Thermal Decomposition of Ethyl N-Nitro-N-isobutyl-carbamate.—A solution of ethyl N-(isobutyl)-N-nitrocarbamate (0.95 g., 5 mmole) in dodecane (20 ml.) was kept at 140° for 89 hr. in a flask fitted with a reflux condenser which was connected to the absorption train used for the rearrangement of ethyl N-nitro-N-(t-butyl)-carbamate. For the last fifteen minutes of the reaction, nitrogen was swept through the reaction mixture. The liquid in the dry ice trap was titrated with a carbon tetrachloride solution of bromine (0.35 M); 2.2 ml. were required equivalent to 16% isobutylene (0.8 mmole). Nitrous oxide was found in the liquid nitrogen trap. It was identified by its infrared spectrum in chloroform. The Ascarite tube increased in weight by 0.060 g. corresponding to 1.4 mmole (28%) of carbon dioxide. The dodecane solution was distilled at 70° (10 mm.) in a short path distillation apparatus to yield isobutyl ethyl carbonate (0.323 g., 2.2 mmole, 44%) identified by means of its infrared spectrum.

The Copper Salt of N-(Isobutyl)-N-nitrosohydroxyl-amine.[29]—Isobutyl magnesium bromide in 150 ml. of ether was prepared under nitrogen from isobutyl bromide (54.8 g., 0.4 mole) in a three-necked flask fitted with stirring motor, condenser and pressure-equalized addition funnel. The condenser was attached to a glass tube the end of which was immersed in a few cm. of mercury. The solution was cooled to −10° and nitric oxide, which had been passed through conc. sulfuric acid and then drierite, was introduced at such a rate that a slight positive pressure was maintained. The temperature rose suddenly to 35°, then fell slowly to 0°. The nitric oxide atmosphere was maintained over the stirred mixture at this temperature for 3 hr. The ether solution was decanted from a gummy residue. The residue was triturated with water (750 ml.) and the triturate was filtered. To the clear aqueous filtrate (slightly basic) was added a saturated copper sulfate solution until the solution reached a pH of 5. The aqueous phase was extracted with carbon tetrachloride until the extracts were no longer colored blue. The organic layers were combined, dried, filtered and the solution evaporated *in vacuo* at room temperature. The deep blue solid which remained weighed 32.6 g. (0.11 mole, 55%). The solid was dissolved in warm ether, n-pentane was added and the solution cooled to yield blue crystals, m.p. 80–82.5°.

Anal. Calcd. for $C_8H_{18}N_4O_4Cu$: C, 32.26; H, 6.09; N, 18.82; mol. wt., 298. Found: C, 32.50; H, 6.22; N, 18.63; mol. wt., 272.[24]

(29) The preparation is a modification of that of J. Sand and F. Singer, *Ann.*, **329**, 190 (1903). See also E. Muller and H. Metzger, *Ber.*, **89**, 396 (1956).

The Sodium Salt of N-(Isobutyl)-N-nitrosohydroxyl-amine.—A 0.1 N sodium hydroxide solution (330 ml., 33 mmole) was added to a solution of the copper salt of N-(isobutyl)-N-nitrosohydroxylamine (4.94 g., 17 mmole) in 95% ethanol (200 ml.) and the mixture was allowed to stand for one half hour at room temperature. A light blue precipitate formed leaving a light blue, alkaline solution. The solid was filtered and the filtrate neutralized with 6 N hydrochloric acid; approximately 3 ml. (18 m-mole) was required. The resulting solution was evaporated at room temperature *in vacuo* to yield a light blue solid. The solid was triturated with ether (60 ml.), the blue color entering the ether phase. The white crystalline solid obtained weighed 3.02 g., and it consisted of sodium chloride and the sodium salt of N-(isobutyl)-N-nitrosohydroxyl-amine (68%) as determined from the band at 245 mμ in the ultraviolet spectrum, (lit. λ_{max} 249 mμ, ϵ 8730[18c]; λ_{max} 243 mμ, ϵ 8300).[30]

The Reaction of the Sodium Salt of N-(Isobutyl)-N-nitrosohydroxylamine with 3,5-Dinitrobenzoyl Chloride.—A mixture of potassium carbonate (4.14 g., 30 mmole), the sodium salt of N-isobutyl-N-nitrosohydroxylamine (2.90 g., 14 mmole) (corrected for NaCl content) and 3,5-dinitrobenzoyl chloride (2.90 g., 13 mmole) was suspended in carbon tetrachloride (25 ml.). The mixture was stirred with a magnetic stirrer in a flask protected by a drying tube. The temperature of the mixture was lowered to 0° while stirring. After forty-five minutes of stirring, the solids were filtered and washed with ether (30 ml.). The ether wash was combined with the filtrate and the solvents were removed *in vacuo* at room temperature to yield a white solid (1.59 g.) which was essentially isobutyl 3,5-dinitrobenzoate. The solid was chromatographed on a silica-gel column (Davison-mesh 28–200) and the esters were quantitatively eluted with 3% ether–97% pentane for a yield of 0.49 g., 1.8 mmoles, 14%. The esters contained 10 ± 2% *sec*-butyl 3,5-dinitro-benzoate as shown by the infrared spectrum. Elution of the column with ether yielded a yellow oil which was probably crude N-(isobutyl)-N-nitroso-O-3,5-dinitrobenzoylhydroxyl-amine. The oil gave a positive Lieberman's nitroso test and the infrared spectrum contained bands at 5.69, 6.45 and 6.67μ.

(30) G. Kortüm and B. Finckh, *Z. physik. Chem.*, **48B**, 32 (1940).

Carbanion Rearrangements. II[2]

BY HOWARD E. ZIMMERMAN[1] AND ARNOLD ZWEIG

2,2-Diphenylpropyllithium has been found to rearrange with phenyl migration to yield 1,2-diphenyl-1-methylethyllithium. The analogous magnesium and mercury compounds have been prepared. Unlike the lithium derivative, the Grignard reagent does not rearrange. Preparation of the organopotassium derivative leads directly to the rearranged carbanion. 2-Phenyl-2-(p-tolyl)-propyllithium has been found to rearrange with preferential phenyl migration. This and other results are interpreted as support for a carbanion rather than a free radical rearrangement mechanism. A molecular orbital treatment of the chemistry of 1,2-shifts is presented.

In our previous publication[2c] dealing with carbanion rearrangements, we noted that while 1,2-

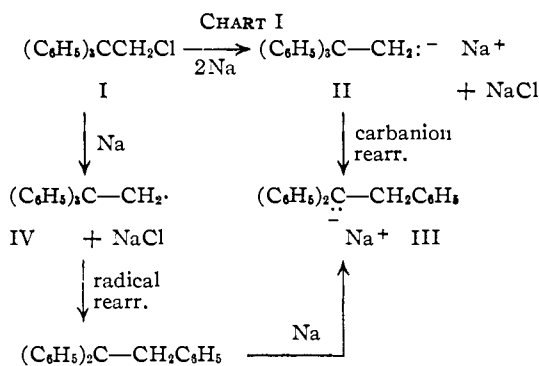(1) Department of Chemistry, University of Wisconsin, Madison, Wis.

(2) (a) Taken largely from the Ph.D. thesis of Arnold Zweig, Northwestern University. A portion of the calculations were completed at the University of Wisconsin. (b) The material described in the present publication was presented in part, April, 1960, at the Cleveland, Ohio, A.C.S. Meeting, Abstracts p. 170. (c) Paper I, H. E. Zimmerman and F. J. Smentowski, *J. Am. Chem. Soc.*, **79**, 5455 (1957).

carbon to carbon rearrangements of carbonium ions, in which a group migrates from one carbon atom to an adjacent and positively charged carbon atom, have been known for a very long time, and while the analogous 1,2-shifts of free radicals are known and have received considerable study, there has been little evidence for the reality of a parallel 1,2-carbon to carbon shift of carbanions.

In this previous publication the rearrangement of 1,1,1-triphenyl-2-chloroethane (I), on treatment

with a sodium dispersion, to afford 1,1,2-triphenyl-ethylsodium (III) was reported.[3]

One of the several reasonable mechanisms possible for this rearrangement involved the formation of 2,2,2-triphenylethylsodium (II) and sodium chloride in a two-electron transfer process followed by a carbanion rearrangement to form the observed product III. A less interesting but equally plausible mechanism pictured the 2,2,2-triphenylethyl free radical IV, formed with sodium chloride by a one-electron transfer process, as rearranging prior to introduction of the second electron. The two[4] mechanistic possibilities (cf. Chart I) thus differ in whether the rearrangement follows or precedes introduction of the second electron and in whether the rearranging species is a carbanion (i.e., II) or instead a free radical (i.e., IV).

CHART I

$$(C_6H_5)_3CCH_2Cl \xrightarrow[2Na]{} (C_6H_5)_3C\!-\!CH_2:^- \quad Na^+$$

I   II   + NaCl

| Na | carbanion rearr.

$(C_6H_5)_3C\!-\!CH_2\cdot$ $(C_6H_5)_2C\!-\!CH_2C_6H_5$

IV   + NaCl   Na⁺   III

| radical rearr.

$(C_6H_5)_2C\!-\!CH_2C_6H_5$ ← Na

In this study[2] all attempts to demonstrate the intermediacy of 2,2,2-triphenylethylsodium (II), thus providing evidence for the carbanion mechanism, were fruitless.

The present investigation began with the objective of preparing an organometallic compound structurally similar to II but rearranging sufficiently less readily to allow its capture and study. Chosen for this purpose was 2,2-diphenylpropyl-lithium (V).

The preparation of V required a synthesis of 1-chloro-2,2-diphenylpropane (VI). This was prepared in two ways (Chart II) to unambiguously establish its structure. In one route 1,1-diphenyl-ethyl methyl ether was converted with potassium metal to 1,1-diphenylethylpotassium as described by Ziegler,[5] and this organopotassium compound was then alkylated with excess methylene chloride.

A more convenient synthesis was found in the free radical chlorination of the known[6] 2,2-di-phenylpropane; this, too, is depicted in Chart II.
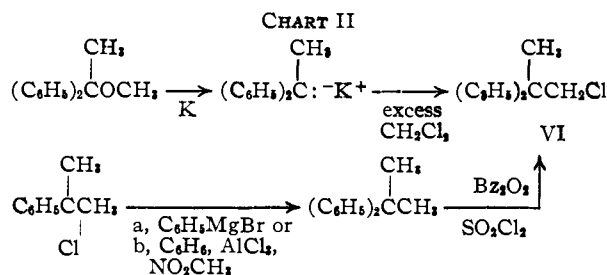
1-Chloro-2,2-diphenylpropane was converted to the corresponding Grignard reagent by reaction with magnesium in tetrahydrofuran. The Grignard reagent on hydrolysis with aqueous ammonium chloride afforded 2,2-diphenylpropane and on

(3) In an independent study, Professor E. Grovenstein, J. Am. Chem. Soc., 79, 4985 (1957), observed the same rearrangement to occur in refluxing dioxane.
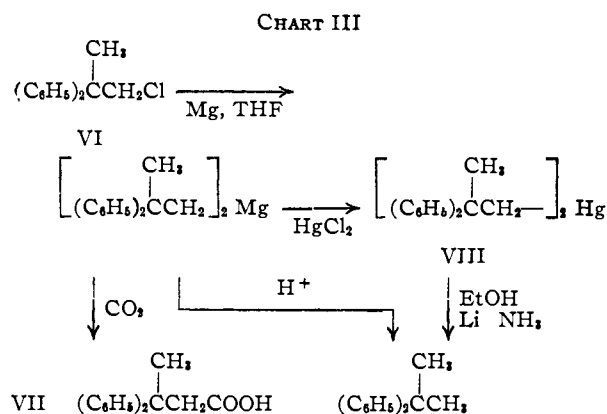
(4) A third reaction mechanism was considered as a possibility in our earlier publication (ref. 2). However, subsequent unpublished results of H. R. Z. with F. Smentowski as well as the presently reported findings fail to support this mechanism, and for brevity it will not be considered further.

(5) K. Ziegler and B. Schnell, Ann., 437, 227 (1924).

(6) (a) P. Sabatier and M. Murat, Compt. rend., 155, 388 (1912). (b) K. T. Serijian and P. H. Wise. J. Am. Chem. Soc., 73, 4768 (1951).

CHART II

$$(C_6H_5)_2COCH_3 \xrightarrow{K} (C_6H_5)_2C:^-K^+ \xrightarrow[\substack{excess \\ CH_2Cl_2}]{} (C_6H_5)_2CCH_2Cl$$
                                                                    VI

$$C_6H_5CCH_3 \xrightarrow[\substack{a, C_6H_5MgBr \text{ or} \\ b, C_6H_6, AlCl_3, \\ NO_2CH_3}]{} (C_6H_5)_2CCH_3 \xrightarrow[SO_2Cl_2]{Bz_2O_2}$$
   |
   Cl

carbonation yielded the known[7] 3,3-diphenyl-butyric acid (VII), m.p. 99°. These experiments showed the Grignard reagent to be unrearranged and confirmed the absence of skeletal rearrangements in the preparation of 1-chloro-2,2-diphenyl-propane itself. Attempts to effect a carbanionic rearrangement of the Grignard reagent by refluxing in dioxane, in pyridine or in pyridine containing anhydrous trisodium phosphate, were fruitless; in each case only unrearranged products were isolated.

CHART III

$$(C_6H_5)_2CCH_2Cl \xrightarrow{Mg, THF}$$
VI

$$\left[(C_6H_5)_2CCH_2\right]_2 Mg \xrightarrow{HgCl_2} \left[(C_6H_5)_2CCH_2\!-\right]_2 Hg$$
                                                            VIII

| CO₂   H⁺ | EtOH / Li NH₃

VII $(C_6H_5)_2CCH_2COOH$ $(C_6H_5)_2CCH_3$

The Grignard reagent was further characterized by conversion to bis-(2,2-diphenylpropyl)-mercury (VIII) with mercuric chloride. The unrearranged structure assigned to VIII was confirmed by the reduction of this compound with lithium and ethanol in liquid ammonia to afford 2,2-diphenyl-propane. A summary of these reactions may be found in Chart III.

The desired 2,2-diphenylpropyllithium (V) was obtained in two ways—from the reaction of lithium with 1-chloro-2,2-diphenylpropane (VI) in ether at 0° and from the similar reaction of lithium with bis-(2,2-diphenylpropyl)-mercury (VIII). Difficulties were encountered because of the requirement for a low reaction temperature (vida infra) coupled with poor reactivity at low temperatures. However, the conversion of 1-chloro-2,2-diphenyl-propane (VI) to 2,2-diphenylpropyllithium (V) proceeded smoothly at 0° in ether when a high speed stirrer was used in conjunction with lithium pieces, as a device for continually exposing fresh surface. Additionally, 2,2-diphenylpropyllithium was obtained by treating bis-(2,2-diphenylpropyl)-mercury (VIII) with lithium metal under similar conditions.

Carbonation of the 2,2-diphenylpropyllithium thus formed afforded 3,3-diphenylbutyric acid

(7) E. Bergmann, H. Taubadel and H. Weiss, Ber., 64, 1500 (1931).

(VII), the same product as obtained from the Grignard reagent (*vide supra*). Non-acidic by-product was found by quantitative infrared analysis to consist almost completely of 2,2-diphenylpropane, the product arising from β-proton abstraction and elimination of the ether solvent by the strong base 2,2-diphenylpropyllithium (V).[8]

Most exciting was the observation that the reaction mixture obtained by first preparing 2,2-diphenylpropyllithium at 0° in the usual way, either from 1-chloro-2,2-diphenylpropane or from bis-(2,2-diphenylpropyl)]mercury, and then refluxing for 3 hours afforded no 3,3-diphenylbutyric acid (VII); instead there was isolated 2-methyl-2,3-diphenylpropionic acid (IX),[9] m.p. 126°. Clearly, this product arose from a 1,2-phenyl rearrangement reaction of 2,2-diphenylpropyllithium (V) and carbonation of the resulting 1-methyl-1,2-diphenylethyllithium (X). These reactions of 2,2-diphenylpropyllithium are presented in Chart IV.

CHART IV
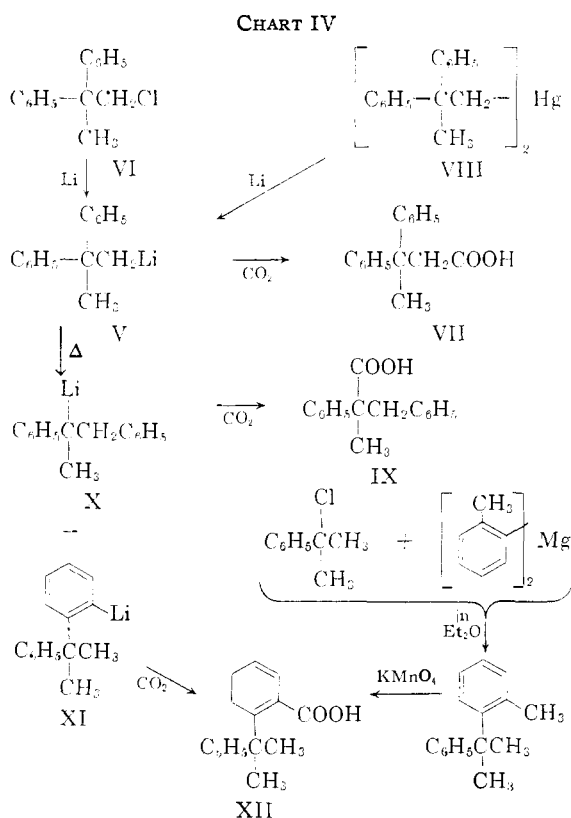
In addition to the major acidic product IX there was isolated an isomeric monocarboxylic acid XII, m.p. 185°. Mixed melting point and infrared comparison demonstrated that this acid was not the known 186° *erythro*-2,3-diphenylbutyric acid.[10] The n.m.r. spectrum (*cf.* Table I), which exhibited only a single, unsplit band in the saturated C–H region, suggested the presence of a *gem*-dimethyl group while the ultraviolet spectrum in the 270 mμ region was too intense to derive from non-

(8) A certain amount of neutral product could arise from incomplete exclusion of moisture in the carbonation process.

(9) V. Meyer and H. Janssen, *Ann.*, **250**, 137 (1889).

(10) (a) A. A. Plentl and M. T. Bogert, *J. Am. Chem. Soc.*, **63**, 991 (1941); (b) W. R. Brasen and C. R. Hauser, *ibid.*, **79**, 395 (1957).

conjugated phenyl and carboxyl groups. The 185° acid was finally established as *o*-(α,α-dimethylbenzyl)-benzoic acid (XII) by independent synthesis of this compound as indicated in Chart IV.

This by-product XII most likely results from an intramolecular rearrangement of 2,2-diphenylpropyllithium (V) in which the strongly basic carbanionic methylene group abstracts a proton from the *o*-position of one of the adjacent phenyl groups.
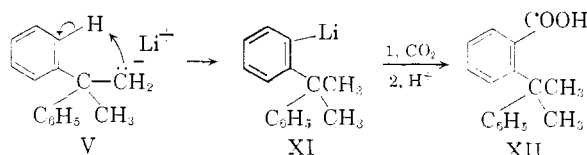
One important point required scrutiny. The best yield of 3,3-diphenylbutyric acid (VII) obtained from carbonation of unrearranged organolithium compound V was 59% while the yield of 2-methyl-2,3-diphenylpropionic acid (IX) obtained from the rearrangement was only 25%. There was no doubt that prior to refluxing there was present at least 59% of unrearranged organolithium compound, 2,2-diphenylpropyllithium (V), while following refluxing there was at least 25% of rearranged organolithium compound, 1-methyl-1,2-diphenylethyllithium (X). However, it was conceivable that X was not formed from V but rather from some unidentified species present to the extent of possibly 41% prior to refluxing. Thus it was the non-acidic material accompanying the 3,3-diphenylbutyric acid (VII) obtained by carbonation prior to refluxing as well as the non-acidic product obtained along with the 2-methyl-2,3-diphenylpropionic acid (IX) by carbonation subsequent to refluxing which had to be characterized.

The neutral material accompanying the carboxylic acids was found to be mainly 2,2-diphenylpropane containing small quantities of 1,2-diphenylpropane. Quantitative infrared analysis showed that the neutral material accompanying the 3,3-diphenylbutyric acid obtained prior to refluxing was 97% 2,2-diphenylpropane while the neutral fraction obtained subsequent to refluxing consisted of 81% 2,2-diphenylpropane and 19% 1,2-diphenylpropane. The 2,2-diphenylpropane was not unexpected, since organolithium compounds were known[11] to effect a slow β-elimination of diethyl ether with β-proton abstraction. The 1,2-diphenylpropane could have arisen in the same fashion by proton abstraction by the less basic 1-methyl-1,2-diphenylethyllithium (X) but more likely resulted from incomplete exclusion of moisture in carbonation. Since the major component of the neutral fraction, 2,2-diphenylpropane, resulted from a side reaction of 2,2-diphenylpropyllithium, and since thus the evidence is against the presence of any other precursor of the rearranged organollithium compound X, the conclusion that X resulted from a rearrangement of 2,2-diphenylpropyllithium (V) was inescapable.

In contrast to the successful preparation of 2,2-diphenylpropylmetal derivatives where the metal was magnesium, mercury or lithium, was the situa-

(11) "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. VIII, 1954, p. 286.

tion where the metal was potassium. The reaction of bis-(2,2-diphenylpropyl)-mercury (VIII) with potassium was found to proceed smoothly but slowly in tetrahydrofuran at room temperature. Carbonation of the resulting red reaction mixture afforded only 2-methyl-2,3-diphenylpropionic acid (IX) while protonation gave 1,2-diphenylpropane. Thus there was no evidence for 2,2-diphenylpropyl-potassium as a stable intermediate in the rearrangement. The simplest interpretation was that 2,2-diphenylpropylpotassium was indeed formed but rapidly rearranged to the red 1-methyl-1,2-diphenylethylpotassium which was then carbonated or protonated.

The failure of the magnesium derivative to rearrange even under drastic conditions, the stability of the lithium reagent at low temperature and rearrangement on heating, and the very facile rearrangement of the potassium derivative correlates with the probable increasing ionic character of the carbon to metal bond in the sequence magnesium, lithium, potassium and provides additional support for a carbanionic rearrangement mechanism.

Nevertheless, there still remained some doubt. While the research described above was predicated on the assumption that identification of the rearrangement precursor as an organometallic species (e.g., V) would provide strong evidence for the carbanionic nature of the rearrangement, such evidence was not iron-clad.[12] For example, in the organolithium rearrangement either one might envision an ionization of the essentially covalent carbon–lithium bond to afford an ion pair intermediate which then would rearrange by a carbanion path (route A) or instead one could picture homolytic dissociation of the carbon–lithium bond to afford the 2,2-diphenylpropyl free radical which might rearrange and recombine with a lithium atom (route B).

CHART V

$$\begin{array}{c} CH_3 \\ | \\ (C_6H_5)_2CCH_2Li \end{array}$$

path A   path B

$$\begin{array}{c} CH_3 \\ | \\ (C_6H_5)_2C{-}CH_2{:}^{-}\ Li^{+} \end{array}$$ $$\begin{array}{c} CH_3 \\ | \\ (C_6H_5)_2C{-}CH_2\cdot\ +\ Li\cdot \end{array}$$

carbanion rearrangement   free radical rearrangement

$$\begin{array}{c} CH_3 \\ | \\ C_6H_5{-}C{-}CH_2C_6H_5 \\ \underline{\ \ } \\ Li^{+} \end{array}$$ ⟵ Li· $$\begin{array}{c} CH_3 \\ | \\ C_6H_5{-}C{-}CH_2C_6H_5 \\ \cdot \end{array}$$
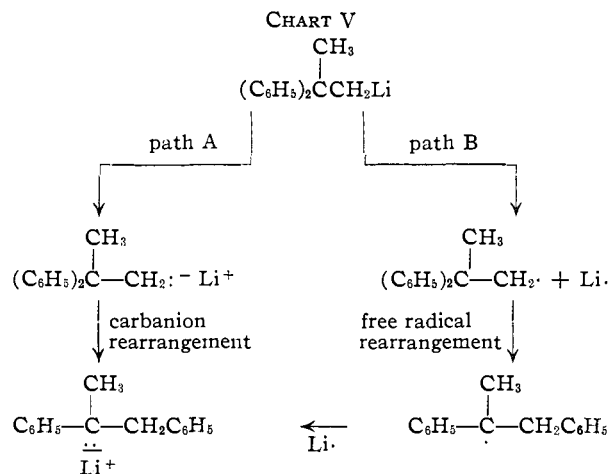
It seemed that investigation of the rearrangement of 2-phenyl-2-p-tolylpropyllithium (XIII) would allow unambiguous characterization of the migration process, for the relative amounts of phenyl and p-tolyl migration in rearrangements de-

(12) A. A. Morton and E. J. Lanpher, J. Org. Chem., 21, 93 (1956), have pointed out very clearly that the circumstance that a reaction begins and ends with ionic species does not necessitate the conclusion that the mechanism is ionic.

pend on and are characteristic of the nature of the rearranging species. Accordingly, 1-chloro-2-phenyl-2-p-tolylpropane (XIV) was prepared; the synthesis utilized the alkylation of 1-phenyl-1-p-tolylethylpotassium with methylene chloride (note Chart VI). Conversion of XIV to the Grignard reagent and carbonation afforded 3-phenyl-3-p-tolylbutyric acid (XV), m.p. 80°. The structure of this previously unknown acid was confirmed by its n.m.r. spectrum (note Table I) as well as by independent synthesis (cf. Chart VI and the Experimental section).

TABLE I

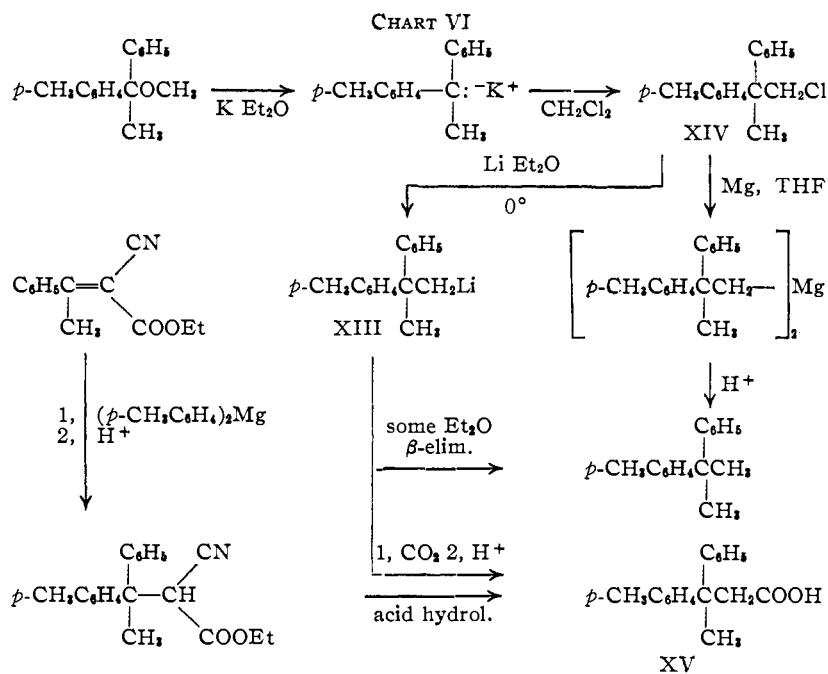NUCLEAR MAGNETIC RESONANCE DATA (τ-VALUES)[a]

Compound, acid	Aliph. methyl	Arom. methyl	Methylene
3,3-Diphenylbutyric (VII)	8.29	..	7.07
3-Phenyl-3-p-tolylbutyric (XV)	8.27	7.78	7.08
2-Methyl-2,3-diphenylpropionic (IX)	8.60	..	6.42, 6.52
2-Methyl-2-phenyl-3-p-tolyl-propionic (XVI)	8.65	7.84	6.88, 7.00
2-Methyl-2-p-tolyl-3-phenyl-propionic (XVII)	8.65	7.75	6.74, 6.85
o-(α,α-Dimethylbenzyl)-benzoic (XII)	8.22	..	....
p-(α,α-Dimethylbenzyl)-benzoic (XIX)	8.33	..	....
p-(α,α-Dimethylbenzyl)-phenylacetic (XVIII)	8.42	..	6.75

[a] Run at 40 mc.

Similarly, both 2-methyl-2-phenyl-3-p-tolylpropionic acid (XVI) and 2-methyl-2-p-tolyl-3-phenyl-propionic acid (XVII), the two possible acidic products of carbonation of rearranged organolithium compounds, were synthesized (cf. Chart VII and the Experimental section).

The preparation of the required reference acids, XV, XVI and XVII—one of unrearranged and two of rearranged skeleton—having been completed, the reaction of 1-chloro-2-phenyl-2-p-tolylpropane (XIV) with lithium was next to receive attention. This compound (XIV) reacted smoothly with lithium metal in ether at 0° under conditions used for the unsubstituted analog. The major products obtained from carbonation of the organolithium compound thus prepared were 3-phenyl-3-p-tolyl-butyric acid (XV) and 2-phenyl-2-p-tolylpropane. The latter was identical with material obtained by protonation of the Grignard reagent as well as by the independent synthesis described in the Experimental section.

Refluxing of the ether solution of 2-phenyl-2-p-tolylpropyllithium (XIII) followed by carbonation afforded, in addition to some 2-phenyl-2-p-tolylpropane, a mixture of carboxylic acids. Chromatography of this mixture led to isolation of three acids. One was 3-phenyl-3-p-tolylbutyric acid (XV), indicating that rearrangement was incomplete. The second was an acid (XVIII), m.p. 74°, which did not correspond to any of the expected rearrangement products. The third acid isolated was identical with 2-methyl-2-p-tolyl-3-phenylpropionic acid (XVII), m.p. 128°, synthesized by an unambiguous route (cf. Chart VII),

Chart VI

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{COCH}_3 \xrightarrow[\text{K Et}_2\text{O}]{} p\text{-CH}_3\text{C}_6\text{H}_4\text{—}\overset{\text{C}_6\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}\text{:}^-\text{K}^+ \xrightarrow[\text{CH}_2\text{Cl}_2]{} p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\text{XIV CH}_3}{\text{C}}}\text{CH}_2\text{Cl}$$

Li Et₂O   0°

Mg, THF

$$\text{C}_6\text{H}_5\text{C}\overset{\text{CN}}{=}\text{C}\underset{\overset{|}{\text{CH}_3}}{\overset{\text{COOEt}}{}}$$

$$p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\text{XIII CH}_3}{\text{C}}}\text{CH}_2\text{Li}$$

$$\left[p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_2\text{—} \right]_2 \text{Mg}$$

1, $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Mg}$
2, H⁺

some Et₂O
β-elim.

H⁺

$$p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_3$$

$$p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\overset{|}{\text{CH}_3}}{\text{C}}}\text{—}\overset{\text{CN}}{\underset{\text{COOEt}}{\text{CH}}}$$

1, CO₂ 2, H⁺
acid hydrol.

$$p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\underset{\text{XV}}{\text{CH}_3}}{\text{C}}}\text{CH}_2\text{COOH}$$

this being the product derived from phenyl rather than p-tolyl migration.

Table II
Product Distribution Determined by Isotope Dilution Technique

Acid	Occurrence in acidic fraction, %
3-Phenyl-3-p-tolylbutyric (XV)	12
2-Methyl-2-phenyl-3-p-tolylpropionic (XVI)	4
2-Methyl-2-p-tolyl-3-phenylpropionic (XVII)	45
p-(α,α-Dimethylbenzyl)-phenylacetic (XVIII)	21

It was clearly necessary to establish the structure of the 74° acid XVIII, since unless it were known not to arise from further reaction of the p-tolyl migration product, a conclusion of lack of p-tolyl migration would be unwarranted. The infrared and n.m.r. spectra indicated the presence of a gem-dimethyl group as well as a methylene group with no adjacent hydrogen atoms (note Table I for n.m.r. data). The ultraviolet spectrum possessed only absorption characteristic of non-conjugated aromatic rings and showed the carboxyl and phenyl groups to be unconjugated. This information together with mechanistic reasoning suggested that XVIII was p-(α,α-dimethylbenzyl)-phenylacetic acid, and this was confirmed by an independent synthesis of the compound as shown in Chart VII. The formation of this product seemed certainly to result from proton abstraction from the tolyl methyl group of 2-phenyl-2-p-tolylpropane by-product by one of the strong bases present. This suggested an experiment in which butyllithium was allowed to react with 2-phenyl-2-p-tolylpropane; there was obtained on carbonation a 6% yield of p-(α,α-dimethylbenzyl)-phenylacetic acid (XVIII).

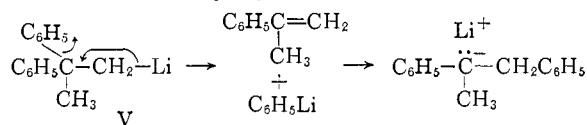Although the only aryl migration product found in the chromatographic separation was 2-methyl-2-p-tolyl-3-phenylpropionic acid (XVII) and it

seemed certain that phenyl migration did predominate, nevertheless, it appeared worthwhile to determine whether small quantities of the product of p-tolyl migration were formed. Accordingly, the rearrangement of 2-phenyl-2-p-tolylpropyllithium (XIII) was repeated and the organometallic product carbonated with radioactive carbon dioxide. Each of four aliquots of the acidic fraction was combined with an authentic sample of one of 3-phenyl-3-p-tolylbutyric acid (XV), 2-methyl-2-p-tolyl-3-phenylpropionic acid (XVII), 2-methyl-2-phenyl-3-p-tolylpropionic acid (XVI), p-(α,α-dimethylbenzyl)-phenylacetic acid (XVIII). Each sample was crystallized until its C^{14} content remained constant (note Table IV in Experimental section); the percentage of these products thus found are recorded in Table II.

Chart VII

Et₂O
reflux

$$p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\underset{\text{XIII}}{\text{CH}_3}}{\text{C}}}\text{CH}_2\text{Li}$$

$$p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{COOH}}{\underset{\text{CH}_3}{\text{CH}}}$$

1, NaNH₂ (2 M)
2, C₆H₅CH₂Br
3, H⁺

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{—}\overset{\text{C}_6\text{H}_5}{\underset{\overset{|}{\text{CH}_3}}{\text{C}}}\text{—CH}_3$$

+

Li⁺

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{—}\overset{}{\underset{\overset{|}{\text{CH}_3}}{\text{C}}}\text{—CH}_2\text{C}_6\text{H}_5 \xrightarrow[\text{2, H}^+]{\text{1, CO}_2} p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{COOH}}{\underset{\underset{\text{XVII}}{\text{CH}_3}}{\text{C}}}\text{CH}_2\text{C}_6\text{H}_5$$

+

$$\text{LiCH}_2\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_3 \xrightarrow[\text{2, H}^+]{\text{1, CO}_2} p\text{-HOOCCH}_2\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\underset{\text{XVIII}}{\text{CH}_3}}{\text{C}}}\text{CH}_3$$

1, Mg Et₂O
2, CO₂
3, H⁺

$$p\text{-CH}_3\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_3 \xrightarrow[\text{Bz}_2\text{O}_2]{\text{SO}_2\text{Cl}_2} p\text{-ClCH}_2\text{C}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_3$$

$$\text{C}_6\text{H}_5\overset{\text{COOH}}{\underset{\text{CH}_3}{\text{CH}}} \xrightarrow[\text{2, }p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br}]{\text{1, NaNH}_2 \text{ (2 }M\text{)}} \text{C}_6\text{H}_5\overset{\text{COOH}}{\underset{\underset{\text{XVI}}{\text{CH}_3}}{\text{C}}}\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$$
3, H⁺

Thus it is quite clear that the phenyl migration product XVII predominated over the p-tolyl

migration product XVI about eleven-fold.[13] This is a result which is clearly not in accord with a free radical rearrangement mechanism. It has been found by University of Chicago research groups that phenyl and p-tolyl groups do not appreciably differ in free radical migratory aptitudes.[14] Furthermore, to the extent that any selectivity were shown in a free radical rearrangement, one would predict p-tolyl to be preferred over phenyl migration (*vide infra*). On the other hand, the observed relative tendency of phenyl *versus* p-tolyl to migrate was in accord with a carbanion rearrangement mechanism (*cf.* discussion to follow).

There still remained a question whether the rearrangement was intramolecular or intermolecular. Thus conceivably the rearrangement of V could have proceeded internally by a carbanion counterpart of a phenonium ion, a phenanion (*e.g.*, XX) or it could have occurred by β-elimination of phenyllithium with subsequent readdition of phenyllithium to α-methylstyrene

$$C_6H_5\overset{\cdot}{\underset{\underset{\text{V}}{CH_3}}{\overset{|}{C}}}\!\!\!-\!\!\overbrace{CH_2}-Li \;\longrightarrow\; \begin{array}{c} C_6H_5C\!\!=\!\!CH_2 \\ CH_3 \\ + \\ C_6H_5Li \end{array} \;\longrightarrow\; C_6H_5\!-\!\underset{\underset{CH_3}{|}}{\overset{\cdot\cdot}{C}}\!\!-\!\!CH_2C_6H_5 \qquad Li^+$$

This latter possibility was, however, excluded by the finding that p-tolyllithium did not add to α-methylstyrene under reaction conditions.[15]

An intramolecular, carbanion rearrangement mechanism having been established, one notes that this picture properly rationalizes the observed preference for phenyl migration. Thus the phenyl rearrangement intermediate XX should be of lower energy than the p-tolyl migration intermediate XXI, since in the latter electron delocalization toward the p-position of the migrating ring is inhibited by the presence of the methyl group[16]; and a similar statement is true of the migration transition states preceding[17] these intermediates.

(13) Since only 82% of the radioactivity was found due to the four acidic products XV, XVI, XVII and XVIII, the possibility remains that an acid deriving from p-tolyl migration was present. Mechanistically, selective destruction of the p-tolyl migration product seems unlikely, and in any event insufficient unidentified acidic product remains to change the conclusion of predominant phenyl migration.

(14) M. S. Kharasch, A. C. Poshkus, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 1458 (1951); W. H. Urry and N. Nicolaides, *J. Am. Chem. Soc.*, **74**, 5163 (1952). The intermediates described were quite reactive and thus small selectivity would be expected even where differences in stabilization might result; if the energy barrier for rearrangement is small for the least likely group to migrate, then the free energy difference, controlling selectivity, must be even smaller.

(15) Arguing against an elimination–readdition mechanism is the fact that if readdition of phenyllithium to α-methylstyrene were possible, then addition of the more basic 2,2-diphenylpropyllithium (V), present in high concentration, should complete successfully in addition. No products expected on this basis were obtained.

(16) A large increase in basicity and nucleophilicity and corresponding decrease in stability is observed in simple alkyllithium reagents and other organometallics as each extra alkyl group is introduced on the metal bearing carbon. Thus, for example, P. D. Bartlett, S. Friedman and M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953), have shown that t-butyllithium and isopropyllithium will add to ethylene whereas primary alkyllithium reagents will not; similarly, isopropyllithium will β-eliminate ethyl ether to ethylene at room temperature in an exothermic reaction while butyllithium does so only slowly. The effect of a methyl group in phenanion intermediates as XX and XXI should be less marked since the negative charge is not localized on the methyl bearing carbon atom.

(17) Of the two free energy barriers, one preceding the phenanion intermediate and one following it, the first should be higher and correspond to the reaction transition state. Proceeding forward and

XX   XXI
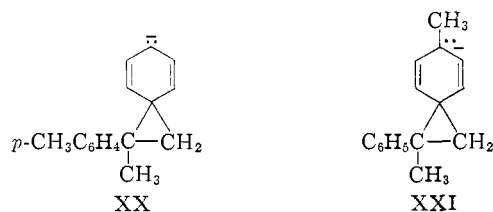
The reality of 1,2-carbanion rearrangements having been demonstrated, a very fundamental and intriguing question remains. This concerns whether the fact that these carbanion rearrangements have so long eluded observation, in striking contrast to the plentiful literature of carbonium ion and free radical 1,2-shifts, derives from an intrinsic difference in ease in migration compared to their carbonium ion and free radical counterparts.

In answering this question it is helpful to consider the energetics of five rearrangement situations: A, alkyl migration between adjacent, non-phenyl-bearing carbon atoms; B, phenyl migration between adjacent, non-phenyl-bearing carbon atoms; C, alkyl migration from a phenyl-bearing carbon atom to an adjacent non-phenyl-bearing carbon atom; D, phenyl migration from a phenyl-bearing carbon atom to a non-phenyl-bearing carbon atom; and lastly, E, phenyl migration from a carbon atom bearing two phenyl groups to a non-phenyl-bearing carbon atom. In each case the simple LCAO molecular orbital theory was applied to the half-migrated species whose energy was then compared with that of the non-bridged ion or radical from which the half-migrated species might, at least in principle, have originated.[18]

The molecular geometry and the orbitals, whose linear combination was used in the calculation, are depicted below for each of the first four half-migrated species—XXIIIa, XXIIIb, XXIIIc and XXIIId—as well as for the parent non-bridged species XXIIa, XXIIb, XXIIc and XXIId. Species XXIIe and XXIIIe differ from XXIId and XXIIId, respectively, only in having an additional phenyl group at carbon one. In each case, A through E, the migration is from carbon atom 1 to carbon atom 2, and the atom actually bonded to atoms 1 and 2 in the bridged species is designated a. In the cases of alkyl migration (A and C) the hybridization at atom a is taken as sp^3 while in the cases of phenyl migration (B, D and E) the hybridization is taken as sp^2. Accordingly, for XXIIIA and XXIIIC ϕ_3 is an sp^3-orbital while for XXIIIB, XXIIID and XXIIIE it is an sp^2 hybrid; all others—χ_1, χ_2, etc.—are taken as atomic 2p-orbitals.[19]

backward from the intermediate, one observes that in the forward direction toward product the negative charge is spread onto a benzylic position with consequent energy lowering, while in the reverse direction, returning to reactant, the charge becomes localized on the single methylenic carbon atom.

(18) The calculation ignored whether the half-migrated species is a transition state or instead an intermediate, the justification being that in either event the half-migrated species will at least approximate the transition state in geometry and parallel it in energy.

(19) Throughout these calculations a number of assumptions and approximations, some drastic, are made. In fact, the one-electron LCAO MO method itself is only an approximation. However, since only differences in behavior are sought and the same approximations are made throughout, it seems quite certain that predictions will be in the proper direction.

CASE A:

XXII A   XXIII A

CASE B:

XXII B   XXIII B

CASE C:

XXII C   XXIII C

CASE D:

XXII D   XXIII D
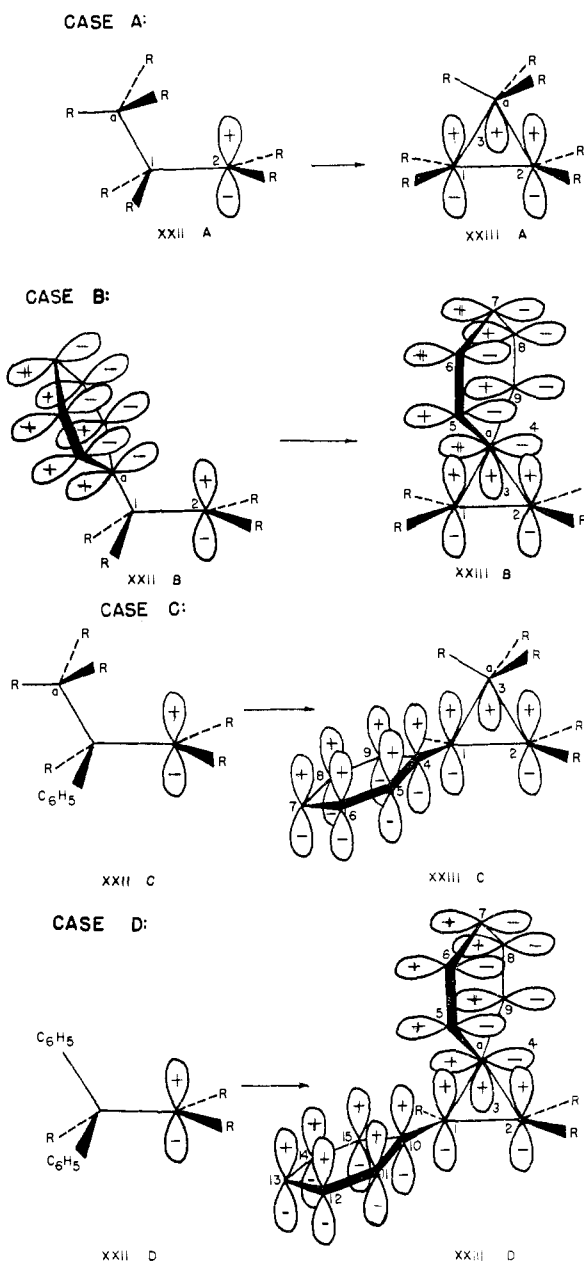
For each bridged species, XXIIIA through XXIIIE, the corresponding secular determinant may be written by inspection and set equal to zero.[20]

$$
\begin{array}{c|ccc}
 & \chi_1 & \chi_2 & \phi_3 \\
\hline
\chi_1 & X & \zeta & \epsilon \\
\chi_2 & \zeta & X & \epsilon \\
\phi_3 & \epsilon & \epsilon & X
\end{array} = 0 \text{ for XXIIIA}
$$

$$
\begin{array}{c|ccccccccc}
 & \chi_1 & \chi_2 & \phi_3 & \chi_4 & \chi_5 & \chi_6 & \chi_7 & \chi_8 & \chi_9 \\
\hline
\chi_1 & X & \zeta & \epsilon & \delta & 0 & 0 & 0 & 0 & 0 \\
\chi_2 & \zeta & X & \epsilon & -\delta & 0 & 0 & 0 & 0 & 0 \\
\phi_3 & \epsilon & \epsilon & X & 0 & 0 & 0 & 0 & 0 & 0 \\
\chi_4 & \delta & -\delta & 0 & X & 1 & 0 & 0 & 0 & 1 \\
\chi_5 & 0 & 0 & 0 & 1 & X & 1 & 0 & 0 & 0 \\
\chi_6 & 0 & 0 & 0 & 0 & 1 & X & 1 & 0 & 0 \\
\chi_7 & 0 & 0 & 0 & 0 & 0 & 1 & X & 1 & 0 \\
\chi_8 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & X & 1 \\
\chi_2 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & X
\end{array} = 0 \text{ for XXIIIB}
$$

(20) E.g., "Les Theories Electriques de la Chimie Organique," by B. Pullman and A. Pullman, Masson and Co., 1952.

and similarly for XXIIIC, XXIIID and XXIIIE. Here X is the energy of a molecular orbital in units of absolute value of β, $|\beta|$, referred to the energy of an isolated p-orbital as the zero, and the non-diagonal elements are the exchange integrals in units of β.[21] The evaluation of the exchange and overlap integrals as well as the values obtained are detailed in the section on Calculations. However, for qualitative purposes one may picture the magnitude of any non-diagonal element A_{ij} as determined by the overlap between orbitals i and j.

Each determinant is of order equal to the number of localized orbitals utilized. Hence, in each case solution of the determinantal equation will afford as many values of X as localized orbitals were fed into the calculation, and these values of X are the energies of the molecular orbitals of the species.

The secular determinants may be broken up into products of smaller determinants, or alternatively these smaller determinants may be set up directly, by use of group theoretical procedures.[22] Details are given in the section on Calculations. The molecular orbital energies obtained[23] for cases A through D are indicated in Chart VIII together with the molecular orbital energies of the non-bridged parent species. The energies for species E are given in the section on Calculations.
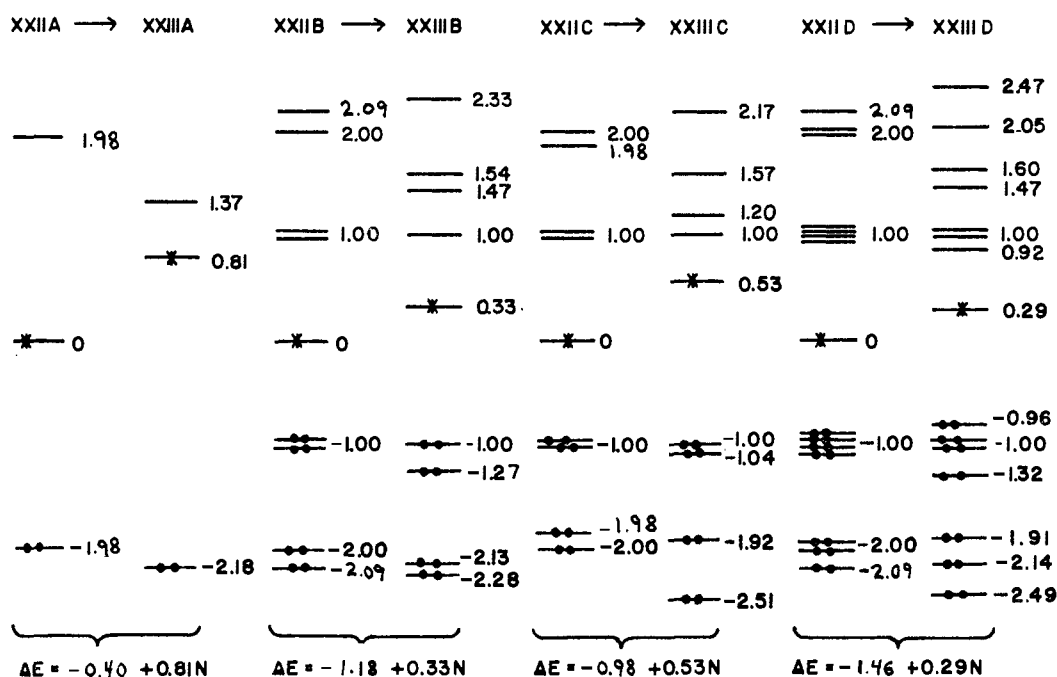
Into the lowest energy molecular orbitals of each species are placed all the electrons available for delocalization, each molecular orbital accommodating at most two electrons. Also included are the two σ-electrons of the C_1-C_a bond of each parent species, since these become available for delocalization in the bridging process; in the parent species these electrons are placed in a localized low energy sigma bonding orbital found to be at -1.98 in XXIIA and XXIIC and at -2.09 in XXIIB, XXIID and XXIIE. Additionally available are any (numbering N) electrons—none, one or two—originally in the carbon-2 p-orbital of the parent species. If the number is none, the parent species is a carbonium ion. If the number is one, the species is a free radical; while, if the number is two, we are dealing with a carbanion. In Chart VIII and in the equations below these N electrons are represented by an asterisk.

For each type system, A through E, an energy of bridging may be calculated. It is of interest to consider the dependence of the bridging energy on the type of system—A, B, C, D, E—as well as on the type of species involved—carbonium ion ($N = 0$), free radical ($N = 1$) or carbanion ($N = 2$). A reasonable assumption is that the bridging energy will be inversely related to the ease of migration.[25] For carbonium ions ($N = 0$) migration

(21) Overlap integrals between adjacent as well as non-adjacent orbitals are taken as zero in this approximation in setting up the determinant. For purposes of evaluating the related exchange integrals they are not taken as zero.

(22) Cf. "Quantum Chemistry" by H. Eyring, J. Walter and G. Kimball, John Wiley and Sons, Inc., New York, N. Y., 1944.

(23) The solution of the larger secular determinants, remaining after maximum simplification by group theory, was effected by use of the facilities of the Northwestern University Computing Center and the University of Wisconsin Numerical Analysis Laboratory; in each an IBM 650 computer was used. We express our appreciation to Mr. Reid Kellogg for the original program and to Mr. Vernon Sande for a modification of this program.

CHART VIII
MOLECULAR ORBITAL REACTION DIAGRAM[A]

XXIIA ⟶ XXIIIA   XXIIB ⟶ XXIIIB   XXIIC ⟶ XXIIIC   XXIID ⟶ XXIIID

$\Delta E = -0.40 +0.81N$ $\Delta E = -1.18 +0.33N$ $\Delta E = -0.98 +0.53N$ $\Delta E = -1.46 +0.29N$

A) EACH DOT REPRESENTS ONE ELECTRON, EACH ASTERISK REPRESENTS N ELECTRONS (ZERO, ONE OR TWO). THE MOLECULAR ORBITAL ENERGIES (X'S) ARE IN UNITS OF |BETA|.

the theory predicts that migration will increase in facility in the sequence: A, alkyl migration from unactivated to unactivated carbon < C, alkyl migration from phenyl substituted to unactivated carbon < B, phenyl migration from unactivated to unactivated carbon < D, phenyl migration from phenyl-bearing to unactivated carbon < E, phenyl migration from doubly phenyl-substituted carbon to unactivated carbon; this sequence accords with observed reactivity sequences[26] in solvolytic and rearrangement reactions.

(24) The value of β is left unassigned since there is no general agreement on its magnitude. Values from −16.5 kcal./mole to close to −50 kcal./mole have been suggested; see A. Streitweiser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959), for a recent discussion.

(25) This will be true even where some precursor leads directly to the bridged species without intermediate formation of the non-bridged "parent." In such an event, in the molecular orbital reaction diagram of Chart VIII we would replace the molecular orbitals of the non-bridged species by the molecular orbitals of whatever precursor engendered the bridged species. In practice this requires only the replacement of the asterisk at zero by two electrons in a σ-orbital whose energy would be insensitive to the type system (A, B, C, D or E) involved; this bonding σ-orbital would be that linking carbon 2 to whatever functional group was present in the precursor and was lost in the formation of the bridged species. Thus, for a given reaction type and given original functional group the ΔE of formation of the bridged species would differ by a constant amount from the ΔE of bridging as given in Chart VIII.
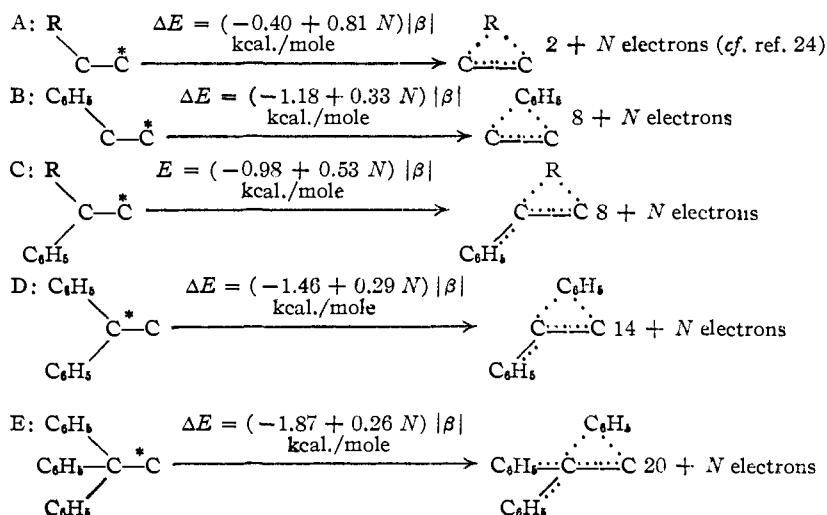
(26) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952), and S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952). M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954), have carried out an interesting calculation in which the energetic importance of phenyl participation with a cationic center is assessed as *ca.* 4.7 kcal./mole without involvement of the σ-bond bearing the phenyl group; here β was taken as −20 kcal./mole.

For each extra electron added to systems A through E it is clear that the bridging process becomes less advantageous.[27] In the case of free radical rearrangements, where $N = 1$, alkyl migration between unactivated carbon atoms is especially unfavorable (ΔE for case A $= +0.41 |\beta|$; 6 to 20 kcal./mole endothermic depending on the value of β assumed). In the remaining cases migration may be predicted to occur with increasing ease in the order C < B < D < E. These predictions are consonant with the observed reluctance of alkyl groups and the known ability of phenyl groups to migrate in free radical arrangements.[28]

Having found the molecular orbital calculations to be reliable in the instances of carbonium ion and free radical rearrangements, it remains to apply these calculations to the problem at hand, namely carbanion rearrangements. One finds that in case A, that of alkyl migration between unactivated carbon atoms, 1.22 $|\beta|$ is required to effect bridging;

(27) On the basis of a simpler model for phenyl migration, one in which the three-membered ring electrons of the bridged species are assumed to be localized, one finds the half-migrated species to have molecular orbitals at 0, ±1, ±1.73 as well as any deriving from additional, but then insulated, phenyl groups. Here the non-bonding MO at zero replaces a slightly anti-bonding one in the more complex model. With this simpler model one would predict no difference in energy between the carbonium ion, carbanion and free radical, since the asterisk would be at zero.

(28) F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **76**, 2732 (1954); for further references and discussion *cf.* J. Hine, "Physical-organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956. p. 446.

A: $\text{R} \diagdown \underset{*}{\text{C}} - \text{C}$ $\Delta E = (-0.40 + 0.81\ N)|\beta|$ kcal./mole $\longrightarrow$ $\text{R} \diagdown \text{C} \cdots \text{C}$ $2 + N$ electrons (cf. ref. 24)

B: $\text{C}_6\text{H}_5 \diagdown \underset{*}{\text{C}} - \text{C}$ $\Delta E = (-1.18 + 0.33\ N)|\beta|$ kcal./mole $\longrightarrow$ $\text{C}_6\text{H}_5 \diagdown \text{C} \cdots \text{C}$ $8 + N$ electrons

C: $\text{R} \diagdown \underset{*}{\text{C}} - \text{C} \diagup \text{C}_6\text{H}_5$ $E = (-0.98 + 0.53\ N)|\beta|$ kcal./mole $\longrightarrow$ $\text{R} \diagdown \text{C} \cdots \text{C} \diagup \text{C}_6\text{H}_5$ $8 + N$ electrons

D: $\text{C}_6\text{H}_5 \diagdown \underset{*}{\text{C}} - \text{C} \diagup \text{C}_6\text{H}_5$ $\Delta E = (-1.46 + 0.29\ N)|\beta|$ kcal./mole $\longrightarrow$ $\text{C}_6\text{H}_5 \diagdown \text{C} \cdots \text{C} \diagup \text{C}_6\text{H}_5$ $14 + N$ electrons

E: $\text{C}_6\text{H}_5 \diagdown \text{C}_6\text{H}_5 - \underset{*}{\text{C}} - \text{C} \diagup \text{C}_6\text{H}_5$ $\Delta E = (-1.87 + 0.26\ N)|\beta|$ kcal./mole $\longrightarrow$ $\text{C}_6\text{H}_5 \cdots \text{C} \cdots \text{C} \diagup \text{C}_6\text{H}_5$ $20 + N$ electrons

thus simple alkyl migration of carbanions is the most energetically unfavorable of cases and may never be observed except under extreme conditions. Even in case C, where the alkyl group migrates from a phenyl-bearing carbon atom, the bridging energy is unfavorable by 0.08 $|\beta|$.

Contrariwise, for phenyl migration (cases B, D and E) the half-migrated species is of lower energy than the free unbridged carbanion. For migration between non-activated carbon atoms 0.52 $|\beta|$ is gained in the bridging process while for migration from a phenyl bearing to a non-phenyl bearing carbon atom, the bridging process is favored by 0.88 $|\beta|$. The latter situation corresponds[29] to the rearrangement of 2,2-diphenylpropyllithium described in the present study and suggests that once a relatively free carbanion results by ion-pair formation from the covalent carbon–lithium bond, bridging is facile. In the case of the 2,2,2-triphenylethyl carbanion system studied earlier,[2a,3] where the phenyl group migrates from a carbon atom bearing two phenyl groups, an even more favorable bridging energy of 1.35 $|\beta|$ is encountered. The conclusion may therefore be drawn, from the theoretical as well as from the experimental results of the present investigation, that 1,2-aryl migrations of carbanions can and do occur.[29]

Experimental[30]

2,2-Diphenylpropane.—To 625 g. (5.3 moles) of α-methylstyrene anhydrous hydrogen chloride was added with cooling below 30° until no more was taken up. The reaction mixture was then placed under vacuum at room temperature to remove unreacted hydrogen chloride. The remaining α-chlorocumene[31] was a viscous liquid weighing 825 g. (theory: 833 g.); this was used without further purification.

A solution of phenylmagnesium bromide, prepared from 4.8 g. (0.20 g. atom) of magnesium and 30 g. (0.19 mole) of bromobenzene and 147 ml. of ether, was cooled in an ice-bath. To this with stirring and continued cooling was

(29) In comparison of the relative ease of carbonium ion, free radical and carbanion rearrangements the present discussion has considered only the energetics of bridging of the free unbridged species once formed. The ease of engendering the three-type species to begin with is another factor which must be reckoned with.

(30) All melting points were taken on apparatus checked with known compounds.

(31) The preparation of α-chlorocumene is patterned after the procedure of H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 20 (1953).

added 23.2 g. (0.15 mole) of α-chlorocumene over a 1-hr. period. When the addition was about three-fourths complete, the reaction mixture thickened with precipitated salt. The reaction mixture was then refluxed for 30 min. and poured into a mixture of 200 g. of ice and 50 ml. of concd. hydrochloric acid. The mixture was ether extracted and the extracts were dried over potassium hydroxide pellets, filtered and concentrated *in vacuo*. The residue was distilled at 3.0 mm. using a modified Claisen apparatus giving the following fractions: (1) 13.51 g. of forerun boiling near room temperature, (2) 5.49 g., b.p. 102-128°; most of fraction 2 appeared to distil at 102-105°. This fraction was subjected to fractionation on a Piros–Glover spinning band column at 6 mm. giving: cut 1, b.p. 80-137°, $n^{25}\text{D}$ 1.5692; cut 2, b.p. 137°, $n^{25}\text{D}$ 1.5706; cut 3, b.p. 137°, $n^{25}\text{D}$ 1.5692; cut 4, b.p. 137°, $n^{25}\text{D} = 1.5682$; pot residue *ca.* 1.5 g. The infrared spectra of cuts 2, 3 and 4 were essentially the same; wt. combined = 3.8 g.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}$: C, 91.78; H, 8.22. Found (cut 2): C, 91.58; H, 7.98. Found (cut 4): C, 91.48; H, 8.22.

Friedel–Crafts Synthesis of 2,2-Diphenylpropane.—To a 3-l. flask fitted with thermometer, stirrer and condenser with drying tube was added 2.2 kg. (28.3 moles) of thiophene-free benzene and 350 g. (2.26 moles) of α-chlorocumene. The mixture was cooled to 10° and a solution of 34 g. (0.255 mole) of aluminum chloride in 68 g. of anhydrous nitromethane was added with stirring. The temperature rose to 15° and a reaction seemed to take place. The temperature was kept at 10° for 1 hr. and then allowed to rise to 20° for a second hr. The reaction mixture was then poured into a mixture of 1000 g. of ice and 200 ml. of concd. hydrochloric acid. The organic layer was separated after thorough shaking and was washed with 500 ml. of 6 N hydrochloric acid, followed by washing with water. The benzene was removed by distillation under reduced pressure and the residual oil was distilled at 5 mm. using a modified Claisen apparatus; a forerun of 5.83 g., b.p. 95-133°, was followed by 179.7 g. (0.917 mole, 40.5%) of pure 2,2-diphenylpropane, b.p. 133-135°. Following this was a fraction boiling at 150-155° and consisting of α-methylstyrene dimer. A pot residue remained and weighed 93.2 g.

In a second run, 936 g. of benzene, 154 g. of α-chlorocumene and 25 g. of aluminum chloride in 50 g. of nitromethane afforded 70.6 g. (36%) of 2,2-diphenylpropane, $n^{25}\text{D}$ 1.5688, was obtained.

In two further runs, each employing 308 g. of α-chlorocumene, 1872 g. of thiophene-free benzene and 25 g. of aluminum chloride in 150 g. of nitromethane, the combined yield was 240 g. (30.3%) of 2,2-diphenylpropane, b.p. 85-87° at 0.5 mm.

Preparation of 1-Chloro-2,2-diphenylpropane from Methylene Chloride and 1,1-Diphenylethyl Methyl Ether.—To a 200-ml. Morton flask fitted with a high speed stirrer, nitrogen inlet, condenser with drying tube and dropping funnel was added 3.128 g. (0.080 mole) of freshly cut potassium together with 30 ml. of redistilled 2,2,4-trimethylpentane and 0.01 g. of Alconox detergent. The mixture was heated to reflux and stirred at 12,000 r.p.m. for 30 min. under oxygen-free (Fieser soln. followed by CaCl$_2$) nitrogen. The stirring was stopped and the flask was cooled with ice. Stirring was then resumed at room temperature.

Fifty ml. of sodium-dried ether was added to the stirred mixture followed by a solution of 8.48 g. (0.04 mole) of 1,1-diphenylethyl methyl ether[5] in 25 ml. of sodium-dried ether. After a 20-min. induction period, the mixture warmed slightly and the color changed from gray to bright red. Stirring was then continued for 2 hr. at room temperature.

Then the mixture was cooled to −65° by means of a Dry Ice–pentane bath, and 10.0 ml. (13.36 g., 0.157 mole) of redistilled methylene chloride was added as rapidly as possible. The bath temperature was then raised to *ca.* −30° when the mixture decolorized leaving a gray suspen-

sion. Stirring was continued for 30 min. The mixture was poured onto 100 ml. of ice and 10 ml. of concd. hydrochloric acid and the product ether extracted.[32] The extracts were washed with water and dried over sodium sulfate. Concentration *in vacuo* left 6.96 g. of yellow oil. The infrared spectrum showed this to be essentially pure 1-chloro-2,2-diphenylpropane.

A 0.50-g. portion of the product was heated in a test-tube over a flame sufficiently to evolve copious quantities of hydrogen chloride gas. The heating was continued for 5 min. when the evolution ceased. On cooling, the reaction mixture crystallized. One crystallization from methanol afforded white crystalline flakes, m.p. 77-78°, not depressing the m.p. of authentic α-methylstilbene. The infrared spectrum of the crude as well as the crystallized pyrolysis product was identical to that of authentic α-methylstilbene.

Synthesis of 1-Chloro-2,2-diphenylpropane by Free Radical Chlorination.—To a 100-ml. flask fitted with reflux condenser topped with a Dry Ice condenser and protecting calcium chloride tube was added 50.0 g. (0.255 mole) of 2,2-diphenylpropane together with 20.2 g. (0.15 mole) of sulfuryl chloride and 1.81 g. (0.0075 mole) of benzoyl peroxide. The mixture was slowly brought to reflux. At the end of 1.5 hr. of refluxing, the reaction mixture was cooled and chromatographed directly on a 60 × 3.5 cm. silica gel column (Davidson 60-200 mesh) slurry packed with 5% benzene in hexane. After elution with 400 ml. of the same solvent, the eluent began to contain unreacted 2,2-diphenylpropane; this fraction consisted of 800 ml. The following 400 ml. contained mainly 1-chloro-2,2-diphenylpropane mixed with some 2,2-diphenylpropane, as indicated by the infrared spectrum. The succeeding liter of eluent consisted of essentially pure 1-chloro-2,2-diphenylpropane, since the infrared spectra of successive portions of the eluent did not vary. In particular, the ratio of intensities of the 7.3 and 12.1 mμ bands remained invariant.

The contents of the last 1400 ml. of eluent weighed 11.05 g. This material was rechromatographed under the same conditions as before. Following elution of some 2,2-diphenylpropane in the first liter of eluent, there was obtained 7.95 g. of oil in 1400 ml. of eluent. The material in the last 100 ml. of this fraction had the same infrared spectrum as that in the first. This product, 1-chloro-2,2-diphenylpropane, had the same spectrum as the compound prepared by reaction of 1,1-diphenylethylpotassium with methylene chloride.

In another run 240 g. (1.212 mole) of 2,2-diphenylpropane was treated similarly with 108 g. (0.8 mole) of sulfuryl chloride and 0.20 g. of benzoyl peroxide. The product in this experiment was purified by distillation. The following fractions were collected at 0.5 mm.: 1, 120.0 g. of 2,2-diphenylpropane, b.p. 83-85° (50% recovery); 2, 118.0 g. of 1-chloro-2,2-diphenylpropane, b.p. 110-112° (63% based on sulfuryl chloride); 3, 36.9 g. of by-products boiling in the range 113-124°; a pot residue of *ca.* 25 g.

Employing the above procedure two further preparations were run, using in the first of these 98 g. of 2,2-diphenylpropane and 47.2 g. of sulfuryl chloride together with 3.0 g. of benzoyl peroxide. The yield of 1-chloro-2,2-diphenylpropane was 32.9 g. (41% based on sulfuryl chloride), distilling at 120-126° at 0.5 mm. In the second of these runs there was obtained from 138 g. (0.7 mole) of 2,2-diphenylpropane, 54 g. (0.4 mole) of sulfuryl chloride and 3.0 g. of benzoyl peroxide, 58.4 g. (63%) of 1-chloro-2,2-diphenylpropane, b.p. 129-130° at 0.5 mm.

Anal. Calcd. for $C_{15}H_{15}Cl$: C, 78.08; H, 6.55. Found: C, 78.49; H, 6.39.

A 1.0-g. sample of the above product was heated in a test-tube with a thermometer. At 180-190° hydrogen chloride gas began to be liberated. This became rapid at 240-250°. The liquid began to reflux, still giving off hydrogen chloride at 280-290°. The test-tube was cooled to room temperature and the liquid solidified. The tan product melted at 74-77°. Its infrared spectrum was that of essentially pure α-methylstilbene.

A small sample of 1-chloro-2,2-diphenylpropane gave an almost immediate precipitate with alcoholic silver nitrate solution. At the end of 30 min. the precipitate was heavy.

(32) Danger of fire was present if small particles of unreacted potassium metal remained when the mixture was poured onto ice. In later runs this difficulty was obviated by addition of *ca.* 5 ml. of abs. ethanol to the reaction mixture prior to pouring onto ice.

Preparation of 2,2-Diphenylpropylmagnesium Chloride in Tetrahydrofuran Followed by Protonation with Aqueous Ammonium Chloride.—A 10θ-ml. flask was fitted with a nitrogen inlet, a reflux condenser and drying tube, and a dropping funnel. The flask was dried by heating and passing dry nitrogen. To the cooled flask was then added 30 ml. of dry tetrahydrofuran and 0.486 g. (0.020 g. atom) of magnesium turnings. A solution of 4.60 g. (0.920 mole) of 1-chloro-2,2-diphenylpropane in 25 ml. of tetrahydrofuran was added in portions. The addition of 0.10 ml. of methyl iodide was required to initiate the reaction. The reaction mixture was stirred for 10 hr. at room temperature and then was poured onto ice and aqueous saturated ammonium chloride. The ether extracts were dried over sodium sulfate and concentrated *in vacuo*. The residue, on distillation with a semi-micro modified Claisen apparatus, afforded 3.62 g. of oil boiling at 80-90° at 0.5 mm. The infrared spectrum of this material showed it to be 2,2-diphenylpropane.

In a second run, magnesium powder rather than turnings was used. The 3.86 g. of oil obtained as before was this time found to be a mixture of 2,2-diphenylpropane and 1-chloro-2,2-diphenylpropane.

Preparation of 2,2-Diphenylpropylmagnesium Chloride Followed by Carbonation.—The Grignard reagent was prepared from 4.6 g. (0.020 mole) of 2-chloro-2,2-diphenylpropane, 0.535 g. (0.022 g. atom) of magnesium powder and a total of 55 ml. of tetrahydrofuran distilled from $LiAlH_4$. Methyl iodide (0.05 ml.) was used to initiate the reaction. The flask became only slightly warm, and the reaction was carried out with an initial 1 hr. of reflux followed by stirring for 20 hr. at room temperature. The reaction mixture was then poured onto powdered Dry Ice. After evaporation of the Dry Ice, the remaining tetrahydrofuran was removed by distillation *in vacuo* and the residue was treated with 5% potassium hydroxide solution and ether extracted. The ether extracts were washed and dried over sodium sulfate. Concentration under vacuum afforded 1.86 g. of neutral oil whose infrared spectrum showed it to be essentially pure 2,2-diphenylpropane. The aqueous potassium hydroxide extract was acidified to a congo red end-point and ether extracted. Drying over sodium sulfate and concentration *in vacuo* gave 2.31 g. (48%) of a waxy solid. Crystallization from methanol-water brought the m.p. to 96-98°. This represented essentially pure 3,3-diphenylbutyric acid.[7]

Reaction of 2,2-Diphenylpropylmagnesium Chloride with Mercuric Chloride to Give Bis-(2,2-diphenylpropyl)-mercury.—A tetrahydrofuran solution of 2,2-diphenylpropylmagnesium chloride was prepared, in the same manner as above, from 13.80 g. (0.060 mole) of 1-chloro-2,2-diphenylpropane, 1.60 g. (0.066 g. atom) of magnesium powder and 100 ml. of tetrahydrofuran freshly distilled from lithium aluminum hydride. An initial 1 hr. of refluxing followed by 16 hr. stirring at room temperature was employed.

To the Grignard reagent was added a solution of 6.80 g. (0.025 mole) of reagent mercuric chloride (stored in a desiccator over P_2O_5) in 25 ml. of dry tetrahydrofuran. The reaction was slightly exothermic. The reaction mixture was then stirred and refluxed for 4 hr., cooled to room temperature, poured into 100 ml. of ice-water and ether extracted. The extract was dried over sodium sulfate and concentrated at reduced pressure, leaving a yellow oil. Treatment of the oil with methanol-ether gave 3.3 g. of colorless crystals which on recrystallization to constant m.p. melted at 109.5-110.0°. The remaining material, weighing 10.3 g., consisted of a yellow oil. This was chromatographed on a 70 × 3.1 cm. silica gel column slurry packed with hexane. The column was eluted with 700 ml. of hexane followed by elution with 500 ml. of 10% benzene in hexane. Elution with 500 ml. of 20% benzene in hexane gave 72 mg. of oil. Elution with 500 ml. of 30% benzene in hexane gave 2.1 g. of solid which was recrystallized to give 1.9 g., m.p. 109°. Elution with 500 ml. of 50% benzene in hexane gave 3.8 g., m.p. 103-107°. Finally, elution with 500 ml. of benzene then 500 ml. of ether gave only traces of oil. Thus a total of 9.0 g. of product had been obtained.

In a second run 23.5 g. (0.10 mole) of 1-chloro-2,2-diphenylpropane was used to prepare the Grignard reagent. Following 1 hr. of reflux and 16 hr. of stirring at room temperature there was added 10.86 g. (0.040 mole) of mercuric chloride in 50 ml. of dry tetrahydrofuran. In this

run the yellow oil obtained on concentration of the original ether extract was seeded with bis-(2,2-diphenylpropyl)-mercury and allowed to stand for 36 hr. There was obtained in this way 11.65 g. (50%) of crystalline product.

Anal. Calcd. for $C_{30}H_{30}Hg$: C, 60.95; H, 5.12. Found: C, 61.41; H, 5.12.

Reduction of Bis-(2,2-diphenylpropyl)-mercury with Lithium in Liquid Ammonia.—A 100-ml. flask was fitted with a liquid ammonia head; this was provided with a connection to an ammonia cylinder, a Dry Ice condenser with sodium hydroxide drying tube, and a capped inlet for addition of reactants. To the flask containing a magnetic stirring bar was added 50 ml. of anhydrous liquid ammonia together with 0.591 g. (0.0010 mole) of bis-(2,2-diphenylpropyl)-mercury in 10 ml. of sodium-dried ether. To this stirred solution was added in small increments 0.0167 g. (0.0024 mole) of freshly cut lithium metal. After completion of the addition the solution was stirred for 1 hr. At the end of this time 1.0 ml. of ethanol was added and stirring was continued for an additional 30 min. Then the ammonia was evaporated and the residue was treated with 25 ml. of cold water and 25 ml. of ether. The ether layer was separated and filtered and washed with water. Drying over sodium sulfate and concentration under reduced pressure afforded 0.24 g. (0.00122 mole, 61%) of oil whose infrared spectrum was that of 2,2-diphenylpropane.

Attempted Rearrangement of 2,2-Diphenylpropylmagnesium Chloride.—A solution of 2,2-diphenylpropylmagnesium chloride in 55 ml. of tetrahydrofuran was prepared as before from 0.535 g. (0.022 mg. atoms) of magnesium powder and 4.60 g. (0.020 mole) of 1-chloro-2,2-diphenylpropane. An initial 2-hr. period of refluxing was employed followed by 13 hr. of stirring at room temperature. It was noted that at room temperature a white complex tended to separate but dissolved on warming. At the end of the reaction period the tetrahydrofuran was replaced by 55 ml. of sodium-dried dioxane, the tetrahydrofuran being removed by distillation. This process took about 1 hr. and the temperature of the mixture rose to 100°. The reaction mixture was then refluxed for 5 hr. The product obtained by pouring onto ice and saturated ammonium chloride solution was ether extracted. The extracts on drying over sodium sulfate and concentrating *in vacuo* left an oil which was distilled. This boiled at 87–90° at 0.5 mm. and the distillate weighed 2.44 g. Its infrared spectrum was that of 2,2-diphenylpropane.

In another run tetrahydrofuran was distilled from the Grignard solution prepared in the above manner and was replaced by 50 g. of anhydrous pyridine. The mixture was stirred for 5 hr. and the deep red solution was poured into a mixture of 100 ml. of ice and 50 ml. of concd. hydrochloric acid. The mixture was ether extracted and the extracts washed, dried over sodium sulfate and concentrated under reduced pressure. Distillation of the residue afforded 2.87 g. of 2,2-diphenylpropane boiling at 85–90° at 0.5 mm.

In a subsequent run the tetrahydrofuran was replaced by pyridine saturated with fused trisodium phosphate. The reaction mixture was refluxed for 1 hr. The same work-up as above afforded 2.88 g. of 2,2-diphenylpropane, b.p. 80–87° at 0.5 mm.

Reaction of Bis-(2,2-diphenylpropyl)-mercury with Potassium in Tetrahydrofuran.—A dispersion of 0.187 g. (0.0048 g. atom) of potassium in 25 ml. of 2,2,4-trimethylpentane under benzophenone ketyl purified nitrogen was prepared. To this with high speed stirring was added at room temperature a solution of 1.182 g. (0.0020 mole) of bis-(2,2-diphenylpropyl)-mercury in 25 ml. of tetrahydrofuran freshly distilled from lithium aluminum hydride. The addition required 20 min. and the red color which had formed darkened to a dark wine color, eventually becoming red-brown. Stirring was continued for 1.5 hr. and the mixture was then poured onto ice and saturated ammonium chloride. Ether extraction, drying over sodium sulfate and concentration *in vacuo* afforded an oil which partially crystallized. This solid was separated by filtration and crystallized once from methanol-ether to give 0.221 g., m.p. 104–106°, whose mixed melting point with the organomercury starting material was not depressed. The oily filtrate was molecularly distilled to yield a colorless oil weighing 0.204 g. whose infrared spectrum was that of 1,2-diphenylpropane. A very strong peak at 9.85 μ as well as several peaks in the 7–8 μ region were characteristic of this compound.

The previous experiment was repeated except that the reaction time after addition was extended to 2.5 hr. and the reaction mixture was poured onto 100 g. of powdered Dry Ice. The tetrahydrofuran was evaporated and the residue was treated with 50 ml. of 5% aqueous potassium hydroxide solution. The mixture was then extracted with ether, and the ether extracts were dried over sodium sulfate and concentrated *in vacuo*, leaving 0.36 g. of semi-solid whose infrared spectrum indicated it to consist of the organomercury starting material. The potassium hydroxide solution was acidified with hydrochloric acid to a congo red endpoint and then ether extracted. These extracts were washed with water, dried over sodium sulfate and concentrated under vacuum to leave a partially crystalline product. One crystallization from methanol-water gave 0.31 g. (32%) of white crystals, m.p. 121–123°. Further crystallization brought the m.p. to constancy at 125–126°; reported[9] m.p. of 2-methyl-2,3-diphenylpropionic acid 126°.

Reaction of 1-Chloro-2,2-diphenylpropane with Lithium; 2,2-Diphenylpropyllithium.—Lithium metal weighing 0.531 g. (0.0768 g. atom) was cut into small cubes and added to a 100-ml. Morton flask fitted with high speed stirrer, dropping funnel, reflux condenser fitted with capillary tube outlet, and a source of ketyl-purified nitrogen which was kept under positive pressure with slight sweeping out the capillary outlet. Also added was 25 ml. of anhydrous ether. The lithium was shredded and dispersed by means of the 12,000 r.p.m. stirrer without the use of heating. A solution of 7.520 g. (0.032 mole) of 1-chloro-2,2-diphenylpropane in 25 ml. of dry ether was added over 15 min. to the stirred lithium suspension which was cooled in ice. The color of the mixture first became green, then brown and finally clear red. Stirring and cooling was continued for 2 hr. followed by pouring onto freshly pulverized Dry Ice. The Dry Ice was allowed to evaporate and the mixture was treated with excess 5% potassium hydroxide solution and then ether extracted. The ether extracts were dried over sodium sulfate and concentrated *in vacuo* leaving 4.54 g. of pale yellow liquid whose infrared spectrum showed it to be largely unreacted 1-chloro-2,2-diphenylpropane. The alkaline extract was acidified with hydrochloric acid to a congo red end-point and was then ether extracted, the extracts dried over sodium sulfate and concentrated under vacuum. The residue consisted of 2.02 g. (26%) of a white solid. Its infrared spectrum was identical with that of pure 3,3-diphenylbutyric acid. It was crystallized with negligible loss of weight from hot hexane affording pure 3,3-diphenylbutyric acid, m.p. 94°. A second crystallization brought the m.p. to 99.0–99.5°, giving no depression with authentic 3,3-diphenylbutyric acid.

In a second run 3.76 g. (0.016 mole) of 1-chloro-2,2-diphenylpropane, 0.266 g. (0.0384 g. atom) of freshly cut lithium pieces and a total of 50 ml. of dry ether were used. The run was made as before except that the reactants were allowed to stir for 8 hr. at 0°. The acidic fraction weighed 1.30 g. (34%) and was essentially pure 3,3-diphenylbutyric acid, m.p. 93–95°.

In a third run 3.76 g. of 1-chloro-2,2-diphenylpropane was treated with 0.277 g. (0.040 g. atom) of lithium. A total of 50 ml. of dry ether was employed. In this case the stirring time was 5 hr. at 0°. The acidic fraction weighed 2.26 g. and melted at 94–96° (yield 59%). An infrared spectrum indicated this to be 3,3-diphenylbutyric acid.

Rearrangement of 2,2-Diphenylpropyllithium in Refluxing Ether.—The previous experiment was reproduced in each detail up to the point where carbonation was effected. However, at this point the reaction mixture was heated to refluxing with continued high speed stirring. At the end of 3 hr. of refluxing the reaction mixture was carbonated as before. The acidic fraction weighed 1.61 g. (42%); the neutral fraction weighed 2.18 g. Quantitative infrared analysis showed this to consist of 19.2% of 1,2-diphenylpropane and 80.8% of 2,2-diphenylpropane.

The acidic fraction was chromatographed on a 70 × 3.1 cm. silica gel column slurry packed with 10% ether in hexane. First 500 ml. of 10% ether in hexane was employed followed by 1 liter of 20% ether in hexane. Only traces of oil appeared in these fractions. Following this, two 250-ml. portions of 30% ether in hexane were used. The material obtained from these fractions was seen from the infrared spectra to be identical and was combined. The weight totaled 0.64 g. Crystallization from hexane brought the m.p. to constancy at 185° with negligible loss to the

filtrate. A mixed m.p. with authentic o-(α,α-dimethyl-benzyl)-benzoic acid was undepressed, and the infrared spectrum was identical with that of authentic material. Characteristic bands were found at 7.7 and 7.9 μ.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.81; H, 6.39.

After 50 ml. more eluent had been collected a new solid material began to appear, and this continued with the following 1325 ml. of 30% ether in hexane. The total weight of these fractions was 0.92 g. and this melted at 119–120°. Recrystallization from hexane afforded 0.84 g. of acid, m.p. 126°, giving no depression with authentic 2-methyl-2,3-diphenylpropionic acid.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.15; H, 6.57.

2-Phenyl-2-o-tolylpropane.—In a 3-liter 3-neck flask fitted with stirrer, dropping funnel and condenser protected with a calcium chloride drying tube was placed 26.3 g. (1.1 g. atoms) of magnesium turnings and 50 ml. of dry ether. To this was added 20.0 g. of o-bromotoluene and the reaction mixture was stirred for a few minutes until an exothermic reaction began. At this point, 100 ml. of ether was added followed by 151 g. of o-bromotoluene (total, 161 g., 1.0 mole) in 700 ml. of ether at such a rate that vigorous reflux was maintained (1 hr.). The reaction mixture was warmed on a steam-bath for 1 hour further, then external heating was removed, and 106 g. (0.90 mole) of α-chlorocumene, freshly prepared and free of dissolved HCl, in 200 ml. of ether was added at a rate such that reflux was vigorous. Half-way through the addition precipitated salt appeared. The reaction mixture was stirred an additional hour at room temperature then 100 g. of ammonium chloride in 500 ml. of water was added. The organic layer was separated, washed once with 500 ml. of water, dried over sodium sulfate, filtered and concentrated *in vacuo*. The concentrated oil was distilled at 0.5 mm. in a modified Claisen apparatus. After a forerun of 0.45 g. of material distilling in the range 60–102°, 23.39 g. of clear oil was collected at 103–110°.

The 103–110° fraction was chromatographed on a 700 × 35 mm. alumina column slurry packed in hexane. The entire fraction was placed without solvent on the column which was then eluted with hexane. The first fraction, obtained by elution with 500 ml. of hexane, contained 0.10 g. of oil. Fraction two, obtained with 500 ml. of hexane, afforded 7.7 g. of clear oil; fraction three, 350 ml., 8.1 g. clear oil; fraction four, 350 ml., 4.8 g. clear oil; fraction five, 300 ml., 1.8 g. clear oil. Finally fraction 6 was obtained by elution with 1 liter of ether and afforded 0.8 g. of material.

Fractions 2–5 had identical infrared spectra, with a characteristic *gem*-dimethyl split 7.2–7.3 μ absorption. These were combined to give 22.4 g. (12%) of clear oil, of which 17.4 g. was subjected to distillation in a Claisen apparatus at 0.1 mm. Essentially all the material distilled at 94–95°. A central cut of 14.3 g. of this 2-phenyl-2-o-tolylpropane was used for elemental analysis.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.62; H, 8.38.

o-(α,α-Dimethylbenzyl)-benzoic Acid.—In a liter flask fitted with a paddle stirrer was placed 400 ml. of water, 20.0 g. of potassium permanganate and 5.0 g. (0.0238 mole) of 2-phenyl-2-o-tolylpropane. To this was added 5 ml. of 10% aqueous NaOH and the mixture was stirred and refluxed vigorously for 24 hours. At the end of this time, excess permanganate color remained. The solution was acidified with 10 ml. of concd. sulfuric acid and refluxed for 0.5 hr. further. Aqueous sodium bisulfite was added until a clear solution resulted. The acid solution was extracted with 100 ml. of ether. The ether was in turn extracted with a total of 50 ml. of 10% aqueous KOH, which was then acidified with HCl and extracted with 50 ml. of ether. The ether extract was dried over sodium sulfate, filtered and concentrated to yield 0.75 g. of white solid, m.p. 181–183°. Recrystallization of this acid from ether–hexane gave 0.68 g. (12%) of o-(α,α-dimethylbenzyl)-benzoic acid, m.p. 184–185°. This material exhibited no mixed m.p. depression with the 185° acid of the rearrangement and carbonation of 2,2-diphenylpropyllithium; similarly, the infrared spectra of the two samples were identical.

Behavior of 2,2-Diphenylpropyllithium in Benzene.—A Morton flask was constructed with a side arm through which a tube could be lowered to the flask bottom. To the flask was added 0.277 g. (0.040 g. atom) of lithium metal in pieces. Also added was 30 ml. of sodium-dried ether. The flask was fitted with a high speed stirrer, a nitrogen inlet, a dropping funnel and a condenser bearing a capillary outlet tube for nitrogen. The nitrogen was purified by passage through benzophenone ketyl in p-xylene and then mineral oil. A mineral oil manometer was employed to maintain slightly positive pressure. The stirrer was operated at 12,000 r.p.m. for 30 min. with ice cooling, and then a solution of 3.76 g. (0.016 mole) of 1-chloro-2,2-diphenyl-propane in 50 ml. of ether was added over 30 min. The mixture was then stirred for 5 hr. at 0°. At the end of this time, the tube, extending through the flask side arm, was lowered below the surface of the reaction mixture and dry, oxygen-free nitrogen was blown through the mixture which was kept at 0°, soon giving a concentrated, thick red sludge. To the reaction mixture then was added 50 ml. of anhydrous thiophene-free benzene. High speed stirring was resumed and the reaction mixture was heated in a 35° oil-bath for 15 hr. more. The mixture was then carbonated by pouring onto 100 g. of powdered Dry Ice and worked up as before. The acidic fraction weighed 1.70 g. (44%) and consisted of white solid, m.p. 93–95°. One crystallization afforded pure 3,3-diphenylbutyric acid, m.p. 98–99°, weighing 1.42 g. (37%) and not depressing the m.p. of an authentic sample. The neutral fraction weighed 1.84 g.

Reaction of Bis-(2,2-diphenylpropyl)-mercury with Lithium Followed by Carbonation.—To a 100-ml. Morton flask fitted with a high speed stirrer, nitrogen inlet, reflux condenser and dropping funnel and protected by a capillary outlet tube was added 0.0553 g. (0.08 g. atom) of freshly cut lithium in 30 ml. of anhydrous ether. This was stirred at 12,000 r.p.m. for 30 min. at 0° and a solution of 1.182 g. (0.0020 mole) of bis-(2,2-diphenylpropyl)-mercury in 30 ml. of dry ether was added over 30 min. The temperature was kept at 0° and stirring was continued for 8 hr. At the end of the first 3 hr. of stirring 0.0553 g. more of lithium metal was added. Finally, the reaction mixture was carbonated by pouring onto 100 g. of Dry Ice and worked up in the usual manner, affording 0.33 g. of acidic fraction. Crystallization from hexane afforded 0.26 g. of 3,3-di-phenylbutyric acid, m.p. 101–102°, giving no depression with an authentic sample. The neutral fraction was molecularly distilled at 70° and 0.5 mm. to give 0.414 g. of colorless oil. Quantitative infrared analysis indicated this to consist of 96.6% 2,2-diphenylpropane. The non-distilled residue was a solid melting at 229–233° and weighing 0.09 g.

In a second run with a stirring time of only 5 hr. there was isolated 0.31 g. of crude acid and 0.28 g. (29.2%) of pure 3,3-diphenylbutyric acid.

Reaction of Bis-(2,2-diphenylpropyl)-mercury with Lithium Followed by Heating and Subsequent Carbonation.—The same procedure and amounts used in the previous experiment were employed here. However, at the end of 5 hr. of stirring at 0°, the reaction mixture was heated to reflux for 3 hr. The mixture was then carbonated and worked up as before. During the reflux period the gray suspension turned to a deep red-brown.

The yield of acid was 0.25 g. (26%) crude, m.p. 121–124°. One crystallization brought the melting point to 125–126°, which showed no depression with authentic 2-methyl-2,3-

TABLE III

INFRARED CALIBRATION[33] OF MIXTURES OF 2,2-DIPHENYL-PROPANE AND 1,2-DIPHENYLPROPANE

Actual % 1,2-isomer	D' (12.59 μ)	D'' (13.59 μ)	R	Q	F	Calcd. % of 1,2-isomer
0	0.0985	0.0362				
24.5	.0794	.1331	0.324	0.332	0.975	25.3
49.1	.0506	.2076	0.965	1.00	0.965	50.6
71.6	.0386	.3010	2.50	2.22	1.127	69.6
100.0	.0088	.3990				

(33) The quantitative infrared method of analysis has been described earlier by H. E. Zimmerman and W. Chang, *J. Am. Chem. Soc.*, **81**, 3634 (1959).

diphenylpropionic acid. The neutral fraction weighed 0.57 g.

Preparation of Authentic 1,2-Diphenylpropane.—A solution of 2.28 g. (0.01175 mole) of α-methylstilbene in 100 ml. of ethyl acetate was hydrogenated using 75 mg. of platinum oxide and a Parr apparatus. It was found necessary to add 200 mg. more of the catalyst for complete hydrogenation. Filtration, concentration and distillation of the residue afforded 1.98 g. of material, b.p. 108–110° at 2.0 mm. The infrared spectrum of the 1,2-diphenylpropane product showed that it did not contain any unreacted α-methylstilbene.

1-Phenyl-1-p-tolylethyl Methyl Ether.—Into a 500-ml. flask was placed 90.0 g. (0.39 mole) of 1-phenyl-1-p-tolylethylethanol[34] together with 200 ml. of toluene and 23.2 g. (0.50 mole) of sodium hydride (52% in oil). The mixture was warmed to 80° and kept at that temperature for 2 hours, then recooled to room temperature and 154 g. (1.0 mole) of methyl iodide was added. The reaction mixture was stirred well and heated to reflux. After 5 hours the internal reflux temperature was 92° and a white solid nearly filled the flask. The product was cooled to room temperature and washed with water. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to yield 99.0 g. of yellow oil.

A 54.0-g. portion of this oil was chromatographed on a 70 × 3.1 cm. silica gel column slurry packed with 5% ether in hexane and eluted with 2.5% ether in hexane. The first 250 ml. of eluent contained only a trace of material. The next 250 ml. gave 17.75 g. of oil. The next liter of eluent gave 21.23 g. of clear colorless oil. In the next liter of eluent was 3.28 g. of oil. This was followed by elution with 500 ml. of 10% ether in hexane which gave an additional 2.1 g. of oil. Distillation of fraction 3 with a modified Claisen apparatus at 0.8 mm. gave 16.82 g. of oil, b.p. 119.5–121°, which represented pure 1-phenyl-1-p-tolylethyl methyl ether.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.13; H, 7.81.

At this point it was apparent that distillative separation was more effective than chromatography. Distillation of chromatographic fractions 2, 4 and 5 combined with the unchromatographed material afforded 43.75 g. of colorless product, b.p. 108–110° at 0.5 mm. The infrared spectrum of this fraction was identical with that obtained from the analyzed sample. The total yield of 1-phenyl-1-p-tolylethyl methyl ether was 60.64 g. (69%).

1-Chloro-2-phenyl-2-p-tolylpropane.—Into a 200-ml. Morton flask fitted with a high speed stirrer (7,500 r.p.m.), dropping funnel, nitrogen inlet and reflux condenser was placed 5.47 g. (0.14 g. atom) of freshly cut potassium metal and 75 ml. of sodium-dried ether. The reaction vessel was continually flushed with purified nitrogen (benzophenone ketyl) and was under a slight positive head of pressure. Stirring was started and soon had cut the potassium into fine slivers. With ice cooling, a solution of 16.92 g. (0.075 mole) of 1-phenyl-1-p-tolylethyl methyl ether in 50 ml. of ether was added over a 0.5-hr. period to the stirred suspension of potassium. A red color formed immediately. After 1 hr. of stirring at room temperature the solution was very thick and red and no particles of potassium could be observed. The reaction mixture was stirred at moderate speed for 8 hr. further then cooled to −65° in a Dry Ice-pentane-bath, and 15 ml. (20.0 g., 0.235 mole) of redistilled methylene chloride was added dropwise over a 0.5-hr. period. The deep red color remained throughout the addition and faded slowly as the temperature was allowed to rise to room temperature during 1 hr. Ten ml. of absolute ethanol in 20 ml. of toluene was added with stirring and the reaction mixture was allowed to stand overnight. The mixture was poured onto 100 ml. of ice and 10 ml. of concd. hydrochloric acid and the product ether extracted. The extracts were washed with water and dried over anhydr. sodium sulfate. Concentration in vacuo gave 15.80 g. of oil. In a small modified Claisen apparatus, 15.20 g. of this oil was distilled at 0.01 mm. After several drops of forerun, 10.28 g. (60%) of an orange oil distilled at 127–128°. Chromatography and treatment with Norite failed to remove the color from the oil.

In another run using the same quantities of starting materials, 9.78 g. (57%) of very pale orange liquid was distilled

(34) C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **49**, 549 (1927).

at 114–115° and 0.001 mm. The infrared spectrum of this material and the distillate from the previous run were identical. This sample of 1-chloro-2-phenyl-2-p-tolylpropane analyzed properly despite a persistent but apparently minor contamination by colored impurity.

Anal. Calcd. for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00. Found: C, 78.59; H, 7.05.

Reaction of 1-Chloro-2-phenyl-2-p-tolylpropane with Lithium; 2-Phenyl-2-p-tolylpropyllithium.—Lithium metal weighing 0.277 g. (0.040 g. atom) was cut into small cubes and added to a 100-ml. Morton flask fitted with a high speed stirrer, dropping funnel, reflux condenser fitted with capillary tube outlet, and a source of ketyl-purified nitrogen which was kept under positive pressure with slight sweeping out of the capillary outlet. Also added was 25 ml. of anhydrous ether.

The lithium was shredded by means of the 10,000 r.p.m. stirrer without the use of heating. About 5 ml. of a solution of 3.67 g. (0.015 mole) of 1-chloro-2-phenyl-2-p-tolylpropane in 25 ml. of dry ether was added. The induction period for the first appearance of the red color was 15 min. and once it had formed, the remainder of the ethereal solution was added over a 15-min. period with cooling in ice. The mixture was stirred at 0° for 5 hr. further, then poured onto freshly pulverized Dry Ice. The Dry Ice was allowed to evaporate and the mixture was treated with excess 5% potassium hydroxide solution and then ether extracted. The ether extracts were dried over anhydr. sodium sulfate and concentrated in vacuo to give 1.09 g. of oil. Distillation of this oil in a molecular still at 85° and 0.01 mm. gave 0.615 g. of clear oil with an infrared spectrum identical with that of 2-phenyl-2-p-tolylpropane. Viscous yellow oil weighing 0.335 g. was recovered from the still but could not be identified by its infrared spectrum. The alkaline extract was acidified with hydrochloric acid to a congo red end-point and was then ether extracted, the extracts dried over anhydr. sodium sulfate and concentrated under vacuum. The residue consisted of 1.85 g. (48.4%) of oil which completely crystallized when seeded with authentic 3-phenyl-3-p-tolylbutyric acid. One crystallization from hexane gave 1.35 g. of white needles, m.p. 79–80°. Mixed m.p. with the authentic acid was undepressed and the infrared spectrum was identical with that of the authentic acid.

Rearrangement of 2-Phenyl-2-p-tolylpropyllithium in Refluxing Ether.—The previous experiment was reproduced in each detail up to the point where carbonation was effected. However, at this point the stirring was slowed to a minimum and the reaction mixture was heated to reflux temperature. At the end of 3 hours of refluxing the reaction mixture was carbonated as before. The neutral fraction weighed 2.17 g. Distillation of this oil in a molecular still at 85° and 0.01 mm. gave 1.32 g. of clear oil with an infrared spectrum identical with that of 2-phenyl-2-p-tolylpropane. The acidic fraction weighed 0.96 g. of which 0.83 g. was chromatographed on a 170 cm. × 2.5 cm. column which had been slurry packed with silica gel in 5% ether in hexane. Elution with 600 ml. of the solvent gave no material. Elution with an additional 1200 ml. of 5% ether in hexane and 4000 ml. of 7% ether in hexane gave a total of 0.064 g. of oil whose infrared spectrum indicated no acidic material. Elution with 1 liter of 11% ether in hexane gave 62 mg. of oil. The next 500 ml. of eluent (11% ether in hexane) gave 96 mg. of solid, m.p. 72–73°. Following this, 500 ml. of eluent (11% ether in hexane) gave 50 mg. of solid, m.p. 72–73°. Elution with 500 ml. of 13% ether in hexane gave 10 mg. more material. As the infrared spectra of the last four fractions were virtually identical, they were combined and recrystallized from hexane to give 177 mg. of crystalline solid, m.p. 73–74°. Mixed m.p. and identical infrared spectra showed this to be p-(α,α-dimethylbenzyl)-phenylacetic acid. The next three fractions were obtained by eluting with 500-ml. portions of 13% ether in hexane. These weighed 70, 128 and 38 mg. in the order in which they came off the column. The next two fractions were obtained by elution with 500-ml. portions of 15% ether in hexane. These fractions weighed 64 and 44 mg., respectively. The infrared spectra of the last five fractions were virtually identical to each other and were also identical with that of 2-methyl-3-phenyl-2-p-tolylpropionic acid. They were combined and crystallized from hexane to give 195 mg. of solid, m.p. 126–127°,

mixed m.p. was undepressed. Elution with 1 l. of 15% ether in hexane gave 55 mg. of oil with an infrared spectrum which did not fit any of the suspected compounds. Elution with 2 l. of 20% ether in hexane yielded 50 mg. of oil, while elution with 2 l. of 30% ether in hexane gave 53 mg. of oil. The last two fractions had infrared spectra which were very similar to that of 3-phenyl-3-p-tolylbutyric acid and by hexane crystallization 59 mg. of this acid, m.p. 79-80°, mixed m.p. undepressed, was obtained.

Rearrangement of 2-Phenyl-2-p-tolylpropyllithium in Refluxing Ether Followed by Carbonation with Carbon Dioxide-C-14.—The previous run was repeated in every detail up to the point where carbonation was effected. At this point, the Morton flask containing the reaction mixture was quickly transferred from the high speed stirring apparatus to a vacuum line where the contents were carbonated at −75° with carbon dioxide generated from 0.5 millicuries of C¹⁴ in 1.9737 g. (0.0100 mole) of barium carbonate.

Work up of the products as before gave 2.26 g. of neutral material and 934 mg. of acid which was a viscous pale yellow liquid.

To determine the specific radioactivity[35] of each acid sample, a 10-50-mg. weighed portion of the acid was introduced into a combustion tube with 2.5 g. of a 2:1 mixture of potassium iodate and potassium dichromate. The portion was combusted by adding 10 ml. of Van Slyke solution[35] and boiling for 0.5 minute (to smoky vapors). The carbon dioxide was generated into a model DC 250 ion chamber of a Dynacon Electrometer (Nuclear-Chicago). The ion chamber was filled with inactive carbon dioxide to atmospheric pressure. The ion chamber was then connected to the electrometer and counts taken by the rate-of-charge method, except in a few cases where the activity was too high for an accurate value by this method. In these cases, the equilibrium method readings were used. In Table IV are recorded specific activities for the crude acidic rearrangement product as well as for successive crystallizations of four authentic acids to which a small and known fraction of crude acidic rearrangement product had been added. The crystallizations were carried out using hexane and four to six crystallizations were interposed between each radioactivity measurement; each sample was vacuum dried before counting.

3-Phenyl-3-p-tolylbutyric Acid.—In a 500-ml. flask was prepared a solution of p-tolylmagnesium bromide from 42.75 g. (0.25 mole) of p-bromotoluene and 6.0 g. (0.25 g. atom) of magnesium turnings in 175 ml. of dry ethyl ether. To this was added 53.8 g. (0.25 mole) of ethyl (1-phenylethylidene)-cyanoacetate[36] dropwise at a rate causing the ether to reflux gently. Stirring was continued during the addition and finally the reaction mixture was refluxed on the steam-bath for 1 hour. The product was cooled to room temperature then poured into 300 ml. of 15% aqueous ammonium chloride. Separation and concentration *in vacuo* yielded 68.5 g. of a viscous oil. Refluxing 65.0 g. of this oil with 200 ml. of concentrated hydrochloric acid for 32 hours followed by cooling to room temperature gave an organic layer which was separated from the hydrochloric acid layer. The diluted hydrochloric acid was ether extracted and the extracts added to the organic layer which was washed with 50 ml. of water then extracted with 100 ml. of 10% aq. potassium hydroxide. The alkaline solution was separated, acidified with hydrochloric acid to a congo red end-point and extracted with ether. The ether extracts were combined, dried over anhydr. sodium sulfate and concentrated *in vacuo* to yield 13.4 g. of oil. Attempts to distil this oil in a modified Claisen apparatus effected decarboxylation. Distillation of the decarboxylated oil at 1 mm. gave 6.06 g., b.p. 170-175°. An infrared spectrum of this material showed the presence of a nitrile function at 4.4 μ, but there was no indication of a carboxylic acid function (bands at 5.8 and 10.8 μ were missing as well as the characteristic broad 3.4 band). This fraction was vigorously refluxed for 24 hr. with 30 ml. of a solution of 84 ml. of concd. sulfuric acid in 115 ml. of water. The mixture was cooled to room temperature and the acidic material was separated from the neutral material in the same manner as described before to give 5.35 g. of acidic oil. This acidic material was chromatographed on a 700 × 35 mm. column of silica gel slurry packed with 10% ether in hexane. Elution with 1 liter of 10% ether in hexane gave 0.48 g. of oil. Elution with 500 ml. of 15% ether in hexane produced less than 0.1 g. of oil. Elution with 20% ether in hexane gave virtually nothing in the first 250 ml. of eluent, but the next 750 ml. of eluent gave 4.24 g. of clear pale yellow oil. On drying on the vacuum pump this fraction completely crystallized. Recrystallization from hexane gave 3.88 g. of white crystals of 3-phenyl-3-p-tolylbutyric acid, m.p. 79-80°.

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.14. Found: C, 80.74; H, 7.07.

2-Phenylpropionic Acid.—To a 500-ml. flask cooled in ice and equipped with a magnetic stirrer was added 150 ml. of water and 20 ml. of concd. sulfuric acid. With stirring at 15°, 20 g. (0.15 mole) of 2-phenylpropionaldehyde was added. Then 16.4 g. (0.104 mole) of potassium permanganate was added in portions over 2 hr. below 20°. The reaction mixture was stirred for an additional hr. at 20° and the solution was decolorized by addition of sodium bisulfite. The resulting oily layer was separated, washed, extracted with 10% potassium hydroxide solution. The alkaline extract was acidified with hydrochloric acid to a congo red end-point and ether extracted. Concentration of the dried ether extract gave 6.1 g. of acidic oil which was distilled at 1.0 mm. to afford 5.0 g. (25%) of 2-phenylpropionic acid[37] as a colorless oil, b.p. 111.5-112.0°, with little forerun and high boiling residue. The infrared spectrum showed the absence of benzoic acid.

2-Methyl-2-phenyl-3-p-tolylpropionic Acid.[38]—A solution of 3.60 g. (0.023 mole) of 2-phenylpropionic acid in 5 ml. of sodium-dried ethyl ether was added to sodium amide prepared from 1.15 g. (0.05 g. atom) of sodium metal in 300

TABLE IV

MEASUREMENT OF ACTIVITIES

The crude acid mixture was found from three measurements to have an activity of 24.4 ± 0.1 μc./mM. For each authentic acid plus crude acid mixture containing the indicated per cent. of active crude acid and having a maximum activity[a] as given, are listed in order: the successive measurement number,[b] the m.p., the activity in μc./mM. and the indicated per cent. of the given acid in the crude mixture.

2-Methyl-2-phenyl-3-p-tolylpropionic acid plus crude acid (10.25% of total), max. possible activity, 2.5 μc./mM.: 1, 105-106°, 0.199, 8.0%; 2, 105-106°, 0.148, 5.9%; 3, 105-106°, 0.133, 5.3%; 4, 105-106°, 0.0907, 3.6%; 5, 105-106°, 0.0884, 3.5%.

2-Methyl-2-phenyl-3-p-tolylpropionic acid plus crude acid (21.2% of total), max. possible activity, 5.18 μc./mM.: 1, 105-106°, 0.247, 4.8%.

3-Phenyl-3-p-tolylbutyric acid plus crude acid (8.92% of total), max. possible activity, 2.18 μc./mM.: 1, 79.5-80°, 0.18, 8.28%; 2, 79.5-80°, 0.14, 6.5%; 3, 79.5-80°, 0.267, 12.2%; 4, 80.0-80.5°, 0.269, 12.3%.

3-Phenyl-3-p-tolylbutyric acid plus crude acid (20.7% of total), max. possible activity, 5.06 μc./mM.: 1, 79.5-80.0°, 0.65, 12.85%.

2-Methyl-2-p-tolyl-3-phenylpropionic acid plus crude acid (21.3% of total), max. possible activity, 5.20 μc./mM.: 1, 127-128°, 2.34, 46.1%; 2, 127-128°, 1.89, 37.:%; 3, 127-128°, 2.32, 44.6%; 4, 127-128°, 2.31, 44.4%.

2-Methyl-2-p-tolyl-3-phenylpropionic acid plus crude acid (29.4% of total), max. possible activity, 7.16 μc./mM.: 1, 127-128°, 3.23, 45.2%.

p-(α,α-Dimethylbenzyl)-phenylacetic acid plus crude acid (17.9% of total), max. possible activity, 4.38 μc./mM.: 1, 72-73°, 1.25, 28.6%; 2, 72.5-73.5°, 1.15, 26.3%; 3, 73-74°, 0.925, 21.1%; 4, 73-74°, 0.905, 20.7%.

p-(α,α-Dimethylbenzyl)-phenylacetic acid plus crude acid (19.5% of total), max. possible activity 4.75 μc./mM.: 1, 73-74°, 1.03, 21.7%.

[a] This is the value which would be observed if the crude acid were completely the acid under consideration. [b] Four to six crystallizations were interposed between successive measurements.

(35) The general procedure is that of D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940); D. D. Van Slyke, J. Plazin and T. R. Weisiger, *ibid.*, **191**, 299 (1951).

(36) A. C. Cope, C. M. Hofmann, C. Wyckoff and E. Hardenbergh, *J. Am. Chem. Soc.*, **63**, 3452 (1941).

(37) M. Tiffeneau, *Ann. chim.*, [8], **10**, 352 (1907).

(38) This procedure was patterned after similar syntheses of C. R. Hauser, D. Lednicer and W. R. Brasen, *J. Am. Chem. Soc.*, **80**, 4348 (1958).

ml. of liquid ammonia. Ten minutes after the acid had been added (greenish solution), a solution of 4.64 g. (0.025 mole) of α-bromo-p-xylene in 5 ml. of ether was added dropwise over 15 min. The reaction mixture was stirred for 0.5 hr. further, then quenched with excess ammonium chloride. The ammonia was allowed to evaporate and the residue was taken up in 5% aqueous potassium hydroxide which was then ether extracted. The alkaline phase was acidified to a congo red end-point with hydrochloric acid and then ether extracted. The extracts were dried over sodium sulfate and concentrated in vacuo. The acidic material weighed 3.86 g. and was distilled in a modified Claisen apparatus. At 1 mm. 1.55 g. of unreacted 2-phenylpropionic acid was collected at 110–111°. The remaining acid did not distil at this pressure with the pot temperature raised to 210°. It was subsequently cooled, dissolved in 5 ml. of ether and chromatographed on a 50 × 1.8 cm. column of silica gel slurry packed with 10% ether in hexane. Eluting with 10% ether in hexane, the first fraction of 250 ml. was virtually empty. The next 250 ml. gave 0.440 g. of white crystalline solid. The next 500 ml. of eluent, obtained with 15% ether in hexane, gave 2.41 g. of solid. Elution with 250 ml. of 15% ether in hexane gave 0.82 g. of solid. The infrared spectra of fractions 2–4 were identical. They were combined and recrystallized from hexane to give 2.44 g. (41.6%) of crystalline 2-methyl-2-phenyl-3-p-tolylpropionic acid.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.14. Found: C, 80.49; H, 7.34.

2-p-Tolylpropionic Acid.—To 20.4 ml. of concd. sulfuric acid in 150 ml. of water was added 13.85 g. of 2-p-tolylpropionaldehyde[39] at 15°. The mixture was stirred vigorously with a magnetic stirrer and kept below 20° by ice cooling as 10.15 g. (0.645 mole) of potassium permanganate was added during 1 hr. After an additional hr. of stirring, sodium bisulfite was added until a clear solution resulted and the mixture was worked up as described above for the preparation of 2-phenylpropionic acid. There was obtained 3.28 g. (21.5%) of 2-p-tolylpropionic acid as a colorless oil, b.p. 119–120° at 1.0 mm. This on standing overnight solidified and melted at 39–40° (reported[40,41] 34–35°, 40–41°).

2-Methyl-2-p-tolyl-3-phenylpropionic Acid.—To a solution of sodium amide prepared from 0.92 g. (0.04 g. atom) of sodium in 300 ml. of liquid ammonia was added 3.30 g. (0.0195 mole) of 2-p-tolylpropionic acid. After 10 min., a solution of 3.42 g. (0.020 mole) of benzyl bromide in 5 ml. of dry ether was added dropwise. After 0.5 hr. of stirring the reaction mixture was quenched by addition of solid ammonium chloride and worked up as described in the preparation of 2-methyl-2-phenyl-3-p-tolylpropionic acid. Concentration of the ethereal solution gave a crystalline solid which on crystallization from hexane to constant m.p. gave 1.87 g. (38%) of 2-methyl-2-p-tolyl-3-phenylpropionic acid, m.p. 127–128°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.14. Found: C, 80.60; H, 6.92.

Bromination of 2,2-Diphenylpropane Affording 2-p-Bromophenyl-2-phenylpropane.—To a 500-ml. flask fitted with stirrer, condenser and thermometer was added 179.7 g. (0.917 mole) of 2,2-diphenylpropane and 96.0 g. (0.60 mole) of bromine. The contents of the flask were heated to 60° with stirring; at this temperature hydrogen bromide gas was evolved. The temperature was maintained for 2 hr.; at the end of this time the evolution of gas had greatly subsided. The temperature was then raised to 80° and 0.5 g. of benzoyl peroxide was added. At the end of 3 hr. the temperature was raised to 90° and kept here for 17 hr. at the end of which time the hydrogen bromide evolution had ceased. The cooled reaction mixture was washed with 10% sodium thiosulfate solution after dilution with benzene. The benzene solution was dried over sodium sulfate and concentrated in vacuo. The residue was distilled to give 81.99 g. (46%) of recovered 2,2-diphenylpropane, b.p. 99–102° at 0.75 mm. As econd fraction distilled at 110–125° and weighed 6.08 g. Fractions 3 and 4 had identical infrared spectra and distilled in the range 125–130°;

(39) Prepared according to P. C. Dutta, *J. Indian Chem. Soc.*, **18**, 233 (1941).

(40) H. Rupe and F. Wiederkehr, *Helv. Chim. Acta*, **7**, 654 (1924).

(41) G. Errera, *Gazz. chim. ital.*, **21**, 81 (1891).

their combined weight was 85.41 g. (52%). Fractions 3 and 4 were analyzed and represented 2-p-bromophenyl-2-phenylpropane.

Anal. Calcd. for $C_{15}H_{15}Br$: C, 65.44; H, 5.47. Found: C, 65.99, 65.94; H, 5.51, 5.41.

Treatment of this compound with alcoholic silver nitrate gave essentially no precipitate. The infrared spectrum showed characteristic *gem*-dimethyl absorption as well as a 12.1 μ band characteristic of p-substituted benzenes. This and other evidence (vide infra) made it clear that free radical bromination on a methyl group had failed and p-bromination had occurred.

Debromination of 2-p-Bromophenyl-2-phenylpropane to 2,2-Diphenylpropane.—A 100-ml. flask was fitted with a liquid ammonia head provided with a connection to an ammonia cylinder, a Dry Ice condenser with sodium hydroxide guard tube, and a capped inlet for adding solids. To the flask, containing a magnetic stirring bar, was added 40 ml. of anhydrous liquid ammonia followed by a solution of 1.20 g. (0.00435 mole) of 2-p-bromophenyl-2-phenylpropane in 20 ml. of anhydrous ether. Following this, with stirring, there was added 0.067 g. (0.0096 g. atom) of freshly cut small pieces of lithium metal; the addition was made over 5 min. Stirring was then continued until the blue color had dissipated, then 3 ml. of ethanol was added to the reaction mixture and the ammonia was allowed to evaporate. The product was isolated by dilution with water and ether extraction. The extracts, after drying over sodium sulfate and concentration in vacuo, afforded 0.72 g. (84%) of oil having an infrared spectrum identical with that of authentic 2,2-diphenylpropane except for an extraneous peak at 9.0 μ. Distillation in a molecular still at 0.10 mm. and 70° gave a colorless oil whose infrared spectrum now was that of authentic material.

p-(α,α-Dimethylbenzyl)-benzoic Acid.—In a 500-ml. flask fitted with a magnetic stirrer, nitrogen inlet, condenser and dropping funnel, was placed 2.43 g. (0.10 g. atom) of magnesium turnings and 50 ml. of sodium-dried ether. With stirring and under a slow stream of ketyl-purified nitrogen, a few ml. of a solution of 27.5 g. (0.1 mole) of 2-p-bromophenyl-2-phenylpropane in 100 ml. of ether was added. An exothermic reaction began in a few minutes and the remainder of the halide solution was added over a 1-hr. period. The solution was refluxed for 1 hr. further, cooled to room temperature and poured onto freshly pulverized Dry Ice. The product was acidified with 25 ml. of 6 N hydrochloric acid and ether extracted. The ether extracts were combined and extracted with 10% aqueous potassium hydroxide. The alkaline solution was acidified with hydrochloric acid to a congo red end-point and this was extracted with ether. The ethereal solution was dried over sodium sulfate and concentrated in vacuo to give a solid mass. Recrystallization from hexane gave 14.5 g. (0.06 mole) (60%) of p-(α,α-dimethylbenzyl)-benzoic acid, m.p. 144–145°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.22; H, 6.40.

p-(α,α-Dimethylbenzyl)-phenylacetic Acid.—In a 25-ml. flask, 11.9 g. (0.10 mole) of thionyl chloride was refluxed with 6.0 g. (0.025 mole) of p-(α,α-dimethylbenzyl)-benzoic acid for 2 hr. The mixture was distilled directly in a modified Claisen apparatus, first at atmospheric pressure to remove excess thionyl chloride, then at 0.05 mm. where 5.1 g. of p-(α,α-dimethylbenzyl)-benzoyl chloride distilled as colorless liquid, b.p. 136–138°.

A diazomethane solution was prepared from 3.0 g. of 70% N,N'-dinitroso-N,N'-dimethylterephthalamide in mineral oil (du Pont EXR-101) and 14 g. of potassium hydroxide. The distilled ethereal solution of diazomethane was dried over potassium hydroxide pellets for 2 hr. then decanted and cooled to 5°; 0.87 g. (0.0035 mole) of p-(α,α-dimethylbenzyl)-benzoyl chloride dissolved in 5 ml. of dry ethyl ether was added dropwise. The flask was held at 10° for 3 hr. Ether and excess diazomethane were removed under vacuum until the remaining material was at room temperature. The remaining semi-solid p-(α,α-dimethylbenzyl)-benzoyldiazomethane was dissolved in 5 ml. of dry dioxane and added dropwise to a stirred solution of 0.10 g. of silver oxide (freshly precipitated), 0.25 g. of anhydr. sodium carbonate and 0.15 g. of sodium thiosulfate in 10 ml. of water at 50–60°. This solution was kept at this temperature for 2 hr. then heated to 90° for 10 min. and

allowed to cool to room temperature. The solution was poured onto 25 ml. of water and acidified with dilute nitric acid. The acidified material was ether extracted. The ether extracts were combined, dried over sodium sulfate and concentrated *in vacuo* to yield a viscous oil. This oil was dissolved in a small quantity of hexane and was crystallized to yield 0.43 g. (44%) of *p*-(α,α-dimethylbenzyl)-phenylacetic acid, m.p. 73–74°.

2-Phenyl-2-*p*-tolylpropane from 2-Phenyl-2-*p*-tolylpropylmagnesium Chloride.—Into a 100-ml. flask fitted with a magnetic stirrer, heater, dropping funnel, condenser and nitrogen inlet was placed 0.365 g. (0.015 g. atom) of magnesium turnings. The flask was flamed and swept through with ketyl-dried nitrogen before use. With stirring, 3.065 g. (0.0125 mole) of 1-chloro-2-phenyl-2-*p*-tolylpropane in 50 ml. of dry tetrahydrofuran (prepared immediately before use by distilling from lithium aluminum hydride) was added together with 1 mg. of iodine. Evidence for the start of the reaction was clouding of the solution, disappearance of the iodine color and etching of the magnesium. The solution was warmed to 50° and kept at that temperature for 16 hr. by which time virtually all of the magnesium had been consumed. A solution of 10 g. of ammonium chloride in 25 ml. of water was added slowly to the Grignard solution. The product was washed with water and the water extracted with ether. The ethereal solutions were combined with the organic layer and dried over sodium sulfate and concentrated *in vacuo*. The pale yellow residue was distilled in a molecular still at 70° and 0.01 mm. to yield 2.49 g. (95%) of 2-phenyl-2-*p*-tolylpropane, a colorless oil whose infrared spectrum was identical with that of 2-phenyl-2-*p*-tolylpropane prepared by an alternative synthesis (*vide infra*).

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.14; H, 8.35.

2-Phenyl-2-*p*-tolylpropane from α-Chlorocumene and *p*-Tolylmagnesium Bromide.—A solution of *p*-tolylmagnesium bromide was prepared from 171 g. (1 mole) of *p*-bromotoluene, 26.7 g. (1.1 g. atoms) of magnesium turnings and 850 ml. of dry ether. To the Grignard solution was added 152.0 g. (0.98 mole) of α-chlorocumene in 200 ml. of ether with stirring at reflux temperature. The addition was complete in 1 hr. and the reaction mixture was stirred and refluxed for an additional hr., by which time a large mass of fine white precipitate had formed. Addition of 50 g. of ammonium chloride in 300 ml. of water was followed by 25 ml. of concentrated hydrochloric acid which completely dissolved the magnesium salts. The ether layer was separated and dried over sodium sulfate. Concentration *in vacuo* left a viscous oil which was distilled in a modified Claisen apparatus at 0.5 mm. After a large forerun distilling in the range 45–80°, 125.0 g. of clear oil was collected at 109–111°. Nothing further was collected until 170° where a very viscous liquid which cooled to a glass was collected. The remaining material in the pot weighed 45 g.

The 109–111° fraction had an infrared spectrum which was identical with that of 2-phenyl-2-*p*-tolylpropane except for an additional strong band at 12.4 μ. When this material was left overnight at 10°, a small amount of white solid separated. This was removed by filtration and was recrystallized from hexane to yield 0.12 g. of *p*,*p*′-dimethylbiphenyl, m.p. 120.5–122° (reported[42] 122°). The infrared spectrum of this compound possessed a very strong band at 12.4 μ.

A 25.0-g. portion of the 109–111° distillation fraction was placed on a 75 × 3.5 cm. alumina (Merck 71707) column and eluted with hexane. The first 500 ml. of eluent was empty. The next liter of eluent contained 21.2 g. of oil which did not have a peak in its infrared spectrum at 12.4 μ and was identical to 2-phenyl-2-*p*-tolylpropane prepared by protonation of 2-phenyl-2-*p*-tolylpropylmagnesium chloride. The next liter of eluent contained 2.2 g. of oil which did have a 12.4 μ peak in its infrared spectrum. Finally, elution with 500 ml. of 10% ether in hexane brought down 1.1 g. of solid *p*,*p*′-dimethylbiphenyl, m.p. 120–122°.

The 21.2-g. chromatographic fraction was redistilled in a modified Claisen apparatus. A 19.4-g. cut of 2-phenyl-2-*p*-tolylpropane distilling at 110–111° at 0.5 mm. was taken. The infrared spectrum of this product was again identical

with that of 2-phenyl-2-*p*-tolylpropane prepared by protonation of 2-phenyl-2-*p*-tolylpropylmagnesium chloride.

_p_-(α,α-Dimethylbenzyl)-phenylacetic Acid from 2-Phenyl-2-*p*-tolylpropane.—Into a 10-ml. flask was placed 3.40 g. (0.016 mole) of 2-phenyl-2-*p*-tolylpropane, 2.0 g. (0.0148 mole) of sulfuryl chloride and 0.010 g. of benzoyl peroxide. The mixture was warmed slowly, finally to 90° for 1 hr., kept at 90° for 1 hr. further, then distilled directly with a modified Claisen apparatus at 0.05 mm. After about 3 drops of forerun containing some benzoic acid, the remaining material distilled at 115–116° with only a trace of dark residue remaining. The distillate of *p*-(α,α-dimethylbenzyl)-benzyl chloride weighed 3.2 g. (88%). It was dissolved in 30 ml. of dry ether and added to 2.4 g. (0.10 g. atom) of magnesium turnings in 30 ml. of ether. The Grignard reaction did not begin spontaneously, but addition of 0.05 ml. of 1,2-dibromoethane initiated a reaction which proceeded vigorously for 15 minutes. The reaction mixture was stirred for 1 hr. further at room temperature under nitrogen, then poured onto excess freshly pulverized Dry Ice. The product was acidified with hydrochloric acid and taken up in ether. The ether was extracted with 10% aqueous potassium hydroxide and the alkaline solution acidified with hydrochloric acid to a congo red end-point and ether extracted. The ether extracts were dried over sodium sulfate and concentrated *in vacuo* to give 2.32 g. of white solid, m.p. 70–72°. One crystallization from hexane gave 2.14 g. (84%) of *p*-(α,α-dimethyl)-phenylacetic acid as a white solid, m.p. 73–74°. The mixed melting point with the acid from the Arndt–Eistert synthesis was undepressed and the infrared spectra of the two samples were identical.

Reaction of 2-Phenyl-2-*p*-tolylpropane with Butyllithium.—A mixture of 10.0 g. (0.0476 mole) of 2-phenyl-2-*p*-tolylpropane and 25 ml. of a 0.92 N solution of butyllithium in ether was refluxed vigorously under ketyl-dried nitrogen with magnetic stirring for 4 hr. The mixture was cooled to room temperature and poured onto excess, freshly pulverized Dry Ice. The product was acidified and taken up in ether. The ether solution was extracted with 10% potassium hydroxide and the alkaline solution acidified with hydrochloric acid to a congo red end-point, then extracted with ether. The ether extracts were dried over sodium sulfate and concentrated *in vacuo* to yield 0.572 g. of oil. This material had an infrared spectrum very similar to that of *p*-(α,α-dimethylbenzyl)-phenylacetic acid but would not crystallize on being seeded. It was chromatographed on a 50 × 1.8 cm. silica gel column slurry packed with 10% ether in hexane. Four 500-ml. fractions were collected by elution with 10% ether in hexane. The first fraction was void. The second fraction contained 11 mg. of oil, the third contained 4 mg. of oil and the fourth contained 79 mg. of oil. The infrared spectra of these fractions indicated the presence of some *p*-(α,α-dimethylbenzyl)-phenylacetic acid, but the fractions did not seem to contain a pure compound. Fraction 5 was collected by elution with 500 ml. of 20% ether in hexane and weighed 0.335 g. It solidified to give material, m.p. 70–72°, and recrystallization from hexane gave 0.294 g. of crystals of *p*-(α,α-dimethylbenzyl)-phenylacetic acid, m.p. 73–74°. Mixed m.p. and infrared comparison with authentic material showed no differences.

Reaction of α-Methylstyrene with *p*-Tolyllithium.—To 100 ml. of 0.108 N *p*-tolyllithium in ether, prepared from *p*-bromotoluene, containing some unreacted lithium metal was added 2.36 g. (0.020 mole) of α-methylstyrene in 25 ml. of ether. The mixture was stirred under ketyl-purified nitrogen at room temperature. As there was no exothermic reaction and no color change during the addition, the reaction mixture was heated to reflux and kept refluxing under nitrogen for 2 hr.; it then was cooled to room temperature and carbonated by pouring onto excess freshly pulverized Dry Ice. Work-up as usual gave 6.21 g. of solid in the neutral fraction, from which was obtained 6.02 g. of recrystallized material, m.p. 92°, whose infrared spectrum indicated it to be di-*p*-tolyl ketone (reported[43] m.p. 95°).

The acidic fraction weighed 3.40 g. and was semi-solid. Two crystallizations from ether gave 2.16 g. of solid of *p*-toluic acid, m.p. 178–179°, mixed m.p. undepressed. The residue was concentrated to give 1.24 g. of material whose infrared spectrum indicated slightly impure *p*-toluic acid. This material was sublimed at 90° and 0.01 mm. to give 990 mg.

(42) F. Ullmann and G. M. Meyer, *Ann.*, **332**, 44 (1904).
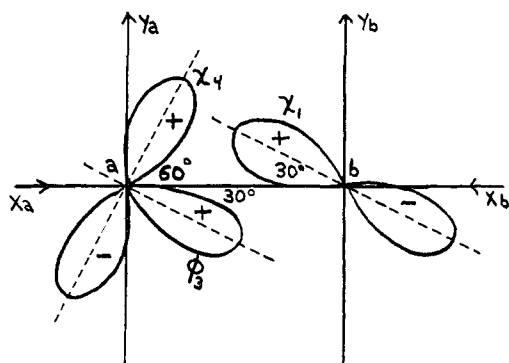
(43) W. D. Cohen, *Rec. trav. chim.*, **38**, 118 (1919).

Fig. 1.

Fig. 2.

of p-toluic acid and 195 mg. of residue. An infrared spectrum of the residue showed that it did not contain 2-methyl-2-phenyl-3-p-tolylpropionic acid, as characteristic bands of the latter compound at 9.3 and 11.6 μ were not present.

Ultraviolet Absorption Data.—The following were run in 95% ethanol. 3,3-Diphenylbutyric acid: 243 mμ shoulder (log ϵ 2.36), 249sh (2.50), 253sh (2.60), 258 peak (2.65), 264sh (2.60), 269 peak (2.53); 2-methyl-2,3-diphenylpropionic acid: 247.7 peak (2.49), 252.5pk (2.57), 257.7pk (2.64), 264.7pk (2.54); p-(α,α-dimethylbenzyl)-benzoic acid: 237pk (4.26); o-(α,α-dimethylbenzyl)-benzoic acid: 260pk (3.11); benzoic acid: 255pk (4.04), 270pk (2.96).

Calculations

Evaluation of Overlap and Exchange Integrals.—The three-membered ring of the bridged intermediate was taken as having the dimensions of cyclopropane. Transposing to a coördinate system (Fig. 1) having the C_a–C_1 bond as the x-axis, a y_a-axis passing through atom a and a y_b-axis passing through atom 1, one finds that he can express χ_1 as a linear combination of p-orbitals, χ_{pxb} and χ_{pyb}, centering at origin b and directed along the coördinate axes x_b and y_b; here the positive direction of χ_b is taken as right to left. Similarly, χ_4 can be expressed as a linear combination of χ_{pxa} and χ_{pya} while the hybrid orbital ϕ_3 is taken as a linear combination of χ_{pxa}, χ_{pya} and χ_{sa}; here the positive direction of x_a is taken as left to right. The orbitals whose linear combinations are used are pictured in Fig. 2. Since overlap integrals for orbitals of type and oriented as in Fig. 2 are given in Mulliken's tables,[44] overlap integrals for the pairs of orbitals in Fig. 1 may be evaluated by expanding the expression for each such overlap integral, $S_{ij} = \int \psi_i \psi_j \, dv$, using the orbitals in Table V for

TABLE V

ORBITALS USED IN EVALUATING OVERLAP INTEGRALS

$\chi_1 = (\sqrt{3}/2)\chi_{pxb} + (1/2)\chi_{pyb}$

$\phi_3 (sp^3) = (1/2)\chi_{sa} + (3/4)\chi_{pxa} - (\sqrt{3}/4)\chi_{pya}$

$\chi_4{}^a = (1/2)\chi_{pxa} + (\sqrt{3}/2)\chi_{pya}$

$\phi_3 (sp^2) = (1/\sqrt{3})\chi_{sa} + (1/\sqrt{2})\chi_{pxa} - (1/\sqrt{6})\chi_{pya}$

^{a} χ_4 here pertains only to cases B, D and E.

ψ_i and ψ_j. In the expansion (due to orthogonality), S-(sa, pyb), S(pxa, pyb) and S(pya, pxb) are zero, $S(\chi_1, \chi_2)$ was taken directly from Mulliken's tables. The expressions for the overlap integrals and the numerical values, assuming R_{ab} to be 1.54 Å., are given in Table VI.

The exchange integrals were evaluated by making use of Winstein's equation, $(H_{ij}/H_{kl}) = (S_{ij}/S_{kl})(1 + S_{kl})/(1 + S_{ij})$, relating exchange to overlap integrals.[45] In the present instance k and l were taken to refer to a pair of adjacent benzene carbon atoms; hence $H_{kl} = \beta$ and $S_{kl} = 0.247$. The values (in units of β) of the exchange integrals obtained and used were $H(\chi_1, \chi_4) = \delta = 0.927$, $H(\chi_1, \phi_3 - sp^3) = \epsilon_{sp_3} = 1.255$, $H(\chi_1, \phi_3-sp^2) = \epsilon_{sp_2} = 1.292$, $H(\chi_1, \chi_2) = \zeta = 0.810$, $H(sp^3-\sigma, sp^2-\sigma; 1.54$ Å.) $= 1.982$,

(44) R. S. Mulliken, C. A. Riecke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(45) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954); F. Wilcox, Jr., S. Winstein and W. G. McMillan, *ibid.*, **82**, 5450 (1960).
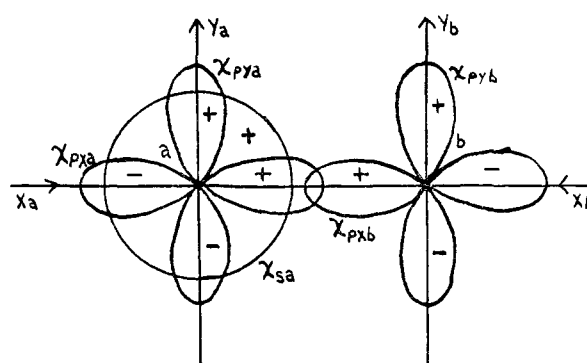
$H(sp^2-\sigma; sp^2-\sigma; 1.52$ Å.) $= 2.093$. Because of the reversal of sign of χ_4 in the direction of χ_2, $H(\chi_3, \chi_4)$ was taken as $-\delta$. The exchange integrals for the six ring p-orbitals were taken as one, in units of β.

Simplification of Secular Determinants.—Use was made of the fact that in secular determinants expressed in terms of symmetry orbitals the element A_{ij} will vanish if the orbitals ψ_i and ψ_j do not have the same symmetry. The secular determinants given earlier may be rearranged, by proper addition and subtraction of rows and columns, so that the secular determinant is expressed in terms of symmetry rather than localized orbitals; the determinants then fall apart into small ones of different symmetry. Alternatively, the smaller determinants may be set up directly.

Species XXIIIA.—Using the C_2 group[22] one finds two orbitals of A symmetry: $\chi_1 + \chi_2$ (not normalized) and ϕ_3 as well as one of the B symmetry: $\chi_1 - \chi_2$. The resulting secular determinant is

$$
\begin{array}{c|ccc}
 & \chi_1 + \chi_2 & \phi_3 & \chi_1 - \chi_2 \\
\hline
\chi_1 + \chi_2 & 2X + 2\zeta & 2\epsilon & 0 \\
\phi_3 & 2\epsilon & X & 0 \\
\chi_1 - \chi_2 & 0 & 0 & 2X - 2\zeta
\end{array}
= 0 \text{ or }
\begin{vmatrix}
2X + 2\zeta & 2\epsilon \\
2\epsilon & X
\end{vmatrix}
$$

$$= 0 \text{ and } (2X - 2\zeta) = 0$$

Hence $X = -2.184$, 1.374 (A symm) and 0.810 (B symm), using the calculated exchange integrals.

Species XXIIIB.—Using the C_{2v} group one finds two A_1 orbitals: $\chi_1 + \chi_3$ and ϕ_3; two A_2 orbitals: $\chi_5 - \chi_9$ and $\chi_6 - \chi_3$; and five B_2 orbitals: $\chi_1 - \chi_2$, χ_4, $\chi_5 + \chi_9$, $\chi_6 + \chi_8$ and χ_7. The symmetry determinants and solutions are

$$
A_1 \quad
\begin{vmatrix}
2X + 2\zeta & 2\epsilon \\
2\epsilon & X
\end{vmatrix} = 0
\qquad
A_2 \quad
\begin{vmatrix}
2X & 2 \\
2 & 2X
\end{vmatrix} = 0
$$

$$X = -2.277, 1.467 \qquad X = \pm 1.000$$

and B_2:

$$
\begin{vmatrix}
2X - 2\zeta & 2\delta & 0 & 0 & 0 \\
2\delta & X & 2 & 0 & 0 \\
0 & 2 & 2X & 2 & 0 \\
0 & 0 & 2 & 2X & 2 \\
0 & 0 & 0 & 2 & X
\end{vmatrix} = 0
$$

IBM 650 evaluation gave $X = -2.131, -1.269, 0.333, 1.543, 2.334$.

Species XXIIIC.—Some simplification was possible as a result of pseudosymmetry; a related species was constructed with the benzene ring symmetric with respect to the plane of the three ring. Two orbitals antisymmetric with respect to this plane gave $X = \pm 1.000$. The remaining seven orbitals symmetric with respect to the plane gave the determinant:

$$
\begin{vmatrix}
X & \epsilon & \epsilon & 0 & 0 & 0 & 0 \\
\epsilon & X & \zeta & 0 & 0 & 0 & 0 \\
\epsilon & \zeta & X & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & X & 2 & 0 & 0 \\
0 & 0 & 0 & 2 & 2X & 2 & 0 \\
0 & 0 & 0 & 0 & 2 & 2X & 2 \\
0 & 0 & 0 & 0 & 0 & 2 & X
\end{vmatrix} = 0
$$

whose solutions as given by the IBM 650 were $X = -2.514, -1.922, -1.035, 0.528, 1.203, 1.568, 2.171$

TABLE VI

OVERLAP INTEGRALS

Overlap integral	Expression	Value
$S(\chi_1, \chi_4{}^a)$	$(\sqrt{3}/4)S(\text{pxa,pxb}) + (\sqrt{3}/4)S(\text{pya,pyb})$	0.225
$S(\chi_1, \phi_3\text{-sp}^1)$	$(\sqrt{3}/4)S(\text{sa,pxb}) + (3\sqrt{3}/8)S(\text{pxa,pxb}) - (\sqrt{3}/8)S(\text{pya,pyb})$	.330
$S(\chi_1, \phi_3\text{-sp}^2)$	$(1/2)S(\text{sa,pxb}) + (\sqrt{3}/2\sqrt{2})S(\text{pxa,pxb}) - (1/2\sqrt{6})S(\text{pya,pyb})$	.344
$S(\chi_1, \chi_2)$		.191
$S(\text{sp}^3\text{-}\sigma,\ \text{sp}^3\text{-}\sigma;\ 1.54\ \text{Å}.)$		.646
$S(\text{sp}^2\text{-}\sigma,\ \text{sp}^3\text{-}\sigma;\ 1.52\ \text{Å}.)$		.673

^{a} χ_4 here refers only to cases B, D, E.

Species XXIIID.—Similar use of pseudosymmetry was made. Eigenvalues for MO's antisymmetric with respect to the plane employed were $X = -1, -1, 1, 1$. Those for symmetric MO's were obtained from the IBM 650 solution of the 11 by 11 determinant remaining: $X = -2.491, -2.138, -1.906, -1.316, -0.9581, 0.289, 0.924, 1.475, 1.599, 2.053$ and 2.471.

Species XXIIIE.—Eigenvalues of orbitals symmetric with respect to the species' plane of symmetry were at $X = -2.727, -2.143, -1.880, -1.346, -1.000, -0.936, +0.2549, +0.897, +1.000, +1.511, +1.644, +2.086, +2.639$. Energies of antisymmetric orbitals were found

as follows: one at -2.000, three at -1.000, three at $+1.000$ and one at $+2.000$.

The Non-bridged Species.—The MO's used here were merely the zero level atomic p-orbital at carbon 2, the molecular orbitals of the unconjugated phenyl groups, as present and the bonding orbital of the σ-bond bearing the group about to migrate.

Benzoyl Peroxide as an Initiator for Hydrocarbon Oxidation

By GEORGE S. HAMMOND AND UMA SANKAR NANDI

The efficiency of benzoyl peroxide as an initiator for tetralin oxidation is anomalously low and the peroxide is essentially no initiator for cumene oxidation. This erratic behavior is somewhat solvent-dependent. The evidence suggests strongly that one of the radicals derived from the peroxide (benzoyloxy, phenyl or an adduct of phenyl to an aromatic nucleus) is incapable of reaction with oxygen and sufficiently long-lived to dominate in the chain-termination step.

For some time we have been using hydrocarbon oxidation as a means of measuring the efficiency of free radical production during the decomposition of azonitriles and ketenimines.[1-5] We considered it worthwhile to investigate benzoyl peroxide by the same technique with the hope that the study might shed new light on the idiosyncracies in the decomposition of the peroxide[6] and on the chemistry of the fragments produced in the decomposition. The results, which show that the behavior of the peroxide as an initiator depends strongly on the nature of the substrate and solvent, are reported in this paper.

Results and Discussion

When tetralin was used as a substrate no alarming results were disclosed. Efficiency measurements were made by measuring the induction periods produced by known amounts of 2,6-di-t-butyl-p-cresol (DBC), an antioxidant which is known[1] to stop two oxidation chains per molecule.

Clearly defined breaks marked the end of the inhibition periods. The rates of decomposition of benzoyl peroxide were measured in the presence of nitrogen and the antioxidant, using iodometric assay for residual peroxide. A plot of the data for typical oxidation runs with added inhibitor is shown in Fig. 1, and the data are summarized in Tables I and II. Since the peroxide decomposition rates are independent of concentration, it appears that the scavenger is effective in eliminating induced decomposition.[7-9]

TABLE I

RATE OF DECOMPOSITION OF BENZOYL PEROXIDE IN THE PRESENCE OF 2,6-DI-t-BUTYL-p-CRESOL AT 70° UNDER NITROGEN

Solvent	Init. concn. of Bz_2O_2, moles l.$^{-1}$	$k_d \times 10^5$, sec.$^{-1}$
Benzene	0.25	1.18
Benzene	.50	1.17
Acetonitrile	.25	1.76
Chlorobenzene	.25	1.35
Dioxane	.25	1.30

Table II includes the apparent efficiency factors a calculated using the measured peroxide decomposition rates and the data for induction periods.

(1) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, J. Am. Chem. Soc., 77, 3233 (1955).

(2) G. S. Hammond, J. N. Sen and C. E. Boozer, ibid., 77, 3244 (1955).

(3) G. S. Hammond, O. D. Trapp, R. T. Keys and D. L. Neff, ibid., 81, 4878 (1959).

(4) C.-H. S. Wu, G. S. Hammond and J. M. Wright, ibid., 82, 5386 (1960).

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(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 474.

(7) K. Nozaki and P. D. Bartlett, J. Am. Chem., Soc., 68, 1686 (1946).

(8) G. S. Hammond, ibid., 72, 3737 (1950).

(9) C. G. Swain, W. H. Stockmayer and J. T. Clarke, ibid., 72, 5426 (1950).