was dried by azeotropic distillation and passed through an alumina column. Concentration of the benzene eluates afforded 17.7 g. (35%) of **10-carbethoxy-8-keto-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene** (**XX**) as a light red oil which did not solidify.

5,10-Dimethyl-3,4-benzpyrene (**XXII**).—A solution of 17.7 g. (0.0493 mole) of 10-carbethoxy-8-keto-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XX), from above, in 100 ml. of anhydrous ether was added over a period of one hour at room temperature to 10 g. (0.26 mole) of lithium aluminum hydride suspended in 500 ml. of anhydrous ether. After refluxing for 2.75 hr. the reaction mixture was cooled and hydrolyzed with 35% sulfuric acid. Benzene was added and the organic layer was filtered, washed with water, and dried by azeotropic distillation. Concentration of the benzene solution afforded **8-hydroxy-10-hydroxymethyl-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene** (**XXI**) as a viscous oil.

The crude diol XXI was directly dehydrated and dehydrogenated by heating with 3.0 g. of 10% palladium–charcoal at 285–355° for 1.25 hr. After cooling, the hard cake was dissolved in boiling benzene and the solution was chromatographed through alumina, and the material obtained by concentration of the benzene eluates was crystallized three times from ethyl acetate producing 2.85 g. of **5,10-dimethyl-3,4-benzpyrene** (**XXII**) as minute yellow plates, m.p. 227.5–230° vac. The material remaining in the mother liquors was purified *via* the picrate providing an additional 0.80 g. of XXII, m.p. 228–230° vac., making the total yield 3.65 g. (26% from XX). An analytical sample, m.p. 229.5–231° vac., was prepared by crystallization from ethyl acetate.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 93.73; H, 5.66.

The hydrocarbon XXII gave an unstable, purple **picrate**, m.p. 195–197°.

Ultraviolet Absorption Spectrum.—The ultraviolet absorption spectrum of 5,10-dimethyl-3,4-benzpyrene (XXII) in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 258 $m\mu$ (4.57), 268 $m\mu$ (4.63), 290 $m\mu$ (4.55), 302 $m\mu$ (4.65), 378 $m\mu$ (4.38) and 398 $m\mu$ (4.47).

5,8,10-Trimethyl-3,4-benzpyrene (**XXV**).—A mixture containing 2.50 g. (0.0089 mole) of 8,10-dimethyl-3,4-benzpyrene (XXIII),[15] 2.55 g. (0.019 mole) of N-methylformanilide, 2.55 g. (0.017 mole) of phosphorus oxychloride and 10 ml. of *o*-dichlorobenzene was warmed on a steam-bath for 2.0 hr. The resulting red solution was cooled, treated with a solution of 17 g. of sodium acetate in 75 ml. of water, and steam distilled. The residual brown solid, **8,10-dimethyl-3,4-benzpyrene-5-aldehyde** (**XXIV**), was filtered, washed with water, and dried. The crude aldehyde was added to 1.5 g. (0.054 mole) of 95% hydrazine, 2.0 g. of C.P. potassium hydroxide and 25 ml. of diethylene glycol. The resulting mixture was heated at 100–115° for 30 min. and then at 210–235° for an additional 90 min. The reaction mixture was allowed to cool and then was acidified with dilute hydrochloric acid. The resulting brown precipitate was filtered, washed with water, and extracted with boiling benzene. The benzene solution was filtered, dried, and passed through an alumina column. Concentration of the benzene eluates yielded 0.67 g. (26%) of **5,8,10-trimethyl-3,4-benzpyrene** (**XXV**) as light yellow plates, m.p. 289–291.5° vac. An analytical sample, m.p. 290–292° vac., was prepared by crystallization from benzene.

Anal. Calcd. for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.92; H, 6.10.

Ultraviolet Absorption Spectrum.—The ultraviolet absorption spectrum of 5,8,10-trimethyl-3,4-benzpyrene (XXV) in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 258 $m\mu$ (4.61), 270 $m\mu$ (4.63), 296 $m\mu$ (4.58), 308 $m\mu$ (4.73), 384 $m\mu$ (4.42) and 404 $m\mu$ (4.45).

ALBUQUERQUE, NEW MEXICO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. XII. The *o*-Tolyl/Phenyl Migration Ratios in the Pinacol Rearrangement and in the Deamination Reaction[1]

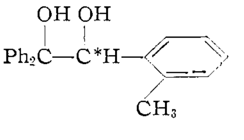
BY VERNON F. RAAEN AND CLAIR J. COLLINS

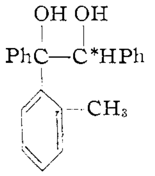
RECEIVED OCTOBER 23, 1957

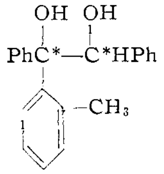
The rearrangements, in cold, concentrated sulfuric acid, of diphenyl-*o*-tolylacetaldehyde (III) and the associated glycols I and II have been studied by means of techniques similar to those previously[2] employed. The *o*-tolyl/phenyl migration ratio has been estimated to be about 3. The *o*-tolyl/phenyl migration ratio in the deamination of 2,2-diphenyl-2-*o*-tolylethyl-1-C^{14}-amine (VI) has been determined as 0.75. These results are explained, in the rearrangement of III, on the basis of open carbonium ion intermediates whose life-times are long enough so that the various conformational isomers are in equilibrium; thus *o*-tolyl group migration predominates over phenyl because of a greater electrical effect and because more steric strain is relieved as a result of tolyl migration. In the deamination of VI, however, it is postulated that the open cationic intermediates are short-lived, do not reach equilibrium with respect to their rotational isomers, and thus phenyl migration predominates over *o*-tolyl migration because conformations VI-1 and VI-2 are sterically more compatible than conformation VI-3.

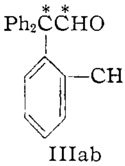
Introduction and Results

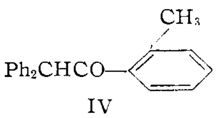
By an application of the same radiochemical techniques previously applied[2] to the acid-catalyzed rearrangements of triphenylethylene glycol,[2a] and closely related trisubstituted glycols and aldehydes,[2b] we have now studied the rearrangements in cold, concentrated sulfuric acid of compounds I, II and III to the ketones IV and V. This series of compounds[3] was selected in order that we might compare the *o*-tolyl/phenyl migration ratio in the aldehyde–ketone rearrangement of III with that

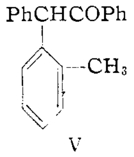

Ia


erythro-IIa


threo-IIab


IIIab


IV


V

---

[1] This paper is based upon work performed at Oak Ridge National Laboratory which is operated for the Atomic Energy Commission by Union Carbide Nuclear Co.

[2] (a) C. J. Collins, THIS JOURNAL, **77**, 5517 (1955); (b) B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4329 (1956).

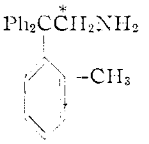
[3] R. Roger and W. B. McKay, *J. Chem. Soc.*, 332 (1933).

previously reported[4] (0.82) in the dehydration of 2-phenyl-2-*o*-tolylethanol-1-C^{14}. This seemed important, since it has been established[2] that the migration ratios in the aldehyde–ketone rearrangement are not necessarily reversed, as had been assumed,[5,6] and are not directly calculable from the simple product ratio. In the case of the rearrangement[2b] of diphenyl-*p*-tolylacetaldehyde[2b] it has been shown that a *p*-tolyl/phenyl ratio greater than one can be justified by means of equation 1 (J. Z. Hearon, ref. 2b) if a mechanism[2b] is assumed, involving a dynamic equilibrium of three carbonium-ion intermediates.

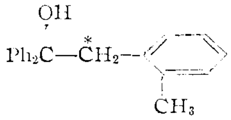
$$\frac{k_{\mathrm{T}}}{k_{\mathrm{P}}} = \frac{k_{\mathrm{H}}}{k\phi} \times \frac{k_{\mathrm{Tol}}}{k'_{\mathrm{H}}} \times r \times \left[\frac{1 + (k'_{\mathrm{H}}/k_{\mathrm{Tol}})}{1 + (k_{\mathrm{H}}/k\phi)}\right] \qquad (1)$$

An application of equation 1 to the rearrangement of diphenyl-*o*-tolylacetaldehyde (III) should permit a calculation of the *o*-tolyl/phenyl migration ratio in the same fashion in which *p*-tolyl/phenyl migration ratios were previously determined[2] for related systems. The specific rate constants of equation 1 have the same significance as in prior work when applied, later in this paper, to the mechanisms of Charts I and II. The value *r* in the present case is the ratio of ketones formed when aldehyde III is rearranged in concentrated sulfuric acid.

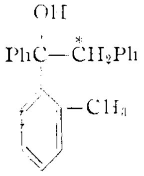
Compounds I, *erythro*- and *threo*-II and III, labeled as shown, were subjected to rearrangement in concentrated sulfuric acid at 0°. The yields of ketones produced in each case were determined by the isotopic dilution method in a manner very similar to that previously described.[2] That no significant fraction of secondary hydroxyl removal occurred from either I or *erythro*-II under these conditions was demonstrated by alkaline cleavage of the products, followed by radioactivity assay of the purified *o*-toluic acid fractions. It was very difficult to separate benzoic from *o*-toluic acid in the acidic portions of the alkaline cleavage products. The mixed acids obtained from the ketones produced on rearrangement of I, therefore, were assayed for radioactivity, and the isotopic dilution method was then employed to determine the percentage of benzoic acid in the mixture. From these data the molar radioactivity of the benzoic acid was calculated to be the same, within experimental error, as the glycol from which it was obtained (see Table V, Experimental section). In the case of product IV, from I or from *erythro*-II, the diphenylmethane fractions obtained upon alkaline cleavage, were oxidized to benzophenone fractions which were then assayed for radioactivity content as the 2,4-dinitrophenylhydrazones. Again, no scrambling of the chain-carbons during rearrangement was indicated. To sum up, then, the evidence is that (a) no scrambling of the chain carbons of IV or V took place during rearrangement of glycol I; and (b) no scrambling of the chain carbons of IV took place during the rearrangement of *erythro*-II. These data indicate also that there was no scrambling of the chain carbons of ketone V during rearrangement of *erythro*-II, since the steric requirements of the *erythro* isomer are such that if secondary hydroxyl removal takes place, phenyl migration should predominate over *o*-tolyl migration. Since our results demonstrate unequivocally that phenyl migration to C-2 does not occur, it then follows also that there should be no migration of *o*-tolyl to C-2. *threo*-II and the aldehyde III were prepared equally labeled in both chain carbons, since for subsequent yield determinations of ketones IV and V produced from these reactants the distribution of radioactivity was unimportant. That no scrambling of the chain carbons of III took place during the rearrangement follows from the fact that glycols I and *erythro*-II exhibited no scrambling of their discrete labels upon rearrangement under identical conditions to IV and V. It has not been proven rigorously that *threo*-II undergoes rearrangement with no secondary hydroxyl removal, for all of our attempts to prepare this material discretely labeled were unsuccessful. Since both ketone IV and V are obtained from *erythro* and *threo*-II in experimentally identical yields, however, we have made the reasonable assumption that *threo*-II, even as *erythro*-II, undergoes no chain scrambling. In Table I are given the yields of IV and V obtained from the reactants I, II or III in cold, concentrated sulfuric acid. In Table II is given a summary of experiments upon the deamination of 2,2-diphenyl-2-*o*-tolylethyl-1-C^{14}-amine (IV) to the carbinols VII and VIII. The radioactivity dilution method[2] was used in the yield determinations of VII and VIII.



VI



VII



VIII

TABLE I

YIELDS OF KETONES IV AND V PRODUCED BY THE ACTION OF SULFURIC ACID UPON I, II AND III

Reactant	Combined yields IV and V, %	Yield[a] of ketone, % IV	V
I	95.0	69.3	30.7
II, *erythro*-form	99.0	50.0	50.0
II, *threo*-form	100.5	49.1	50.9
III	103	62.0	38.0

[a] Adjusted to 100%. The data upon which these yields are based are given in Table III.

TABLE II

MIGRATION RATIOS OBSERVED IN THE DEAMINATION OF VI AS DETERMINED BY THE ISOTOPE DILUTION METHOD

Expt.	Yield, % VII	VIII	Total yield, % of carbinols	*o*-Tolyl/phenyl migration ratio
1	16.2	43.6	59.8	0.746
2	15.1	40.5	55.6	0.746

Finally, the yields of aldehyde III produced upon rearrangement of I and *erythro*-II in 98% formic acid at 27.6°, were determined by the radioactivity dilution method to be, respectively, 29 and 77%.

---

[4] B. M. Benjamin and C. J. Collins, THIS JOURNAL, **75**, 402 (1953).

[5] G. W. Wheland, "Advanced Organic Chemistry," 2d Edition, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 501–502.

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 479.

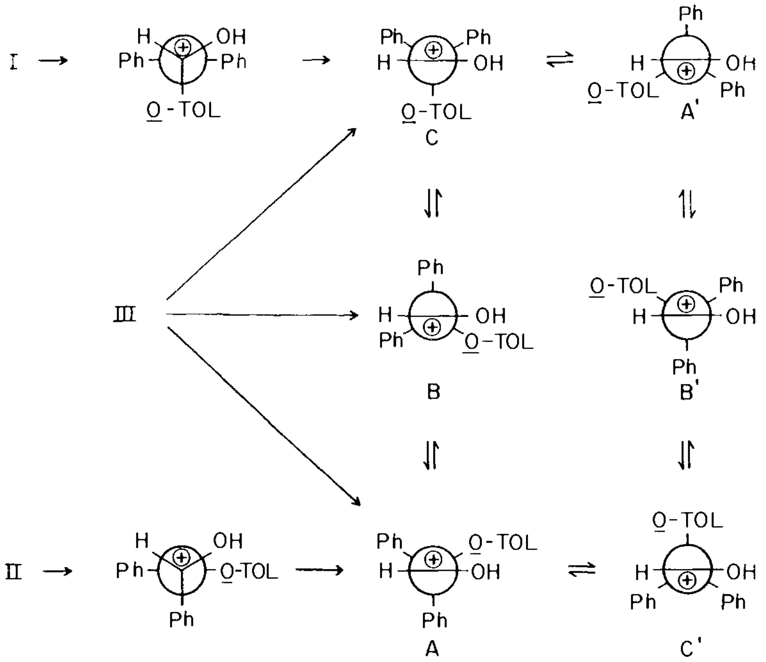


CHART III

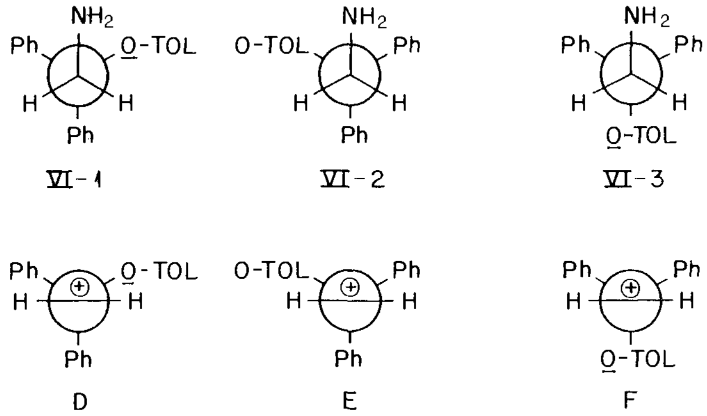


CHART IV

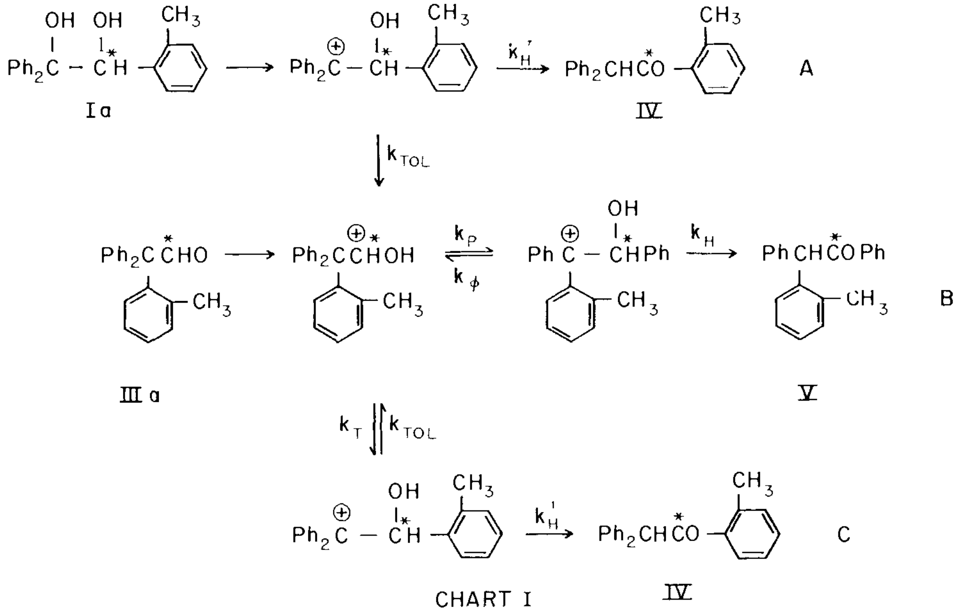


CHART I

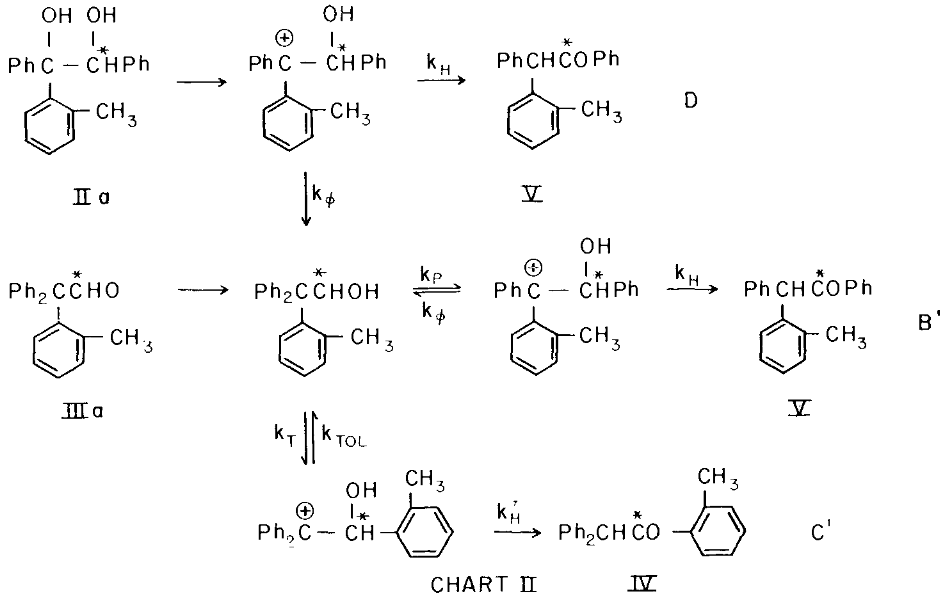


CHART II

Discussion

In Charts I and II are given the schemes by which we presume the rearrangements of glycols I and II and of the aldehyde III to take place. If we define m_a, m_b, m_c and, separately, m_d, m'_b and m'_c as the mole fractions, respectively, of reactants I and II which proceed to products by the corresponding paths of Charts I and II, then these mole fractions can be calculated (see Experimental section) to have the values: m_a, 0.193; m_b, 0.307; m_c, 0.500; m_d, 0.193; m'_b, 0.307 and m'_c, 0.500.

By the same type of mathematical treatment formerly applied[2b] it can be shown that equation 1 is applicable to the rearrangement (Charts I and II) of diphenyl-*o*-tolylacetaldehyde (III). The symbols employed for the specific rate constants of Charts I and II are the same as those used before[2b]; these identical symbols have been used purposely for the different systems in order to permit easy comparison. It must be remembered, however, that the symbols do not possess the same absolute values when applied to the separate and distinct systems.

The specific rate-constant ratios of equation 1 may now be evaluated

$$\frac{k_{\mathrm{Tol}}}{k'_{\mathrm{H}}} = \frac{m_b + m_c}{m_a} = 4.18, \text{ and } \frac{k_{\mathrm{H}}}{k\phi} = \frac{m_d}{m'_b + m'_c} = 0.241$$

From these values and from the ratio r (1.63) it can be shown (by means of equation 1) that $k_T/k_P = 1.64$, and thus the *o*-tolyl/phenyl migration ratio $(2k_T/k_P) \cong 3$. In order to establish whether the value of 3 for $2k_T/k_P$ is a reliable number, we have made the arbitrary and highly improbable assumptions that all of the yield determinations given in Table I are in error by 2 reaction per cent. in such a direction as to make $2k_T/k_P$ a minimum; thus it has been shown that if such be the error, then $2k_T/k_P$ becomes 1.4. If the assumption is made, conversely, that all of the yield determinations given in Table I are in error by 2 reaction per cent. in such a direction as to make $2k_T/k_P$ a maximum, then this value becomes 9.7 (see calculations given in Experimental section). From these data, therefore, we infer that the *o*-tolyl group migrates in preference to phenyl during the rearrangement of III in cold, concentrated sulfuric acid.[7] Because of this fact, the deamination of 2,2-diphenyl-2-*o*-tolylethyl-1-C^{14}-amine (VI) to the carbinols VII and VIII was undertaken, since III and VI contain identical trisubstituted carbon atoms, and might thus be expected to exhibit similar migration ratios. From Table II, however, it appears that VI undergoes deamination with an *o*-tolyl/phenyl ratio of 0.8.[8]

The reasons for the foregoing results may now be sought through a consideration of the various conformations of the conjugate acid of diphenyl-*o*-tolylacetaldehyde which may be formed from I, II and III (Chart III). Now it is only through C and C′ that the shift of *o*-tolyl can take place. It is likely, however, that $A \rightleftarrows B \rightleftarrows C \rightleftarrows A' \rightleftarrows B' \rightleftarrows C' \rightleftarrows A$ are all in a rapid, reversible equilibrium because of stabilization by solvent (cold, concentrated sulfuric acid) and by the electron-rich hydroxyl group. The relative proportion of *o*-tolyl which migrates, therefore, will not be limited by the populations of C and C′, but will be determined by the electrical properties and the steric "requirements" of the *o*-tolyl group.[7] Additional support for the concept that sulfuric acid, being capable of stabilizing the ionic intermediates, thus removes the steric restriction to *o*-tolyl migration imposed by conformational control, is to be found in a comparison of the ratios

$$\text{in sulfuric acid, } k_{\mathrm{Tol}}/k'_{\mathrm{H}} = k\phi/k_{\mathrm{H}} = 4.2$$

$$\text{in formic acid, } k_{\mathrm{Tol}}/k'_{\mathrm{H}} = 0.41;\ k\phi/k_{\mathrm{H}} = 3.3$$

Steric effects must be quite important, for considerable strain must be relieved through *o*-tolyl shift as compared with the shift of a phenyl; the preference, then, for *o*-tolyl migration does not seem at all unusual when examined in light of these circumstances. The question now arises, however, as to the preference for phenyl over *o*-tolyl migration during the deamination of VI. Shown in Chart IV are the three conformations (VI-1, VI-2 and VI-3) for 2,2-diphenyl-2-*o*-tolylethylamine. From molecular models it seems likely that the equivalent conformations VI-1 and VI-2 are sterically more compatible, and thus more likely than conformation VI-3. Upon deamination these conformations yield, respectively, ionic conformations, D, E and F. Ion DEF, being primary, is much less stable than ion ABC of Chart III. Further, the environment of the deamination reaction (water–acetic acid) is much less able to stabilize a carbonium-ion than the sulfuric acid environment used in the rearrangements (Charts I and II) of compounds I, II and III. We propose, therefore, that the interconversions $D \rightleftarrows E \rightleftarrows F \rightleftarrows D \rightleftarrows$ etc., are slow compared to the rates at which phenyl and *o*-tolyl migrate to generate product. Here the populations of the conformations D, E and F control the relative amounts of the products, and since conformation F, through which the *o*-tolyl shift occurs, is less important than the two equivalent conformations D and E, *o*-tolyl migrates less frequently than either of the two phenyls. This explanation finds much support in the recently published[9] observations on the deamination of optically active, stereospecifically phenyl-labeled 1,1-diphenyl-2-aminopropanol-1. By this[9] work it was demonstrated that the labeled phenyl migrates during deamination to yield product of *inverted* configuration at the migration terminus, whereas the unlabeled phenyl migrates to produce material whose configuration is *retained*, thus demonstrating that the ionic intermediate does not achieve rotational equilibrium prior to its destruction by the entering hydroxyl group.

---

(7) An *o*-tolyl/phenyl ratio of 3.6 in the solvolyses of *o*-methylphenyldimethylcarbinyl chloride and phenyldimethylcarbinyl chloride has been reported by H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957).

(8) Since the combined yields of VII and VIII are only 55–60%, some caution must be used in transposing the data of Table II into migration ratios. In a study of the deamination of 2,2-diphenyl-2-*p*-tolylethyl-1-C^{14}-amine [B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4952 (1956)], however, it was possible to establish that the ratio of yields of the two carbinols produced was invariant even though in separate runs the combined yields varied from 42–74%.

(9) B. M. Benjamin, H. J. Schaeffer and C. J. Collins, *ibid.*, **79**, 6160 (1957).

Experimental

1,1-Diphenyl-2-*o*-tolylethylene-2-C^{14} Glycol (Ia).[10]—Methyl *o*-methylmandelate-C^{14} was prepared through a series of conventional reactions in which carbonyl labeled *o*-toluic acid was employed as the starting material. A Grignard reagent prepared from 0.95 mole of bromobenzene and 0.95 mole of magnesium turnings was added to 0.26 mole of methyl *o*-methylmandelate to produce 40 g. of crude glycol. After three crystallizations from ethanol and one crystallization from benzene–hexane (1:10), there was obtained 26 g. of purified material with a m.p. of 126–127°.

1,2-Diphenyl-1-*o*-tolylethylene-2-C^{14} Glycol (*erythro*-IIa).—Carbonyl-labeled desoxybenzoin was converted to desyl bromide[11] and thence to benzoin-C^{14} by the method of Ward[12]; the yield of material of m.p. 132–135° was 70%. Benzoin-C^{14}, 0.11 mole, was added to a Grignard reagent prepared from 0.40 mole of *o*-bromotoluene and 0.40 mole of magnesium; 300 ml. of tetrahydrofuran was added and most of the diethyl ether was distilled off. After being heated at reflux temperatures for 16 hours, the reaction mixture was poured on 500 g. of ice and was then heated with ammonium chloride solution. The glycol (*erythro*-IIa) was isolated after four crystallizations from 90% ethanol and had a m.p. of 157–158°.[13] It had a radioactivity assay of 1.630 mc./mole.

1,2-Diphenyl-1-*o*-tolylethylene-1,2-C^{14} Glycol (*threo*-IIab).—Carbonyl-labeled benzil was obtained upon oxidation of the benzoin obtained from carbonyl-labeled benzaldehyde. Upon addition of *o*-tolyllithium (prepared from 0.50 mole of lithium wire and 0.20 mole of *o*-bromotoluene) to 0.20 mole of benzil-C^{14} there was produced in 75% yield an oil, b.p. 185–195° (0.5 mm.). After two crystallizations from toluene–hexane the ketol, m.p. 80–82°,[10b] was obtained. The ketol was treated with lithium aluminum hydride to yield the glycol (*threo*-IIab) which, after one crystallization from methanol–water and six crystallizations from hexane, had a m.p. of 144–145°[10b] and a radioactivity assay of 7.57 ± 0.03 mc./mole.

Diphenyl-*o*-tolylacetaldehyde-C^{14} (IIIab).—1,2-Diphenyl-1-*o*-tolylethylene-2-C^{14} glycol (IIa), 12 g., was added with vigorous stirring to 200 ml. of 98–100% formic acid; the mixture was stirred for 16 hours, then cooled, and the aldehyde which precipitated was collected on a filter. The precipitate was washed with cold 95% ethanol; the aldehyde, having a m.p. of 163–164°,[14] weighed 7.7 g. A slight yellow color was removed after this material had been crystallized from 95% ethanol.

Radiochemical Structure Determination of 1,2-Diphenyl-1-*o*-tolylethylene-2-C^{14} Glycol (*erythro*-IIa).—*erythro*-IIa (0.002 mole) which had a specific radioactivity of 2.163 mc./mole was dissolved in 20 ml. of glacial acetic acid and to it was added slowly, with stirring, a solution of 0.270 g. of CrO_3 in 2–3 ml. of water. After being stirred for 20 minutes, 0.2 ml. of 65% sulfuric acid was added to the mixture and it was heated on the steam-bath for an additional 20 min. The mixture was poured onto ice and extracted with chloroform. The neutral fraction containing 2-methylbenzophenone was treated with 2,4-dinitrophenylhydrazine reagent. After three crystallizations from tetrahydrofuran–ethanol the 2,4-dinitrophenylhydrazone had a sharp m.p. of 184° and a radioactivity assay of 0.307 ± 0.005 mc./mole. Thus the 2-position contained 85.8% of the total radioactivity. In two other preparations by the same method this distribution of radioactivity was the same within ±1%.

Ketones V and VI.—Benzhydryl *o*-tolyl ketone[10a] and *o*-tolyldesoxybenzoin[14] for use in yield determinations were prepared by the reaction of diphenylacetyl chloride with di-*o*-tolylcadmium and the reaction of 2-phenyl-2-*o*-tolylacetyl chloride with diphenylcadmium, respectively. Both ketones crystallized with difficulty from hexane, requiring three months in the refrigerator to produce the first crop of crystals. After six crystallizations from hexane the benzhydryl *o*-tolyl ketone had a m.p. of 45–46° and the *o*-tolyldesoxybenzoin a m.p. of 53–54.5°. A mixture of the two ketones exhibited m.p. in the range 30–35°.

Rearrangement of Compounds I, *erythro*-IIa, *threo*-IIab and IIIab with Concentrated Sulfuric Acid.—In a typical experiment 3.000 g. of glycol or aldehyde was added to concentrated sulfuric acid which had been cooled to 0°. The mixture was maintained at 0° and stirred by means of a magnetic stirrer until solution was complete. The amount of time required varied from 20 min. to two hours. The contents of the flask were then poured over 300 g. of chipped ice and extracted several times with 50-ml. portions of ether. The combined ether solutions were washed with sodium bicarbonate solution and evaporated to dryness. The residual, light-yellow oil was taken up in tetrahydrofuran and diluted to 250 ml. in a volumetric flask for use in determining yields of carbon-14 distribution.

Rearrangement of Glycols Ia and *erythro*-IIa in Formic Acid.—Glycols Ia and *erythro*-IIa (0.300 g.) were added separately with vigorous stirring to two 50.0-ml. portions of 98% formic acid, respectively; the mixtures were stirred for 24 hours at 27.6°. To each flask was added 0.300 mg. of dead diphenyl-*o*-tolylacetaldehyde and the resulting mixture was washed onto excess sodium carbonate and ice. The oily, yellow layer was extracted twice with ether. The ether layer was washed with water, the oily material remaining after evaporation of the ether was dissolved in hot 95% ethanol and cooled to cause crystallization. After two additional crystallizations from ethanol the two aldehyde fractions had a m.p. of 164–165°. Assay data and yields are summarized in Table III.

TABLE III

YIELDS OF III FROM REARRANGEMENT OF GLYCOLS Ia AND *erythro*-IIa IN FORMIC ACID AS DETERMINED BY THE ISOTOPIC DILUTION METHOD

Glycol	Ia	*erythro*-IIa
Weight of glycol, g.	0.3000	0.3000
Radioactivity of glycol, mc./mole	5.110 ± 0.017	2.163 ± 0.000
Experimental conditions	50.0 ml. HCOOH 24 hr. at 27.6°	50.0 ml. HCOOH 24 hr. at 27.6°
Wt. of dead III added, g.	0.3000	0.3000
Radioactivity of diluted III, mc./mole	0.710 ± 0.003	0.8082 ± 0.0019
Yields, % III	28.6	77.1

Yield Determinations. Ketones IV and V.—Aliquots of the tetrahydrofuran solutions of products from the various acid-catalyzed reactions were added to carefully weighed portions of the ketones. Since neither ketone could be crystallized in the presence of the other, no attempt was made to isolate the ketones in this series. To obviate this difficulty the ketone mixtures were treated with excess lithium aluminum hydride in ether solution. The resulting carbinols were converted to the acetates,[15] and crystallized six times from hexane. The yields were calculated from the assay data as described previously.[2a] The acetate derived from ketone IV had a m.p. of 116–117° and the acetate derived from ketone V had a m.p. of 133–134°. The experiments are summarized in Table IV.

Determination of Distribution of Carbon-14 in Ketones IV and V.—Solvent was evaporated from the aliquots of the products of various acid-catalyzed rearrangements. To each residue was added 75 ml. of 25% potassium hydroxide in methanol; ketone cleavage[16] was accomplished by heating at reflux temperature for 24 hours. The light-yellow solution was poured on ice and extracted 3 times with 50-ml. portions of ether. The alkaline residue was acidified and the precipitated acid fraction was crystallized three times from 20% methanol–water and sublimed at reduced pressure to yield pure *o*-toluic acid. A mixture of benzoic and toluic acids was recovered from the methanol–water mother liquor and sublimed twice at reduced pressure. Since pure

---

(10) (a) R. Roger and F. C. Harper, *Rec. trav. chim.*, **56**, 202 (1937); (b) J. F. Eastham, J. E. Huffaker, V. F. Raaen and C. J. Collins, THIS JOURNAL, **78**, 4327 (1956).

(11) W. Staedel and F. Kleinschmidt, *Ber.*, **13**, 837 (1880).

(12) A. M. Ward, *J. Chem. Soc.*, 1549 (1929).

(13) R. Roger and W. B. McKay, *ibid.*, 2234 (1931).

(14) R. Roger and W. B. McKay, *ibid.*, 335 (1933).

(15) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 212.

(16) P. J. Pollack and D. Y. Curtin, THIS JOURNAL, **72**, 964 (1950).

TABLE IV

SUMMARY OF DATA USED IN YIELD DETERMINATIONS OF IV AND V FROM REARRANGEMENT OF I, II AND III IN COLD, CONCENTRATED SULFURIC ACID

Starting compound[a]	Radioactivity, mc./mole	Weight, g.	Aliquot used to determine yield IV	Aliquot used to determine yield V	Weight of ketone added to aliquot, g. IV	Weight of ketone added to aliquot, g. V	Radioactivity of diluted ketone[b,c] IV	Radioactivity of diluted ketone[b,c] V
I	5.110 ± 0.017	2.000	2/5	2/5	2.000	2.000	1.012 ± 0.008	0.5049 ± 0.0021
erythro-IIa	2.163 ± .000	2.000	2/5	2/5	2.000	2.000	0.3385 ± .0005	0.3395 ± .0025
threo-IIab	7.565 ± .025	3.000	2/5	2/5	2.000	2.000	1.645 ± .005	1.701 ± .019
IIIab	5.272 ± .008	3.000	1/5	1/5	2.000	2.000	0.8490 ± .0045	0.5561 ± .0041

[a] All rearrangements were catalyzed by 96% sulfuric acid at 0°. [b] Radioactivities of diluted ketones were determined for the corresponding carbinol-acetates. [c] The combined yields of IV and V were in all cases essentially quantitative. For the yields of IV and V see Table I.

TABLE V

SUMMARY OF RADIOACTIVITY DISTRIBUTION DETERMINATIONS FOR REACTANTS AND PRODUCTS OF REACTIONS CATALYZED BY 96% H_2SO_4 AT 0°

Reactant	Radioactivity in mc./mole: Starting compound	Tertiary carbon position	Toluic acid fraction of products	Benzoic acid fraction of products	Benzophenone fraction of products
Ia	5.150 ± 0.022	0.000	5.206 ± 0.047	0.7465 ± 0.0025[a]	0.0190
erythro-IIa	2.163 ± .000	0.307	1.885 ± 0.003	....	0.307
threo-IIab	7.580 ± .060	3.790			

[a] Value obtained for diluted benzoic acid isolated after adding 0.400 g. of non-radioactive benzoic acid to a mixture of *o*-toluic and benzoic acids. The mixed acids had a specific activity of 0.04031 ± 0.00006 mc./g.

benzoic acid could not be isolated, the percentage of benzoic acid present was estimated indirectly by first determining the radioactivity of the mixture, diluting 0.1000 g. of the mixture with 0.4000 g. of pure, dead benzoic acid and then recrystallizing three times from water, subliming at reduced pressure and assaying the pure diluted benzoic acid for radioactivity. The neutral diarylmethane fraction was recovered as an oily residue by evaporation of the ether. The neutral fractions were oxidized with an equal weight of chromic acid in 30 ml. of glacial acetic acid and heating on the steam-bath for one hr. An insignificant amount of *o*-benzoylbenzoic acid, m.p. 91–93°, was isolated. The neutral ketone fraction was treated with excess 2,4-dinitrophenylhydrazine reagent and the 2,4-dinitrophenylhydrazones were crystallized from tetrahydrofuran–ethanol. Only the benzophenone derivative, m.p. 239–240°, was isolated and assayed for radioactivity. Using these data it can be demonstrated that secondary hydroxyl removal does not occur to a significant extent. The experiments are summarized in Table V.

2,2-Diphenyl-2-*o*-tolylacetonitrile-1-C^{14}.—*o*-Tolyl phenyl ketone was treated with phenylmagnesium bromide and heated under reflux in ether solution in an atmosphere of nitrogen for 18 hr. The product after hydrolysis was crystallized once from benzene–light petroleum ether to give a 40% yield of the carbinol which had a m.p. of 99–101°. The alternate preparation using benzophenone and *o*-tolylmagnesium bromide proved unsatisfactory. The carbinol (37 g., 0.135 mole) was converted to 30 g. of chloride (m.p. 133–136°) by the method of Bachmann.[17] The chloride was then placed in a round-bottom flask, heated to 140°, and treated with 13 g. of cuprous cyanide-C^{14}. The mixture was heated at 130–140° with occasional shaking for 30 min. and was then extracted with several small portions of toluene and distilled at reduced pressure. The resulting oil was triturated with 50 ml. of hexane to induce crystallization. The crude nitrile was purified by one crystallization from toluene–hexane and two recrystallizations from 95% ethanol to yield 15 g. of pure nitrile which had a m.p. of 110–111°. A second preparation yielded a product whose m.p. was 122–123°, and which, when added to the first product, gave no depression of the m.p. However, when maintained at 108° for a short time in the presence of the higher melting form the 110–111° form changed to the higher melting variety.

Anal. Calcd. for $C_{21}H_{17}N$: C, 89.02; H, 6.04. Found: C, 89.22, 89.30; H, 6.09, 6.20.

2,2-Diphenyl-2-*o*-tolylethylamine-1-C^{14} (VII).—2,2-Diphenyl-2-*o*-tolylacetonitrile-1-C^{14} (15 g., 0.053 mole), 17 g. of platinized[18] W-2 Raney nickel catalyst, and 400 ml. of ethanol were placed in a 500-ml. flask. The mixture was heated to 45° in the presence of hydrogen at 1 atmosphere and stirred vigorously with a magnetic stirrer for one week, after which the reaction mixture was filtered and evaporated to produce an oil. It was taken up in dry ether and treated with excess dry hydrogen chloride. The precipitated hydrochloride (12.2 g.) was filtered and crystallized from ether–tetrahydrofuran to yield about 10 g. of product having a m.p. of 150–152° dec. An attempt to reduce the nitrile to the amine with lithium aluminum hydride resulted in a nearly quantitative cleavage of the nitrile group leading to diphenyl-*o*-tolylmethane and hydrogen cyanide. Hellerman[19] has reported similar cleavage reactions involving other reducing agents with triarylnitriles. An alternate synthesis for the non-labeled amine involved the reduction of the aldehyde III oxime with excess sodium in alcohol.

Rearrangement of 2,2-Diphenyl-2-*o*-tolylethylamine (VI).—The amine (3.000 g., 0.0097 mole) was dissolved in 100 ml. of water and was heated to 80.0 ± 0.5°, at which time 100 ml. of a hot (80°) solution containing 3.00 g. of sodium nitrite was added with vigorous stirring. Stirring was continued for 1 hr., during which time temperature was maintained at 80.0 ± 0.5°. The mixture was cooled and extracted with four 50-ml. portions of ether. The ether layer was washed with water and evaporated to a viscous oil weighing 2.68 g. The oil was taken up in methanol and was diluted to 250 ml. in a volumetric flask. Aliquots were taken and added to carefully weighed portions of 1,2-diphenyl-1-*o*-tolylethylene and 1,1-diphenyl-2-*o*-tolylethylene. The solvents were evaporated and the residues were heated under reflux with 75 ml. of glacial acetic acid for 2 hours or longer. The acetic acid solutions were cooled and 2.80 g. of chromium trioxide was added. The mixtures were stirred with magnetic stirrers for 45 min. and then heated for 15 min. on the steam-bath before being poured on ice and extracted with chloroform. The acid fractions were extracted from the chloroform layer with 10% sodium hydroxide solution. Acids were purified by 3 crystallizations from water, each crystallization being followed by a sublimation. Ketone fractions were isolated by evaporating the neutral chloroform fractions followed by the addition of alcohol and 2,4-dinitrophenylhydrazine reagent. The 2,4-dinitrophenylhydrazones were crystallized from tetrahydrofuran–ethanol. They were found to be non-radioactive. The experiments are summarized in Table VI.

1,2-Diphenyl-1-*o*-tolylethylene.—Excess benzylmagnesium chloride in ether was added to an ether solution containing 80 g. of *o*-tolyl phenyl ketone and the reaction mix-

---

[17] E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 509.

[18] M. Delepine and A. Horeau, *Compt. rend.*, **201**, 1301 (1935).

[19] L. Hellerman, THIS JOURNAL, **49**, 1735 (1927).

TABLE VI

SUMMARY OF DATA USED IN DETERMINING PRODUCT YIELDS FROM THE DEAMINATION OF VI AS DETERMINED BY THE ISOTOPIC DILUTION METHOD[a]

Experiment	1	2
Wt. of hydrochloride of VI, g.	3.000	3.000
Radioactivity of VI, mc./mole	8.77 ± 0.04	8.77 ± 0.04
Experimental conditions	3.00 g. $NaNO_2$ 200 ml. H_2O 1 hr. at 80.0 ± 0.5°	3.00 g. $NaNO_2$ 200 ml. H_2O 1 hr. at 80.0 ± 0.5°
Aliq. used to determine yields, VII	2/5	2/5
Aliq. used to determine yields, VIII	2/5	2/5
Wt. of carbinol added to aliq. (g.), VIII	3.000	
Wt. of olefin added to aliq. (g.), VII	3.002	2.703
Wt. of olefin added to aliq. (g.), VIII		2.703
Radioact. of toluic acid derived from diluted carbinol, VII	0.4365 ± 0.0030	0.4516 ± 0.0008
Radioact. of benzoic acid derived from diluted carbinol, VIII	1.147 ± 0.004	1.114 ± 0.0015
Radioact. of 2,4-dinitrophenylhydrazones derived from VII and VIII	0.000	0.000

[a] For summary of actual yields see Table II.

ture was heated at reflux temperature for two hours. The resulting carbinol was isolated and added to 300 ml. of glacial acetic acid. The solution was heated at reflux temperature for 24 hours and was then distilled, 80 g. of viscous oil which distilled being collected in the range 145–150° (0.5 mm.). The 1,2-diphenyl-1-*o*-tolylethylene was taken up in hexane and crystallized. Two further crystallizations from tetrahydrofuran–ethanol gave a product which had m.p. 76–77°.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.40, 93.30; H, 6.71, 6.62.

1,1-Diphenyl-2-*o*-tolylethylene.—*o*-Tolylacetyl chloride (68 g., 0.40 mole) was heated under reflux for 1 hr. with a benzene solution of 0.35 mole of diphenylcadmium. The resulting ketone was isolated and distilled, the fraction boiling in the range 130–140° (0.5 mm.) being collected. Three crystallizations from light petroleum ether yielded 30 g. of pure *o*-methyldesoxybenzoin, m.p. 67–68°.[20] Addition of this compound to excess phenylmagnesium bromide presumably yielded the tertiary carbinol. However, all attempts to crystallize the product of this reaction resulted in dehydration. The oily product was therefore dehydrated without further purification by refluxing for 3 hr. in 150 ml. of glacial acetic acid. The mixture was then distilled through a 12-inch Vigreux column, and the fraction boiling from 140–142° (0.5 mm.) was collected. The oil formed seed crystals after standing for 1 month and three crystallizations from tetrahydrofuran–methanol yielded the pure 1,1-diphenyl-2-*o*-tolylethylene, m.p. 55–57°.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.21, 93.23; H, 6.63, 6.64.

Oxidation of the olefin with potassium permanganate in acetone containing a little acetic acid yielded nearly pure *o*-toluic acid, m.p. 102°, not depressed by the addition of pure *o*-toluic acid, m.p. 104°.

Calculations of Contributions in Mole Fractions of Each Path of Chart I and Chart II.—From Table I the ratio of ketones IV/V upon rearrangement of aldehyde III = r = 1.63.

For the rearrangement of glycol I

$$m_a + m_c = 0.693$$
$$m_b = 0.307$$
$$m_c = m_b r = 0.307 \times 1.63 = 0.500$$
$$m_a = 0.693 - 0.500 = 0.193$$

For the rearrangement of glycol II

$$m_d + m'_b = 0.500$$
$$m'_c = 0.500$$
$$m'_b = m'_c/r = 0.500/1.63 = 0.307$$
$$m_d = 0.500 - 0.307 = 0.193$$

Estimation of Probable Errors in the Determination of $2k_T/k_P$. (a) Calculation of Maximum Value for $2k_T/k_P$.—In making this calculation it has been assumed that all of the data of Table I are in error by 2 reaction per cent. in such a direction as to give a maximum value of $2k_T/k_P$ from equation 1; thus the ratio of ketones IV/V from aldehyde III = 0.640/0.360 = 1.78. For the rearrangement of glycol I we assume

$$m_a + m_c = 0.673$$
$$m_b = 0.327$$
$$\text{then } m_c = 0.327 \times 1.78 = 0.581$$
$$\text{and } m_a = 0.673 - 0.581 = 0.092$$

For the rearrangement of glycol II we assume

$$m_d + m'_b = 0.520$$
$$m'_c = 0.480$$
$$\text{then } m'_b = 0.480/1.78 = 0.270$$
$$\text{and } m_d = 0.520 - 0.270 = 0.250$$

from which

$$\frac{k_{\text{Tol}}}{k'_{\text{H}}} = \frac{m_b + m_c}{m_a} = 9.9 \text{ and } \frac{k_{\text{H}}}{k\phi} = \frac{m_d}{m'_b + m'_c} = 0.333$$

Thus, from equation 1, $2k_T/k_P$ = 9.7.

(b) Calculation of Minimum Value for $2k_T/k_P$.—In this calculation it has been assumed that all of the data of Table I are in error by 2 reaction per cent. in such a direction as to give a minimum value of $2k_T/k_P$ from equation 1; thus the ratio of ketones IV/V from aldehyde III = 0.600/0.400 = 1.50. For the rearrangement of glycol I we assume

$$m_a + m_c = 0.713$$
$$m_b = 0.287$$
$$\text{then } m_c = m_b \cdot r = 0.287 \times 1.5 = 0.415$$
$$m_a = 0.713 - 0.415 = 0.298$$

For the rearrangement of glycol II we assume

$$m_d + m'_b = 0.480$$
$$m'_c = 0.520$$
$$\text{then } m'_b = 0.520/1.5 = 0.347$$
$$\text{and } m_d = 0.480 - 0.347 = 0.133$$

from which

$$\frac{k_{\text{Tol}}}{k'_H} = \frac{m_b + m_c}{m_a} = 2.4 \text{ and } \frac{k_{\text{H}}}{k\phi} = \frac{m_d}{m'_b + m'_c} = 0.154$$

Thus, from equation 1, $2k_T/k_P$ = 1.4.

Analytical Determinations.—The carbon and hydrogen analyses were performed by the Huffman Microanalytical Laboratories, Wheatridge, Colo.

OAK RIDGE, TENNESSEE

---

(20) M. S. Newman and R. Gaertner, THIS JOURNAL, **72**, 264–273 (1950).