an oven at 150° for 2 days. The particle size of these inert ingredients did not appear to be critical.

The preparation of diphenylketene-*p*-tolylimine (I) represents a general procedure for the preparation of ketenimines. Modifications, where used, are noted.

Diphenylketene-*p*-tolylimine (I).—To a stirred solution of 10.0 g. of N-(*p*-tolyl) diphenylacetamide (XIII) in 300 ml. of dry pyridine were added 25.0 g. of phosphorus pentoxide, 50.0 g. of alumina, and 200 ml. of pyridine. The mixture was refluxed for 7 hr., then allowed to cool, and filtered. The residue was leached with pyridine and the pyridine was evaporated under reduced pressure from the combined filtrates. The crystalline mass was dissolved in dry petroleum ether, filtered, concentrated, and allowed to crystallize. Bright yellow stout needles of ketenimine (I), 8.2 g. (87%), m.p. 82–84°,[5a] were obtained.

The replacement of alumina with Florisil or sand yielded approximately the same results. In the absence of these materials the reaction was very slow, although an 80% yield was obtained.

The *o*-methoxyketenimine (VIII) was prepared using Florisil instead of alumina. The *p*-bromoketenimine (II) was prepared in the stated yield with no inert ingredients added; using alumina in the dehydrating mixture lowered the yield to 26%.

In the preparation of the aromatic ketene aliphatic imine (IX), triethylamine was preferred to pyridine. In the preparation of the aliphatic ketene aromatic imine (X), 2,4,6-collidine was the preferred base. In the preparation of *p*-methylthiophenyl compound (IV), 10 equivalents of phosphorus pentoxide instead of the usual 5 equivalents were required to obtain 75% yield.

Hydrolysis of Ketenimines.—For proof of structure, all the ketenimines were hydrolyzed to the starting amides.[5b] For this purpose, 200 mg. of the ketenimine was dissolved in 10 ml. of acetone and 1 ml. of 4 *N* hydrochloric acid was added. The solution was allowed to stand until the characteristic yellow color of the ketenimine was discharged. The reaction mixture was made turbid by the addition of water, if necessary, and allowed to stand overnight. The resulting solid was filtered and recrystallized from the proper solvent. The yield of recrystallized amide in all cases was over 75%. Mixture melting points with the original amide were undepressed in all cases.

Asymmetric Reductions. XI. The Grignard Reagent from (+)-1-Chloro-2-phenylbutane[1]

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Reduction of a series of alkyl phenyl ketones by the optically active Grignard reagent from (+)-1-chloro-2-phenylbutane in ether at room temperature has produced the corresponding alkylphenylcarbinols with the following optical purities: methyl, 37%; ethyl, 52%; isobutyl, 53%; isopropyl, 82%; and *t*-butyl, 14%. These per cent asymmetric reductions parallel, but, with the exception of the *t*-butyl case, are much higher than those observed when the same ketones were reduced with the Grignard reagent from (+)-1-chloro-2-methylbutane. The use of tetrahydrofuran instead of ether solvent reduced the stereoselectivity from 82 to 75% at 35°. The effect of a 66° variation in temperature on this reaction in tetrahydrofuran was to increase the per cent asymmetric reduction from 69% at 66° to 78% at 0°; however, the difference in free energy of activation, $\Delta\Delta F^*$, did not vary over this range. The 82% asymmetric reduction of the isoproply phenyl ketone (which corresponds to the production of 91% *l*-, 9% *d*-carbinol ($\Delta\Delta F^*$ = 1.45 kcal./mole) is the highest asymmetric synthesis reported for a reagent containing a single asymmetric center. The factors contributing to this high stereoselectivity and the surprisingly low value obtained in the phenyl *t*-butyl case are discussed.

With the specific purpose of finding variations which will lead to stereoselectivities approaching those of enzyme systems, we have continued our studies on the asymmetric Grignard reduction reaction. The highest asymmetric reductions which we observed with the Grignard reagent from (+)-chloro-2-methylbutane were 24% in the reduction of isopropyl ketone and 25% in the reduction of cyclohexyl phenyl ketone.[3,4]

Vavon and Angelo[5] reported a 72% asymmetric synthesis in the reduction of *t*-butyl phenyl ketone using the Grignard reagent from "pinene hydrochloride." The reducing agent in this case (isobornylmagnesium chloride) has three asymmetric centers and after the hydrogen is transferred the olefin formed (bornylene) still retains two of these three centers and is optically active. The reduction of 1-deuteriobenzaldehyde with isobornyloxymagnesium in a Meerwein–Ponndorf type reaction by Streitwieser and Wolfe[6] produced optically active 1-deuteriobenzyl alcohol which has been assumed to approach optical purity.[7] In this case the reducing agent has three asymmetric centers, only one of which is lost during the reduction.

The reduction of methyl *t*-butyl ketone by "diisopinocamphenylborane," prepared from diborane and α-pinene, carried out by Brown and Bigley,[8] has given methyl-*t*-butylcarbinol of 35% optical purity, and hydroboration of *cis*-2-butene followed by peroxide oxidation has given 2-butanol of better than 90% optical purity.[9] Again, this has been brought about with a reagent containing multiple asymmetric centers which are not destroyed in the reaction.

We believe that in a properly designed system containing only one asymmetric center the difference in the energies of activations between the *d*- and *l*-transition states may be sufficient to permit asymmetric reductions approaching 100%. In order to elucidate further the effect of structural variations in the Grignard reagent upon the degree of asymmetric reduction we have investigated the reduction of some alkyl phenyl

(1) We acknowledge with gratitude support of these investigations by the U. S. Public Health Service (RG-5248) and the National Science Foundation (GF-955).

(2) National Science Foundation Post Doctoral Fellow, 1962.

(3) R. MacLeod, F. J. Welch, and H. S. Mosher, *J. Am. Chem. Soc.*, **82**, 876 (1960).

(4) E. P. Burrows, F. J. Welch, and H. S. Mosher, *ibid.*, **82**, 880 (1960).

(5) G. Vavon and B. Angelo, *Compt. rend.*, **224**, 1435 (1947).

(6) A. Streitwieser, J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 340 (1959).

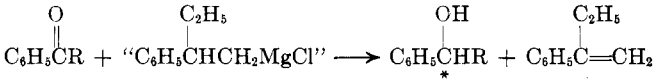
(7) In a preliminary investigation [H. S. Mosher, and V. Althouse, paper presented at the 140th National Meeting of the American Chemical Society Chicago, Ill., September, 1961] it was reported that reduction of 1-deuteriobenzaldehyde by actively fermenting yeast produced 1-deuteriobenzyl alcohol with a rotation 2.2 times that obtained from the isobornylmagnesium reduction. This case is still under investigation by the present authors and by Dr. Streitwieser (private communication.)

(8) H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, **83**, 3166 (1961).

(9) H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961).

TABLE I

ACTIVE PHENYLAKLYLCARBINOLS FROM GRIGNARD REDUCTIONS

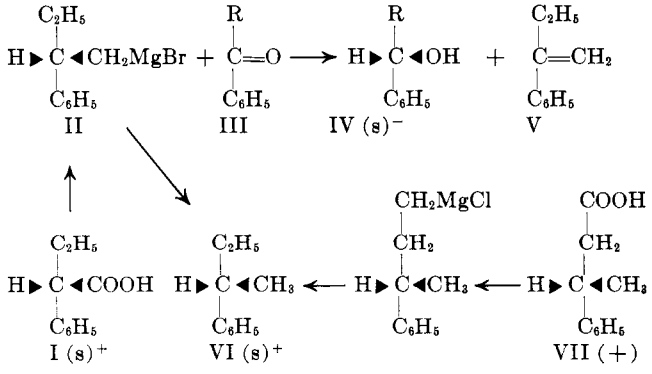


Alkyl group, R	Solvent (T, °C.)	Carbinol yield,[a] %	Minimum carbinol purity,[b] %	Rotation observed,[c] [α]D, deg. (T, °C.)	Specific rotation corrected[d] [α]D, deg.	Maximum lit. rotation[e] [α]D, deg. (T, °C.)	Asymmetric reduction,[f] %	ΔΔF*,[g] kcal./mole
Me	Ether (25)	19	98	−19.86 (28)[h]	−20.6[o]	43.6 (25)	47.2	0.606
Et	Ether (25)	89	95	−14.65 (27)[h]	−15.2[p]	29.1 (27)	52.2	0.686
i-Bu	Ether (25)	63	98	−6.34 (28)[i]	−17.2[p]	32.3 (26)	53.2	0.729
i-Pr	Ether (25)	69	97	−3.67 (27)[j]	−39.2[p]	47.7 (20)	82.1	1.446
i-Pr	THF (66)	44	99	−3.06 (28)[k]	−32.9[q]	47.7 (20)	69.1	1.148
i-Pr	THF (35)	48	97	−2.98 (27)[l]	−35.7[r]	47.7 (20)	74.8	1.147
i-Pr	THF (0)	45	99	−3.58 (28)[m]	−37.4[q]	47.7 (20)	78.4	1.146
t-Bu	Ether (25)	77	99	−1.05 (27)[n]	−5.72	36.2 (20)	15.8	0.189

[a] Based on gas chromatographic analysis after simple distillation. [b] Estimated from the gas chromatograms of the products after purification *via* preparative gas chromatography (Beckman Megachrom). [c] All rotations were taken in center filled tubes with the zero reading determined without altering the caps and are to 0.03° or better, usually 0.01°. [d] The corrected specific rotations are for the same temperatures as the observed rotations and were calculated by correcting for the per cent purity of the carbinol, assuming that the impurities (mostly ketone) were optically inactive and correcting for the optical purity of the chloride used for the Grignard preparation. The optical purity of the chloride was based on a value of $[\alpha]^{27}D$ 5.95° for optically pure 1-chloro-2-phenylbutane. [e] See ref. 3 and 4. Concentrations and solvents were comparable to those reported for the maximum literature values. [f] The per cent asymmetric reduction is defined as 100 × [α] corrected/[α] maximum. [g] $\Delta\Delta F^*$ is calculated from $\Delta\Delta F^* = -RT \ln k_l/k_d$. [h] Neat liquid, $l = 1$. [i] *n*-Heptane solvent, c 19.00, $l = 2$. [j] Ether solvent, c 5.00, $l = 2$. [k] Ether solvent, c 4.965, $l = 2$. [l] Ether solvent, c 4.473, $l = 2$. [m] Ether solvent, c 5.010, $l = 2$. [n] Ether solvent, c 9.49, $l = 2$. [o] Optical purity of chloride used for Grignard reagent, 98.5%. [p] Optical purity of chloride, 97.7%. [q] Optical purity of chloride, 93.3%. [r] Optical purity of chloride, 93.6%.

ketones with the Grignard reagent from (+)-1-chloro-2-phenylbutane.

The Grignard reagent (II) from (+)-1-chloro-2-phenylbutane was prepared from (+)-2-phenylbutanoic acid (I) by the sequence illustrated. The resolved 2-phenylbutanoic acid was 97.3% optically pure based on the maximum values reported.[10] That the sequence of reactions went without significant racemization was verified by decomposing an aliquot of the Grignard reagent (II) with water to give (+)-2-phenylbutane (VI) which had a rotation that was 97.7% of the value reported by Cram[11] who prepared it by a similar sequence of reactions, but started from resolved 3-phenylbutyric acid (VII). Furthermore, this sequence of reactions interrelates 2-phenylbutyric (I) and 3-phenylbutyric (VII) acids and verifies the consistency of the assigned[11,12] configurations as shown.



The Grignard reagent (II) was treated with each of the alkyl phenyl ketones listed in Table I with the results shown. In each case the preponderant alkylphenylcarbinol isomer was levorotatory and thus had the absolute s configuration[13] as represented by IV. From a consideration of the cyclic transition state mechanism for the hydrogen transfer process in which the interactions of the two phenyl groups are minimized by occupying unopposed positions, as in VIII, one predicts the s configuration (IV) for these products as observed. Thus the predictive value of these assumptions from a configurational standpoint is verified in spite of the fact that this must represent an oversimplification of the problem.

From a quantitative standpoint, the results in Table I can be compared to those obtained with the Grignard reagent from (+)-1-chloro-2-methylbutane[3] where a methyl group is substituted for the phenyl group in the Grignard reagent of the present investigation. One would predict that the greater steric requirement imposed on the transition state resulting from the incorporation of the more bulky phenyl group would lead to greater stereoselectivity. This also has been verified, and in a dramatic fashion, in the case of isopropyl phenyl ketone where 82% asymmetric reduction was observed with the Grignard reagent from (+)-1-chloro-2-phenylbutane as compared to 25% asymmetric reduction with the Grignard reagent from (+)-1-chloro-2-methylbutane.

It is thus seen that a *single* asymmetric center in the reducing agent is capable of inducing a rather high order of asymmetry in the product. The 82% asymmetric reduction using diethyl ether solvent at 35° represents the production of 91% of the s isomer and 9% of the R isomer and corresponds to a difference in the free energies of activation ($\Delta\Delta F^*$) of the competing transition states of about 1.45 kcal./mole at 25°.

(10) (a) K. Petterson, *Arkiv. Kemi*, **10**, 283 (1956); (b) M. Delépine and F. Larèze, *Bull. soc. chim. France*, [5] **22**, 104 (1955); (c) B. Sjöberg, *Acta Chem. Scand.*, **14**, 273 (1960); (d) P. A. Levene, L. A. Mikeska, and K. Passoth, *J. Biol. Chem.*, **88**, 27 (1930).

(11) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952). The values for the asymmetric reductions reported in Table I have been corrected on the basis of a value of $[\alpha]^{25}D$ 5.95° as the rotation of optically pure 1-chloro-2-phenylbutane.

(12) Cram used the (−) isomer of VII and obtained the (−) enantiomorph of VI opposite to that represented here.

(13) The configurational assignments have been discussed in previous papers in this series, ref. 3 and 4.

This represents a fourfold increase in the $\Delta\Delta F^*$ value (0.35 kcal./mole at 25°) for the asymmetric reduction of the same ketone by the previous Grignard reagent from (+)-chloro-2-methylbutane.

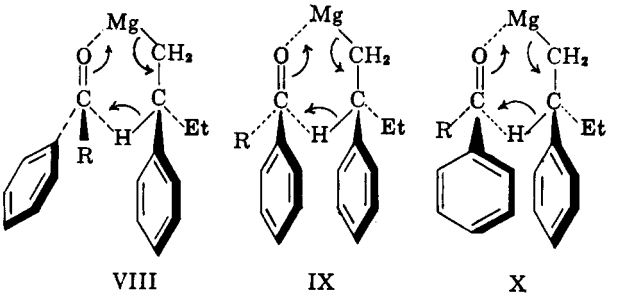
A large gap still exists between these values and the *total* asymmetric synthesis of enzyme systems; nevertheless, these results clearly indicate that the steric requirements at the immediate site of reaction are of utmost importance in the organic chemical reaction and, by inference, in biochemical enzyme processes dealing with low molecular weight substrates as well.

Of special interest in the experiments using the present Grignard reagent (II) is the dramatic drop in stereoselectivity in going from isopropyl phenyl ketone (82%) to more hindered *t*-butyl phenyl ketone (16%). A decrease, but of a smaller amount, of from 25% to 16% was previously noted[3] for the asymmetric reduction of the same two ketones by the less hindered Grignard from (+)-1-chloro-2-methylbutane; thus the trend is confirmed, although greatly magnified, in the present case. From a purely steric interpretation one would conclude that the phenyl group is much larger than the tertiary butyl group, although it is not obvious that this should be so. It is recognized under the same conditions of solvent and temperature that there are at least three major factors contributing to the over-all extent of asymmetric reduction: steric, electronic, and rate.

In a study of the rate of reduction of a series of alkyl phenyl ketones by sodium borohydride, Brown and Ichikawa[14] observed that the relative rates of reduction of alkyl phenyl ketones was in the order: methyl, 0.136; ethyl, 0.076; isopropyl, 0.071; isobutyl, 0.011; and *t*-butyl, 2.47. The fact that the rate of reduction of the highly hindered *t*-butyl phenyl ketone increased instead of decreased was attributed to the large steric strain which forced the phenyl group out of coplanarity with the carbonyl group and thus allowed the former to exert its natural inductive effect without resonance interaction. The inhibition of resonance interactions between the carbonyl and phenyl groups has been independently demonstrated on spectroscopic grounds.[15]

The same factors must be operative on the Grignard reduction reaction although the steric requirements for the Grignard reagent must be much greater than those for the borohydride reagent. It may be reasoned than that the decrease in stereoselectivity has its origin in either the noncoplanar conformation of the *t*-butyl phenyl ketone or in the enhanced rate of reduction which this noncoplanarity allows. It is difficult to evaluate properly this role of coplanarity in the transition state under consideration but a study of models in which only steric considerations are evaluated seems to indicate that noncoplanarity should lead to enhanced steric interactions and, therefore, greater stereoselectivity contrary to what is observed. On the other hand, a faster over-all rate of reduction should result in decreased stereoselectivity.

In the transition states of the reactions being considered, that one leading to the predominant alcohol of the s configuration may be represented by VIII and that leading to the less favored enantiomorph by IX. It is the difference in energies of activation ($\Delta\Delta F^*$) of these two transition states which is responsible for the asymmetric reduction observed. The transition of the carbonyl carbon atom of the ketone from trigonal to tetrahedral, and the concomitant reverse transition of the carbon atom attached to the phenyl group of the Grignard reagent from tetrahedral to trigonal as the reaction proceeds, will tend to increase the planarity of the cyclic transition states and will tend to bring the two phenyl groups face to face in the nonpreferred transition state IX. The electronic repulsions of these two phenyl rings, which are minimized in VIII, rather than steric interactions may be the factor accounting for the high stereoselectivity in this series.



VIII IX X

In the case of the extreme steric effect of the *t*-butyl group, which reduces the coplanarity of the phenyl group attached to the carbonyl carbon atom, the nonpreferred transition state may be represented as X. Although this conformation apparently increases the steric interactions, it may decrease the electronic repulsions even more and at the over-all expense of stereoselectivity.

It is difficult to assess the relative importance of these factors. In addition, no absolute rate data are available in order to evaluate this additional variable. Investigations on further examples in which the steric and electronic factors may be separated are in progress.

Experimental

Materials.—The alkyl phenyl ketones were distilled under nitrogen before use, and their purity verified by gas–liquid chromatography using a Wilkens Model A-90 Aerograph fitted with a 10% Ucon Polar column. Tetrahydrofuran was purified by allowing it to stand over potassium hydroxide for 24 hr., refluxing with lithium aluminum hydride for 3 hr., and finally distilling. It was stored over sodium wire.

Resolution of 2-Phenylbutanoic Acid.—The procedure of Levene, Mikeska, and Passoth[10d] was followed. From 400 g. of racemic acid was obtained, after five crystallizations, 143.1 g. of (+)-2-phenylbutanoic acid, $[\alpha]^{26}D$ +93.2° (neat, l = 1), b.p. 126–127° (2 mm.). On the basis of the maximum value in the literature[10a] of $[\alpha]^{23}D$ −95.8°, this acid is 97.3% optically pure.

Reduction of (+)-2-Phenylbutanoic Acid.—To lithium aluminum hydride (37.3 g., 0.98 mole) in anhydrous ether (400 ml.) was added (+)-2-phenylbutanoic acid (143.1 g., 0.87 mole, $[\alpha]^{26}D$ +93.2, neat, l = 1) dissolved in 100 ml. of ether. After addition was complete, the mixture was refluxed for 4.5 hr. A small amount of ice was added to decompose the excess lithium aluminum hydride, and the reaction mixture was hydrolyzed with 10% sodium hydroxide solution. Ether extracts of the aqueous basic solution were dried over anhydrous magnesium sulfate and distilled to yield (+)-2-phenylbutanol, 119.6 g., b.p. 94–96° (2 mm.), $[\alpha]^{25}D$ +16.5° (neat, l = 1). V.p.c. failed to detect the presence of any impurities.

(+)-1-Chloro-2-phenylbutane.—To 119.6 g. (0.81 mole) of (+)-2-phenylbutanol, $[\alpha]^{25}D$ +16.5° (neat), in 121.5 g. (1.5 mole) of dry pyridine was added slowly 152 g. (1.3 mole) of thionyl chloride with stirring at 0–10°. The resulting thick mixture was stirred for 4 hr. at 0–10° and then warmed. At approxi-

(14) H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **84**, 373 (1962).
(15) G. D. Hedden and W. G. Brown, *ibid.*, **75**, 3744 (1953).

mately 70° a vigorous evolution of gas was observed and after heating for 17 hr. at 90°, the reaction mixture was cooled, and the excess thionyl chloride was decomposed with ice. The upper layer was separated and combined with ether extracts of the lower layer, washed successively with cold saturated sodium bicarbonate solution (three times) and with water (once), dried over anhydrous magnesium sulfate, and distilled to give (+)-1-chloro-2-phenylbutane, b.p. 74–75° (4 mm.), 110.4 g. (81%), $[\alpha]^{28}D$ +5.75 ± 0.01° (neat, l = 1), 97.7% optically pure based on its conversion to (+)-2-phenylbutane.

Asymmetric Reductions.—The Grignard reagent was prepared under purified nitrogen from (+)-1-chloro-2-phenylbutane in anhydrous ether (or tetrahydrofuran) in the usual manner[3,4] using highly purified magnesium.[16] An aliquot of this Grignard solution (about 0.06 mole of an 0.2 *M* solution) was added dropwise with stirring to the solution of alkyl phenyl ketone (about 0.06 mole in 25 ml. of ether or tetrahydrofuran) maintained in water bath at the specified temperature. The runs reported in Table I in ether solvent, with the exception of the first, used (+)-1-chloro-2-phenylbutane described earlier, $[\alpha]^{28}D$ +5.75° (neat, l = 1). The runs in tetrahydrofuran were made with a sample of (+)-1-chloro-2-phenylbutane with $[\alpha]^{27.5}D$ +5.55°. A suitable correction for the optical purity of the Grignard reagent, as determined by conversion to the (+)-2-phenylbutane, is made in the calculated per cent asymmetric reduction. After 18 hr., the reaction mixture was hydrolyzed with an ice-cold ammonium chloride solution. The ether layer was combined with several ether extracts of the aqueous layer and dried over magnesium sulfate. The ether extracts were fractionated through a short column, and the fractions were analyzed with an Aerograph A-90 vapor phase chromatograph. The carbinol fraction was then purified on a Beckman Megachrom preparative gas chromatograph fitted with a 12-ft. 10% Ucon Polar column, using helium as the carrier gas. Under a vacuum of less than 1 mm. the carbinol was distilled from the collection trap into a specially designed centrifuge tube. The purity of the alcohol was then established on an Aerograph A-90 gas chromatograph. The results are summarized in Table I.

(+)-2-**Phenylbutane.**—An aliquot of the prepared Grignard reagent from (+)-1-chlorophenylbutane (0.04 mole) was added to an ice-cold solution of ammonium chloride, and the mixture extracted with ether. The ether extracts were washed with saturated brine, dried over anhydrous magnesium sulfate, and distilled to give (+)-2-phenylbutane, b.p. 31–33° (4 mm.), 4.11 g., $[\alpha]^{26}D$ +23.76 ± 0.02° (neat, l = 1).[17] Analysis by gas chromatography failed to detect any impurity.

Acknowledgment.—We are indebted to Professor Kurt Mislow for valuable discussions concerning these experiments.

(16) We gratefully acknowledge a gift from Dow Chemical Co. of sublimed magnesium with the following upper limits of elemental impurities in parts per million: Al, 1; Cu, 1; Fe, 4; Mn, 2; Ni, 4; Pb, 10; Si, 10; Sn, 10; Zn, 100; Ba, 1; Ca, 18; K, 5; Na, 6; Sr, 1.

(17) This value is 97.7% of the maximum value of $[\alpha]^{28}D$ 24.3° (neat, l = 1) reported by Cram.[11] Based on this hydrocarbon value the Grignard reagent and the chloride from which it was prepared will be considered 97.7% optically pure.

Alicyclic Syntheses. I. The Diels–Alder Reaction of 2-Phenylbutadiene with Citraconic Anhydride and 5-*p*-Tolylthiotoluquinone

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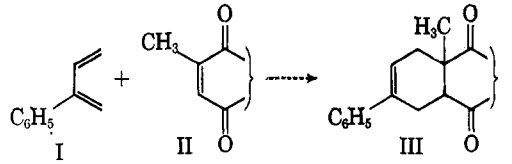
The identity of the adduct of 2-phenyl-1,3-butadiene and citraconic anhydride has been established as *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV), contrary to what would have been predicted from a consideration of polar factors. The significance of this and related Diels–Alder reactions is discussed and a mechanism to account for the results is propounded. The stereochemical configurations of the hydrogenation products VII and IX of the adduct IV and of its *trans* isomeride VIII, respectively, have been assigned on the basis of a conformation analytical argument. Use of an arylthiotoluquinone X has been made in an analogous addition to phenylbutadiene to force the generation of angularly methylated decalin systems XI, XII, XIII. Substance XI was desulfurated and reduced in one operation with zinc–acetic acid. Substances XII and XIII were desired as models in the synthesis of steroids lacking ring B.

It was desired to acquire an understanding of the mode of addition of 2-phenyl-1,3-butadiene to unsymmetrical dienophiles of the type II as an introduction to projected syntheses of substances incorporating



I II III

part structure III. Such structures bearing a 1,4-arylmethyl relationship were desired in projected syntheses[2] of 19-nor steroidal compounds lacking ring B.

Subsequent to the inception of this work, there have appeared disclosures of similar activity from other laboratories aimed at the synthesis of such substances,[3] and one case, that of estrone and estradiol lacking ring B,[4] was shown to possess considerable estrogenic activity.

2-Phenyl-1,3-butadiene[5] was treated with citraconic anhydride, and the product was isolated in good yield more conveniently as the diacid. The orientation of the angular methyl group and the identity of the adduct as *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV) were established as follows.

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(2) Additionally, polycyclic substances containing styryl moieties and available by Diels–Alder reactions were desired to test the acid-catalyzed benzyl hydroperoxide transformation of such to oxo derivatives in another synthetic problem. The facile conversion of α-methylstyrene or the derived tertiary alcohol or chloride therefrom to phenol and acetone by Kharasch and co-workers, *J. Org. Chem.*, **15**, 748 (1950), and later papers [see also H. Kwart and R. T. Keen, *J. Am. Chem. Soc.*, **81**, 943 (1959), for a related transformation] suggested the possibility of utilizing such a sequence in synthetic work to introduce carbonyl groups at sites suitably earmarked initially as styryl functions. This scheme, an additional portion of which is presented in paper II of this series, V. Georgian and J. Lepe M., *J. Org. Chem.*, **29**, 45 (1964), is under investigation.

(3) A. J. Birch, E. Pride, and H. Smith *J. Chem. Soc.*, 4688 (1958); R. H. Jaeger, *Tetrahedron*, **2**, 326 (1958).

(4) F. C. Novello, U. S. Patent 2,886,589 (May 12, 1959).

(5) C. C. Price, F. L. Benton, and C. J. Schmidle, *J. Am. Chem. Soc.*, **71**, 2860 (1949).