal in autoxidized α-pinene also has been suggested.[9] The verbenyl hydroperoxide is obviously the precursor of the verbenol and verbenone, but the source of the sobrerol and pinol has been in doubt. Recently, Schenck[10] has reported the secondary formation of α-pinene epoxide when the α-pinene was oxidized at room temperature. This oxide is very readily hydrated to sobrerol in the presence of dilute acid. Subsequently, Lombard[11] has suggested that the intermediate is the cyclic peroxide analogous to pinol.

Quantitative data regarding the autoxidation products are in all cases meager and there seems to have been no attempt to make a complete examination of the volatile oxidation products obtained under a given set of conditions. Furthermore, the oxidation conditions used have usually involved uneconomically long reaction times and low temperatures.

The present report concerns the volatile products of the non-catalyzed autoxidation of α-pinene at 100° in the absence of light. Under such conditions, a vigorous exothermic reaction occurs with rapid absorption of oxygen and somewhat less rapid accumulation of peroxides (Fig. 1). Reduction of the hydroperoxides with sodium sulfide and fractional distillation of the recovered neutral fraction gave an oil whose composition is summarized in Table I.

TABLE I

Compound	% of distillate	Compound	% of distillate
α-Pinene	45	*trans*-Pinocarveol	8
Verbenene	Trace	*trans*-Verbenol	16
α-Pinene epoxide	13	Verbenone	9
Myrtenal	1	*trans*-Carveol	2

Dupont[12] has pointed out that the production of verbenyl hydroperoxide III, verbenol and verbenone is in accord with the modern theory of α-methylenic attack in autoxidation of olefins.[13] The ver-

(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

(2) Presented, in part, at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

(3) C. M. Murphy, J. G. O'Rear and W. A. Zisman, *Ind. Eng. Chem.*, **45**, 119 (1953).

(4) V. M. Loeblich, F. C. Magne and R. R. Mod, *ibid.*, **47**, 855 (1955).

(5) Margueron, *Ann. Chim.*, **21**, 174 (1797).

(6) C. T. Kingzett and R. C. Woodcock, *J. Soc. Chem. Ind.*, **31**, 265 (1912).

(7) A. Blumann and O. Zeitschel, *Ber.*, **46**, 1178 (1913).

(8) K. Suzuki, *Bull. Inst. Phys. Chem. Res. Japan*, **15**, 70 (1936).

(9) G. Dupont, W. Zacharewicz and R. Dulou, *Compt. rend.*, **198**, 1699 (1934).

(10) G. O. Schenck, H. Eggert and W. Denk, *Ann.*, **584**, 177 (1953).

(11) R. Lombard and A. Kohler, *Bull. soc. chim.*, 639 (1954).

(12) G. Dupont, *Bull. soc. chim. France*, 838 (1948).

(13) (a) E. H. Farmer and A. Sundralingham, *J. Chem. Soc.*, 121 (1942); (b) E. H. Farmer, H. P. Koch and D. A. Sutton, *ibid.*, 541 (1943). (c) J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950); (d) L. Bateman, *Quart. Rev.*, **8**, 147 (1954).