It is the behavior in the acid solvents that is most striking. Catalysis by acid as found by Blomquist and Ferris[12] for *t*-butyl perbenzoate in several solvents containing trichloroacetic acid and as suggested by our experiment with heptafluorobutyric acid, is not apparent in most of the acids shown in Table IV. In acetic, α-chloropropionic, propionic and *n*-butyric acids, the rates are not greatly different from those in chlorobenzene, and in the case of the last two are slightly lower. Although α-chloropropionic acid is a much stronger acid than acetic acid, the rate in it is smaller. Examination of the structures of these four acids suggested that their effects may be related to the number and strength of binding of the hydrogen atoms on the carbon atom alpha to the carboxylate group. This further suggested trying an acid with no hydrogen in the α-position, which explains the choice of α-chloroisobutyric acid.

The great effect of the absence of hydrogen atoms on the α-carbon atom is shown by the more than fivefold increase in rate in α-chloroisobutyric acid above that in α-chloropropionic acid. When a mixture of 10 mole-per cent. of isobutyric acid and 90 mole-per cent. of α-chloroisobutyric acid was used as solvent with *t*-butyl permyristate at 110°, the 10^5k value was 29.5 sec.$^{-1}$, showing the inhibitory effect of the presence of the isobutyric acid.

These results show that the acid catalysis expected of a carboxylic acid is diminished greatly if the acid has one or more hydrogen atoms on its α-carbon atom. This stabilizing or inhibitory effect shows a dependence also upon the other atoms attached to the α-carbon atom and in the case of propionic and butyric acids is great enough to render the net rate of decomposition of the perester lower than in pure chlorobenzene.

Other evidence of combined inhibitory action and acid catalysis by carboxylic acids is found in the observations of Blomquist and Ferris[12] with *t*-butyl perbenzoate. They found that the rate in acetic acid was higher than in aromatic solvents such as chlorobenzene at the same temperature but that while addition of trichloroacetic acid to the ester in *p*-chlorotoluene had a marked catalytic effect, addition of dichloroacetic acid had practically no effect. An effect of the presence and the nature of the hydrogen atoms on the α-carbon of the acid is thus apparent in their work also.

The exact nature of the action of carboxylic acids must be determined by extensive further research and we do not wish to speculate upon it at present. No good clue to that nature is provided by the analysis of the products produced in *n*-butyric acid (Table VII) since that analysis is not sufficiently different from the one obtained for the decomposition in chlorobenzene. On the other hand, the effects of the acids on the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values (Table VI) do not fit well with the correlations found for peresters undergoing simple or "concerted" cleavage free of radical-induced reaction.[2]

Acknowledgment.—M. Trachtman expresses his grateful acknowledgment of the aid and encouragement given him by the Research Division of the Frankford Arsenal and of the support of the U. S. Army Research Office. The advice and interest given us by Leonard S. Silbert, Frank D. Verderame and Robert J. Witonsky are also gratefully acknowledged.

(12) A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3412 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

Cyclopropanes. XIII. The Absolute Configuration of 1-Methyl-2,2-diphenylcyclopropane[1]

BY H. M. WALBORSKY AND C. G. PITT

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The absolute configuration of 1-methyl-2,2-diphenylcyclopropane has been determined by a direct chemical correlation with (+)-R-propylene oxide and with (−)-S-2-methyl-3,3-diphenylpropionic acid. The absolute configuration of the latter was established from the optical rotatory dispersion curves of the corresponding methyl ketone, aldehyde and morpholinothiocarbamide derivatives. The above findings are compared with a previous tentative assignment of absolute configuration to 2,2-diphenylcyclopropanecarboxylic acid, which had been based on the results of partial asymmetric syntheses. The results of the chemical correlation and the asymmetric syntheses are shown to be compatible if one assumes that a "diazo-exchange" reaction has occurred in the addition of diazodiphenylmethane to the menthyl acrylate and methacrylate.

Introduction

Prelog,[2] Cram,[3] and their co-workers have studied the course of asymmetric syntheses in a variety of systems and have found that the configuration of the newly created asymmetric center is dependent on the conformation of the original asymmetric moiety. The concepts derived from this work have been applied, with much success, to the correlation of configuration. This has been notably true for the atrolactic acid system of Prelog.[2,4] However, certain anomalous results have recently been reported. For example, Collins and co-workers[5]

(1) This study was supported by the U. S. Army Research Office (Durham) and by the National Science Foundation.

(2) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

(3) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952)

(4) For a review of this work, see J. A. Mills and W. Klyne, Ch. 5, in "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., pp. 198–201; E. Eliel, "Stereochemistry of Carbon Compounds," McGraw–Hill Book Co., Inc., New York, N. Y., 1962.

(5) J. H. Stocker, P. Sidisunthorn, B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 3913 (1960).

have shown that in the addition of Grignard reagents to phenylacetoin the use of phenylmagnesium chloride or bromide resulted in a preponderance of the *threo* isomer, whereas with phenylmagnesium iodide the *erythro* isomer predominated. Therefore a subtle change of reagents has resulted in a reversal of stereoselectivity. Temperature,[6] solvent[7] and catalyst[8] have also been shown to have a marked effect on the course of asymmetric syntheses.

By partial asymmetric synthesis the addition of diazodiphenylmethane to (−)-menthyl acrylate and (−)-menthyl methacrylate yielded, respectively, (−)-2,2-diphenylcyclopropanecarboxylic acid and (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid.[9] The acids were shown, by an independent method, to have the same relative configuration and by making use of the Prelog–Cram model a tentative absolute configuration was assigned to them.[9]

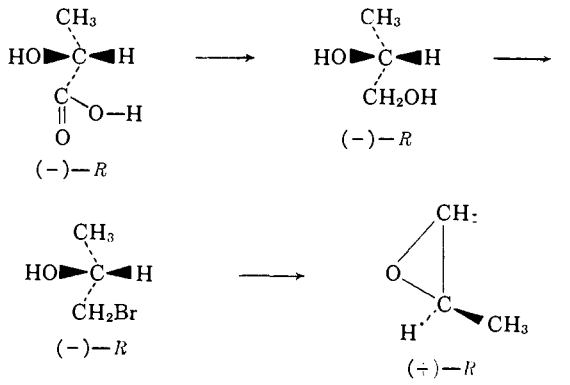
In order to employ a hypothesis such as the Prelog–Cram model, it is necessary, *a priori*, to have some knowledge of the geometry and nature of the transition state as well as the mechanism of the reaction in question. It therefore seemed essential to establish the absolute configuration of the above acids by a direct chemical correlation in order to ascertain whether or not the Prelog–Cram model can be applied to this type of a reaction. To this end the absolute configuration of 1-methyl-2,2-diphenylcyclopropane was determined by a direct chemical correlation. This in turn provides the absolute configuration of 2,2-diphenylcyclopropanecarboxylic acid since this acid has been related by unambiguous means[10] to 1-methyl-2,2-diphenylcyclopropane.

Based on the results of optical rotatory dispersion data (−)-2-methyl-3,3-diphenylpropionic acid has been assigned the *S*-configuration. This acyclic acid has also been related to 1-methyl-2,2-diphenylcyclopropane by a direct chemical correlation.

Results and Discussion

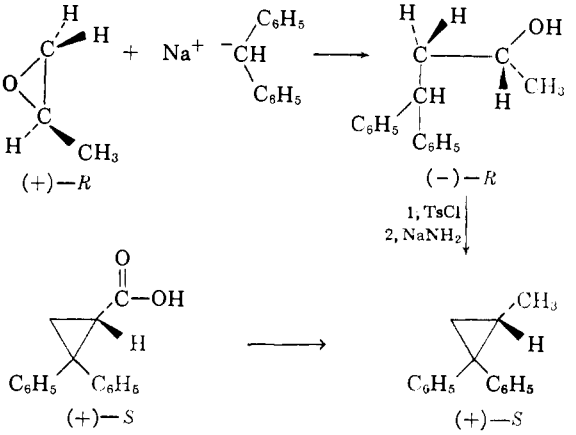
Chemical Correlations.—(+)-R-Propylene oxide was selected as the starting material for the synthetic route to the cyclopropane system under consideration. Levene[11] has demonstrated that the dextrorotatory epoxide is related to (−)-R-lactic acid by the first sequence of reactions.

The only questionable step, in which the asymmetric carbon atom may be involved, is in the conversion of propylene glycol to the bromohydrin. However, Levene and Walti[11] have shown that treatment of (−)-1-bromopropanol-2 with potassium cyanide, followed by hydrolysis of the nitrile, yields (−)-3-hydroxybutyric acid which, in turn, has been related[12] to (−)-R-butanol-2. It should



be pointed out that treatment of the bromohydrin with aqueous potassium hydroxide, without isolation of the intermediate epoxide, regenerates the original (−)-propylene glycol (see Experimental).

(+)-R-Propylene oxide was converted to (+)-S-1-methyl-2,2-diphenylcyclopropane



Addition of an ether solution of (+)-R-propylene oxide to sodium diphenylmethide in liquid ammonia gave (−)-R-4,4-diphenylbutanol-2 in 80% yield. The structure proposed for this alcohol, which results from nucleophilic attack of the diphenylmethyl carbanion at the less hindered ring carbon of the epoxide,[13] is consistent with the method of preparation,[13] elemental analysis, infrared and n.m.r. spectra (see Experimental). The isomeric alcohol, 2 - methyl - 3,3 - diphenylpropanol, which would have resulted from attack at the more hindered ring carbon of the epoxide, was prepared and its physical properties (n.m.r. and infrared) compared and shown to differ from 4,4-diphenylbutanol-2. Since the asymmetric carbon atom is not involved in this displacement reaction, the absolute configuration (−)-R-4,4-diphenylbutanol-2 assigned.

The benzhydryl moiety in 4,4-diphenylbutanol-2 is the potential source of a carbanion or strong nucleophile. Thus cyclization to a cyclopropane ring should be feasible if a group which is capable of nucleophilic displacement is introduced in the γ-position in the molecule. To this end, the *p*-toluenesulfonate ester of (−)-R-4,4-diphenylbutanol-2 was prepared and added to a solution of sodium amide in liquid ammonia. Examination

(6) H. Pracejus, *Ann.*, **634**, 9 (1960).

(7) Y. Inouye, S. Inamasu, M. Ohno, T. Sugita and H. M. Walborsky, *J. Am. Chem. Soc.*, **83**, 2962 (1961).

(8) H. M. Walborsky, L. Barash and T. C. Davis, *J. Org. Chem.*, **26**, 4778 (1961).

(9) H. M. Walborsky, L. Barash, A. E. Young and F. J. Impastato, *J. Am. Chem. Soc.*, **83**, 2517 (1961).

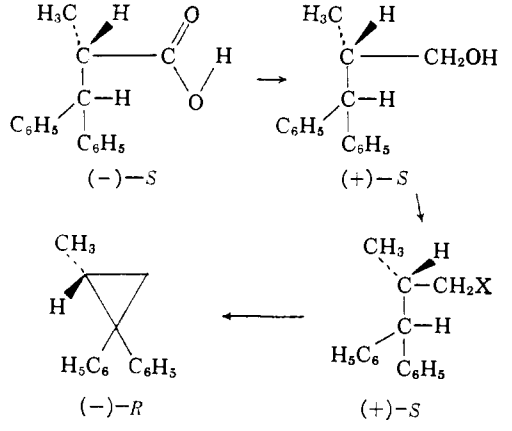
(10) H. M. Walborsky and F. J. Impastato, *ibid.*, **81**, 5835 (1959).

(11) P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **67**, 329 (1926); P. A. Levene and A. Walti, *ibid.*, **68**, 415 (1926).

(12) P. A. Levene and H. L. Haller, *ibid.*, **71**, 465 (1929).

(13) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

of the products of this reaction showed that cyclization, or γ-elimination,[14] had occurred to give 1-methyl-2,2-diphenylcyclopropane in 50–80% yield. As in the case of 3,3-diphenylpropyltrimethylammonium iodide,[14] γ-elimination had occurred to the exclusion of β-elimination, for gas liquid chromatography indicated that less than 1% of isomeric olefins were present in the reaction product. The specific rotation of the 1-methyl-2,2-diphenylcyclopropane formed was $+126.8 \pm 1.8°$, which represents an optical purity of 100%[10] within the limits of experimental error. The overall complete retention of optical activity is consistent with the view that this reaction involves an intramolecular displacement with inversion at the asymmetric carbon atom. It is interesting to note that when the above cyclization was attempted at 0–5° using dimethoxyethane as the solvent, β-elimination predominated over γ-elimination. The product obtained consisted of 4,4-diphenyl-1-butene (77.5%), 1,1-diphenylbutene[15] (8.8%) and 1-methyl-2,2-diphenylcyclopropane (13.7%) as determined by gas–liquid chromatography. Utilizing these figures the specific rotation of the 1-methyl-2,2-diphenylcyclopropane was calculated to be $+115 \pm 4°$. The predominance of β-elimination using dimethoxyethane as a solvent, in contrast to liquid ammonia where exclusively γ-elimination resulted, is in all probability a consequence of going to a less solvating medium and a higher temperature which would favor the β-elimination.[16]



If one could establish the absolute configuration of 2-methyl-3,3-diphenylpropionic acid, then the above sequence of reactions would provide an alternative means of establishing the absolute configuration of 1-methyl-2,2-diphenylcyclopropane. This route is particularly attractive since it does not involve any reactions at the asymmetric carbon. Conversely, if the absolute configuration of 1-methyl-2,2-diphenylcyclopropane is known, then one would arrive at the absolute configuration of 1-methyl-2,2-diphenylpropionic acid. Assuming, therefore, the correctness of the correlation of (+) - S - 1 - methyl - 2,2 - diphenylcyclopropane with (+)-R-propylene oxide, then (−)-2-methyl-3,3-diphenylpropionic acid would possess the S-configuration.

As shown above, (−)-2-methyl-3,3-diphenylpropionic acid was reduced with lithium aluminum hydride to (+)-2-methyl-3,3-diphenylpropanol, which was converted with thionyl chloride to (+) - 1 - chloro - 2 - methyl - 3,3 - diphenylpropane. When the (+)-chloride was treated with sodium amide in liquid ammonia, the product was found to be a mixture of two hydrocarbons. These were identified as (−)-1-methyl-2,2-diphenylcyclopropane (38%) and 1,1-dimethyl-2,2-diphenylethylene (62%). The latter olefin is formed by the base-catalyzed rearrangement of the initially formed dehydrohalogenation product, 2-methyl-3,3-diphenyl-1-propene. The facility of this rearrangement was confirmed by separate experiment. When the *p*-toluenesulfonate ester of (+)-2-methyl-3,3-diphenylpropanol was treated in an identical manner to that of the chloride, the sole product isolated was optically pure (−)-1-methyl-2,2-diphenylcyclopropane and no olefin could be detected. Thus, the relationship between (−)-2-methyl - 3,3 - diphenylpropionic acid and (−) - 1-methyl - 2,2 - diphenylcyclopropane is established and, based on the earlier correlation of (+)-S - 1 - methyl - 2,2 - diphenylcyclopropane with (+)-R-propylene oxide, the absolute configuration of the acyclic acid is (−)-S-2-methyl-3,3-diphenylpropionic acid.

As a further check on the correctness of the above assignment of absolute configuration, it was thought desirable to determine independently the absolute configuration of (−)-2-methyl-3,3-diphenylpropionic acid. The most attractive method seemed to be optical rotatory dispersion.[17] The (−) - acid was converted to the (+) - morpholinothiocarbamide derivative[18] which was found to exhibit a negative Cotton effect (Fig. 1). Based on the empirical conclusions of Djerassi,[19] the absolute configuration can be assigned as (−)-S-2-methyl-3,3-diphenylpropionic acid.

Treatment of (−) - 2 - methyl - 3,3 - diphenylpropionic acid with methyllithium gave (−)-3-methyl - 4,4 - diphenyl - 2 - butanone, and reduction of the (−)-acid with lithium aluminum hydride to the (+)-carbinol followed by chromic oxide oxidation gave (−)-2-methyl-3,3-diphenylpropionaldehyde. Both the aldehyde and the ketone exhibited positive Cotton effects (Fig. 1). Barring unusual conformational effects, these two compounds may be compared with (+)-S-2-methylbutyraldehyde and (+)-S-3-methyl-2-pentanone, respectively, where the two β-hydrogens of the ethyl group have been replaced by phenyl groups. Since the latter two compounds both exhibit positive Cotton effects,[20] (−)-2-methyl-3,3-diphenylpropionaldehyde and (−)-3-methyl-4,4-di-

(14) C. L. Bumgardner, *J. Am. Chem. Soc.*, **83**, 4420, 4423 (1961).

(15) Probably arose from the based catalyzed isomerization of 1,1-diphenyl-2-butene, see, T. W. Campbell and W. G. Young, *ibid.*, **69**, 688 (1947).

(16) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(17) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(18) C. Djerassi and K. Undheim, *J. Am. Chem. Soc.*, **82**, 5755 (1960).

(19) C. Djerassi, K. Undheim, and A. M. Weidler, *Acta. Chem. Scand.*, **16**, 1079 (1962).

(20) C. Djerassi and L. E. Geller, *J. Am. Chem. Soc.*, **81**, 2789 (1959).

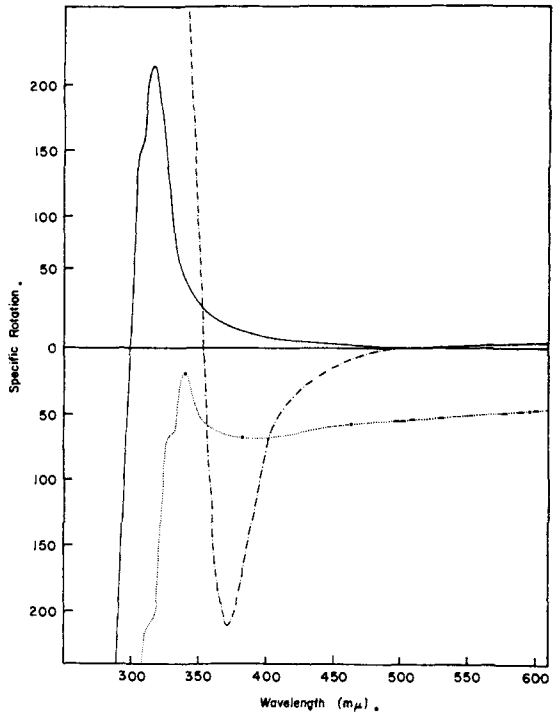


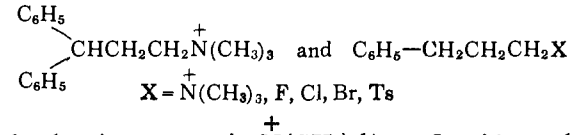
Fig. 1.—The optical rotatory dispersion curves of: ———, (−)-3-methyl-4,4-diphenyl-2-butanone in isooctane; ·····, (−)-2-methyl-3,3-diphenylpropionaldehyde in isooctane; — . —, morpholinothiocarbamide of (−)-2-methyl-3,3-diphenylpropionic acid in methanol (specific rotation $\times 10^{-1}$).

phenyl-2-butanone may be assigned the S-configuration. These results are in agreement with the absolute configuration derived by chemical correlation.

Comments on Displacement and Elimination Reactions in Liquid Ammonia.—A number of reasonable conclusions may be drawn from the stereochemical results of the cyclization reactions in liquid ammonia. Cyclization of (+)-4,4-diphenyl-2-butyl *p*-toluenesulfonate in liquid ammonia gives rise to (+)-1-methyl-2,2-diphenylcyclopropane with little or no racemization. It therefore appears that the intramolecular displacement, with inversion of configuration, is operative in liquid ammonia. By the same argument an α-elimination[21] mechanism may be ruled out, for this would be expected to result in extensive or total racemization in the formation of 1-methyl-2,2-diphenylcyclopropane.

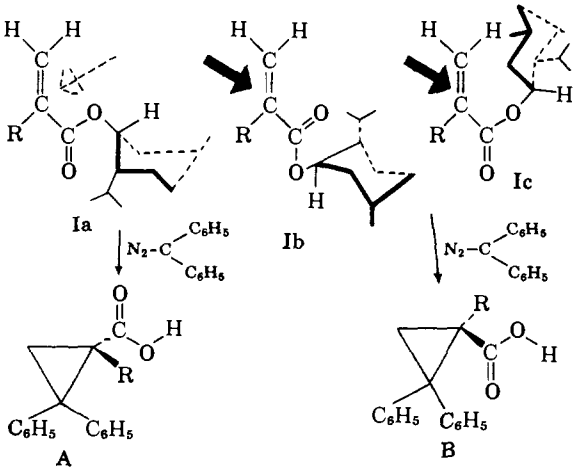
Considering the mechanism of olefin formation from 1-chloro-2-methyl-3,3-diphenylpropane, *i.e.*, β-elimination, a reversible removal of β-proton (E_{1cb}) cannot be occurring, for this, too, would lead to a partially or completely racemized 1-methyl-2,2-diphenylcyclopropane.

Bumgardner[22] has recently studied two very similar systems as given at the top of the next column. He has shown that when the leaving group (X) is bromide only olefin formation is observed. When



the leaving group is $\overset{+}{N}(CH_3)_3$[14] or fluoride, only γ-elimination is observed, whereas the chloride and tosylate[23] results in both β- and γ-elimination. Bumgardner has explained these results reasonably in terms of the increasing importance of beta (and gamma) proton removal in the rate-determining step as the polarizability of the leaving group decreases. It is difficult to understand, however, why with 4,4-diphenyl-2-butyl *p*-toluenesulfonate and with 2-methyl-3,3-diphenylpropyl *p*-toluenesulfonate (secondary and primary tosylates) one should obtain complete γ-elimination, whereas with the primary chloride, 1-chloro-2-methyl-3,3-diphenylpropane, one obtains a mixture. It would seem that the product composition depends on a rather subtle interplay between the acidity of the β- and γ-protons and the polarizability of the leaving group.[22]

Partial Asymmetric Synthesis.—Although the partial asymmetric syntheses of (−)-2,2-diphenylcyclopropanecarboxylic acid and (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, by addition of diazodiphenylmethane to (−)-menthyl acrylate and methacrylate, predicted the correct relative configurations of the acids, this method did not predict the correct absolute configurations.[9] The prediction of the absolute configuration was based on the Prelog–Cram model[2,3] in which one assumes menthyl acrylate and methacrylate to be in the transoidal conformation, with the menthyl ring flanking the carbonyl of the ester group (Ia). This model would predict attack of the diazodi-



phenylmethane preferably from below the plane, to produce configuration A in excess of B. However, if the conformation of the esters is cisoidal (Ib), or the menthyl ring flanks the olefinic bond (Ic), the product of opposite (and correct) configuration (B) will predominate. Unfortunately, there are no data available concerning the position of the cisoidal–transoidal rotamer equilibrium. However, such an equilibrium must surely exist and furthermore one would expect it to be sensitive to

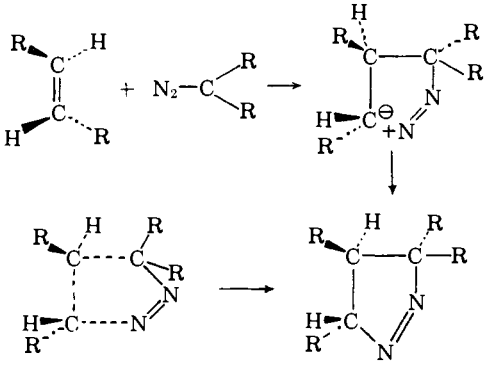
(21) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 492 1961).

(22) C. L. Bumgardner, reported at the Southwest and Southeast A. C. S. Meeting, New Orleans, La., Dec. 7–9, 1961.

(23) C. L. Bumgardner, private communication.

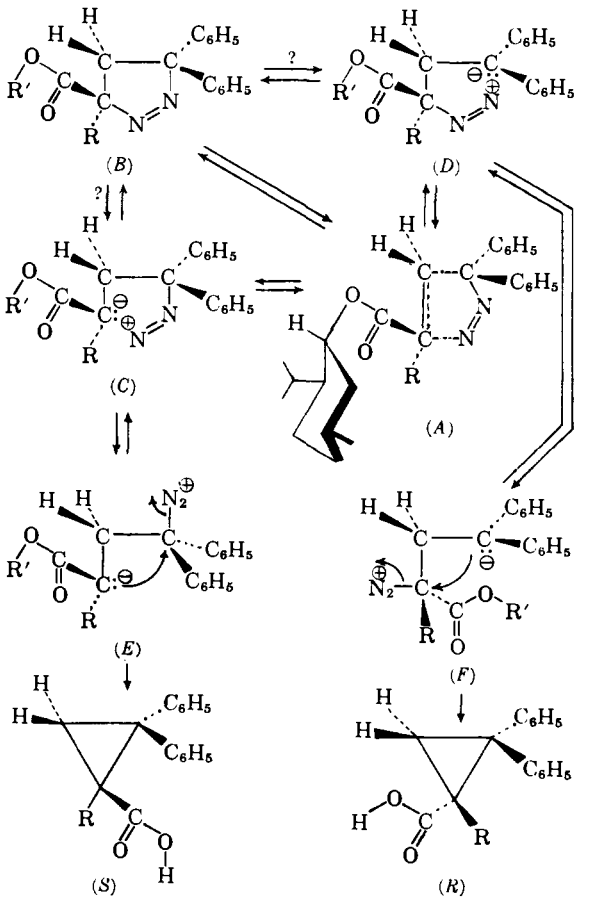
solvent. This may, perhaps, account for the solvent effects that have been observed in other asymmetric syntheses.[24]

Stereochemical studies have revealed that the addition of diazoalkanes to *cis*- and *trans*-olefins to yield 1-pyrazolines is a stereospecific process.[25a-e] The stereochemical results can be accommodated by postulating an attack by the nucleophilic diazoalkane on the olefin which is then followed by a fast ring closure to yield the pyrazoline or alternatively by postulating a concerted 1,3-dipolar addition[26] to yield the pyrazoline directly.



The stereochemistry of the decomposition of 1-pyrazolines to yield cyclopropanes is in doubt. Some workers[27a-d] have claimed that the thermal decomposition of 1-pyrazolines to the corresponding cyclopropane is a non-stereospecific process, whereas others[27a-d] have claimed that it is a stereospecific one. The thermal addition of diazodiphenylmethane to dimethyl fumarate and maleate has been shown to be non-stereospecific[28] since the only product isolated from these reactions was *trans*-dimethyl 3,3 - diphenyl - 1,2 - cyclopropropanedicarboxylate. An identical result was obtained on the addition of 9-diazofluorene to these olefins at room temperature[29] and, furthermore, no pyrazoline could be detected. In contrast to the latter observation, the reaction of diphenyldiazomethane with dimethyl fumarate and maleate at 40° in a variety of solvents is reported to yield the 2-pyrazoline derivative.[26] Also, the rate of addition was not appreciably affected by the polarity of the solvent and this has been cited[26] as evidence for the 1,3-dipolar addition mechanism rather than the stepwise zwitterion-ion intermediate.[30] If indeed, the reaction of diazoalkanes with olefins at high temperatures does proceed through the 1-pyrazoline as an intermediate, then another question arises. Does the 1-pyrazoline decompose to yield a diradical or an ionic intermediate? Overberger[27d] suggests, by analogy with other cyclic azo systems, that *trans*-3,5-diphenyl-1-pyrazoline decomposes to a diradical intermediate which in contrast to the seven- and eight-membered ring compounds cyclizes stereospecifically to yield *trans*-1,2-diphenylcyclopropane. To date there is no compelling evidence that decomposition of 1-pyrazolines in general yields diradicals. An ionic intermediate is just as plausible and may well be the case when the 1-pyrazoline is unsymmetrically substituted in the 3- and 5-positions in such a manner that one of the substituents is capable of delocalizing a positive charge and the other substituent a negative charge. This is analogous to the unsymmetrically substituted diacoyl peroxides and perbenzoates which have been shown to decompose by an ionic mechanism.[31] However, whether 1-pyrazolines are intermediates in the thermal addition of diazoalkanes to olefins and whether they decompose by a radical or an ionic mechanism is still an open question.

On the basis of the preceding discussion, the following ionic reaction paths suggest themselves for the addition of diazodiphenylmethane to methyl acrylate and methacrylate (R = H or CH_3).



(24) Y. Inouye, S. Inamasu, M. Ohno, T. Sugita and H. M. Walborsky, *J. Am. Chem. Soc.*, **83**, 2962 (1961).

(25) (a) K. von Auwers and F. Kōnig, *Ann.*, **496**, 27 (1932); (b) J. van Alphen, *Rec. trav. chim.*, **62**, 334 (1943); (c) K. L. Rinehart, Jr. and T. V. van Auken, *J. Am. Chem. Soc.*, **82**, 5251 (1960); (d) W. M. Jones and Wun-Ten Tai, *J. Org. Chem.*, **27**, 1030 (1962), and preceding papers; (e) for a general review see, T. L. Jacobs in R. C. Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. 5, 1957.

(26) R. Huisgen, H. Stangl, J. J. Sturm and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).

(27) (a) K. von Auwers and F. Konig, *Ann.*, **470**, 284 (1924); **496**, 252 (1932); (b) *Ber.*, **66**, 1198 (1932); (c) J. von Alphen, *Rec. trav. chim.*, **62**, 210 (1943); (d) C. G. Overberger and J. P. Anselme, *J. Am. Chem. Soc.*, **84**, 870 (1962).

(28) W. M. Jones, *ibid.*, **81**, 3776 (1959).

(29) L. Horner and E. Lingnau, *Ann.*, **591**, 21 (1955).

(30) B. Eistert, *Angew. Chem.*, **54**, 99, 127 (1941).

(31) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956.

The Prelog-Cram model for menthyl acrylate will be assumed and therefore the diazodiphenylmethane will attack preferentially from the right to yield, in a 1,3-dipolar-addition (the initial asymmetric synthesis step), transition state A. This transition state can form pyrazoline B or it can collapse to form intermediates C or D. These same intermediates, C and D, could also be formed from the pyrazoline B if indeed the pyrazoline is an intermediate in the thermal addition reaction. It should be noted that the formation of D is tantamount to the transfer of a diazo group, a reaction first noted by Farnum and Yates.[32] It can therefore be seen that the stereochemical consequences of the asymmetric synthesis will be dependent on the ratio of intermediates C and D in the reaction. The decomposition of C will lead to the predominant formation of (S)-2,2-diphenylcyclopropanecarboxylic acid. Since the asymmetric synthesis was found to produce the (−)-enantiomer in excess and since the (−)-enantiomer was shown to have the (R)-absolute configuration it is suggested that the formation of intermediate D predominates in this reaction.

More work is obviously necessary in order to establish firmly the suggested "diazo-exchange" reaction as well as the general mechanism of the addition of diazoalkanes to olefins.[33]

Experimental

The optical rotatory dispersion curves were obtained on a recording Rudolf spectropolarimeter using a xenon high-pressure arc lamp as a light source. F and M model-55 gas chromatograph, Infracord and Cary-14 spectrophotometer were the other instruments used in this work. All melting points and boiling points are uncorrected. The n.m.r. data was obtained on a 60 mc. Varian high resolution spectrometer using tetramethylsilane as a standard.

(+)-R-Propylene Oxide.—(+)-R-Propylene oxide was prepared by the method of Levene and Walti.[34]

Acetol (75 g.), from chloroacetone and potassium acetate in methanol, was reduced microbiologically with reductase of yeast (Fleischmann brand) to (−)-R-propylene glycol to yield 47 g. (61%), b.p. 64–65° (3 mm.), $n^{27}D$ 1.4300, $\alpha^{26}D$ −16.32 ± 0.03° (1 dm., neut); reported for (−)-propylene glycol, α_D −16.03°,[35] −16.3°,[36] $n^{20}D$ 1.4323.

(−)-R-Propylene glycol (27 g.) was treated with anhydrous hydrogen bromide at 0°, until the theoretical increase in weight had been gained, to give (−)-R-propylene bromohydrin, 27.2 g. (55%), b.p. 55–56° (19 mm.), $n^{26}D$ 1.4764, $(\alpha)^{26}D$ −11.34 ± 0.70° ($CHCl_3$, c 2.741); reported for (−)-propylene bromohydrin, $(\alpha)D$ −10.53° ($CHCl_3$),[37] $n^{25}D$ 1.4775.[37]

(−)-R-Propylene bromohydrin (22 g.) was cyclized by treatment with 40% aqueous sodium hydroxide to give (+)-R-propylene oxide, 7.5 g. (81%), b.p. 34–35°, $(\alpha)^{24}D$ 15.16 ± 0.1° (ether, c 28.87); reported for (+)-propylene oxide, $(\alpha)D$ +15°, +14.5°.

Solvolysis of (−)-R-Propylene Bromohydrin.—Sodium hydroxide (0.8 g., 0.02 mole) was added to 1.4 g. of (−)-R-propylene bromohydrin (0.01 mole) and 40 ml. of water in a 60-ml. round-bottomed flask, fitted with water and Dry Ice condensers. A reaction was immediately observed, and the lower layer of bromohydrin disappeared concurrently with the appearance of a top layer of propylene oxide. The contents of the flask were warmed slowly to 120°, over a period of 5 hours, when the reaction mixture and the refluxing liquid became homogeneous. The aqueous solution was cooled to room temperature, and the water was evaporated under reduced pressure. The residue was made acidic with glacial acetic acid. The excess of acetic acid was evaporated under reduced pressure, and the residual salts were extracted several times with hot ether. The combined ether extracts were evaporated and the residue was distilled under reduced pressure to give 0.35 g. (46%) of propylene glycol. The product was redistilled and its physical constants were determined: b.p. 70–76° (6 mm.), $n^{25}D$ 1.4259, $(\alpha)^{26}D$ −27.1 ± 1.0° ($CHCl_3$, c 3.035); reported[37] for (−)-propylene glycol, $(\alpha)D$ −28.6° ($CHCl_3$), $n^{20}D$ 1.4334. The identity of the product was confirmed by infrared analysis and gas–liquid chromatography.

(−)-R-4,4-Diphenylbutanol-2.—Diphenylmethane (16.8 g., 0.1 mole) in anhydrous ether (100 ml.) was added to a stirred solution of sodium amide (0.1 mole) in liquid ammonia (250 ml.) to form sodium diphenylmethide. After stirring the reaction mixture for 15 min., (+)-R-propylene oxide (5.8 g., 0.1 mole) in anhydrous ether (50 ml.) was added. The red color of sodium diphenylmethide gradually disappeared during the addition. The liquid ammonia was allowed to evaporate overnight. Excess of sodium amide was treated with aqueous ammonium chloride, and the product was separated from the inorganic phase by extraction with ether. The combined ether extracts were washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate and water, and finally dried over sodium sulfate. After removal of the solvent, the crude product was purified by elution chromatography from an alumina column, followed by distillation, to yield 18 g. of (−)-R-4,4-diphenylbutan-2-ol, 79.7%, b.p. 107–109° (0.1 mm.), $n^{27}D$ 1.5698, $(\alpha)D$ −27.10 ± 0.90°, ($CHCl_3$, c 2.768).

Although the product contains the MeCHOH group, it failed to give a positive iodoform test. However, the assigned structure was supported by n.m.r. (singlet at 431.1 c./sec. phenyl; triplet at 249.3 c./sec., benzhydryl; sextet at 217.0 c./sec., −CHOH; quartet at 125.4 c./sec., methylene; and doublet at 62.9 c./sec., methyl (standard T.M.S.), and by comparison (infrared, n.m.r.) with the alternative product, 2-methyl-3,3-diphenylpropanol.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.92; H, 8.03. Found: C, 84.85; H, 8.21.

(+)-R-4,4-diphenyl-2-butyl *p*-Toluenesulfonate.—A solution of 3.1 g. of (−)-R-4,4-diphenyl-2-butanol ($[\alpha]D$ −27.1°) in dry pyridine (25 ml.) was added to 7 g. of *p*-toluenesulfonyl chloride in dry pyridine (25 ml.) at 0°, and the combined solutions were refrigerated for 48 hours. The pyridine solution was diluted with chloroform, and washed with dilute hydrochloric acid until the aqueous phase was acidic. The chloroform layer was washed with aqueous sodium bicarbonate and then water before drying over sodium sulfate. Removal of the solvent, by distillation under reduced pressure, gave a viscous liquid which could not be purified further by elution chromatography, and would not crystallize from any of a variety of solvents.

Examination of the infrared spectrum of the crude product showed it to be essentially identical with that of the pure racemic tosylate, and to be free from carbinol. The specific rotation of the product was $(\alpha)^{25}D$ +8.27 ± 0.90° ($CHCl_3$, c 1.874).

In a similar experiment, treatment of the racemic carbinol (0.05 mole) with *p*-toluenesulfonyl chloride in pyridine gave 15 g. of the racemic tosylate. The crude product was isolated as a white solid by pouring the pyridine solution onto crushed ice, and was purified by crystallization from chloroform–petroleum ether; yield 68.5%, m.p. 89.5–90.0°.

Anal. Calcd. for $C_{23}H_{24}O_3S$: C, 72.60; H, 6.36; S, 8.43. Found: C, 72.83; H, 6.52; S, 8.86.

Cyclization of (+)-R-4,4-diphenyl-2-butyl *p*-Toluenesulfonate. A. Liquid Ammonia as Solvent.—The sulfonate (3.8 g., 0.01 mole, $(\alpha)D$ + 8.27°) in dry ether (200 ml.) was added dropwise, over a period of 45 minutes, to a stirred solution of sodium amide (0.02 mole) in liquid ammonia (250 ml.). The color of the reaction mixture was a dark green, slowly fading to brown as the addition was completed.

(32) D. G. Farnum and P. Yates, *Proc. Chem. Soc.*, 224 (1960).

(33) Based on our previous tentative assignment of absolute configuration we had reported[9] that the Brewster method (J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 1959), had failed to predict two out of three configurations. As a result of our new assignment this method predicts two out of three correctly.

(34) P. A. Levine and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926); P. A. Levene and A. Walti, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 5, 545.

(35) W. Fickett, H. K. Garner and H. J. Lucas, *J. Am. Chem Soc.*, **73**, 5063 (1951).

(36) E. Farber and F. F. Nord, *Biochem. Z.*, **112**, 316 (1920).

(37) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956); C. C. Price and Nan Shieh, *J. Org. Chem.*, **24**, 1169 (1959).

The liquid ammonia was allowed to evaporate overnight. Excess of sodium amide was destroyed with aqueous ammonium chloride, and the product was separated from the inorganic material by extraction with ether. The combined ether extracts were successively washed with dilute hydrochloric acid, aqueous sodium bicarbonate and water. The solvent was removed, and the high-boiling residue was distilled under reduced pressure to give (+)-S-1-methyl-2,2-diphenylcyclopropane, 1.1 g. (52.5%), b.p. 60–65° (0.05 mm.), $n^{26}D$ 1.5739, $(\alpha)^{26}D$ + 126.75 ± 1.8° ($CHCl_3$, *c* 1.064); reported[38] for 1-methyl-2,2-diphenylcyclopropane, $(\alpha)D \pm 127°$ ($CHCl_3$). In a duplicate run a yield of 84% was obtained. The identity of the product was confirmed by gas–liquid chromatography, n.m.r. and infrared analyses. Gas–liquid chromatography of the undistilled reaction product showed less than 1% of impurity formed from competing elimination reactions was present.

B. 1,2-Dimethoxyethane as Solvent.—A solution of 3.8 g. of the sulfonate (0.01 mole, $(\alpha)D$ + 8.27°) in anhydrous 1,2-dimethoxyethane (125 ml.) was added dropwise to a stirred suspension of potassium amide (0.03 mole) in 1,2-dimethoxyethane (150 ml.) maintained at a temperature of 0 to 5°. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was stirred overnight. The color of the reaction mixture was initially dark green, turning slowly to brown. Excess potassium amide was destroyed with aqueous ammonium chloride, and the bulk of the resulting solution was reduced to 25 ml. by evaporation under reduced pressure. The residue was diluted with pentane, and was washed successively with aqueous ammonium chloride and water before drying over sodium sulfate. The solvent was removed, and the residue, was distilled under reduced pressure. A fraction (1.1 g.) boiling at 93–95° (0.25 mm.) was collected. Gas–liquid chromatography showed the distillate to contain three components, in the ratio of 78.5:13.7:8.8. The retention time of the smaller fraction indicated that it was 1-methyl-2,2-diphenylcyclopropane.

The infrared spectrum of the distillate showed a strong absorption band at 920 $cm.^{-1}$, and the ultraviolet spectrum showed an absorption band, λ_{max} (EtOH) 254 mμ, ε 1700. The ultraviolet absorption is too strong to be assigned to the benzene nuclei, and suggests a structure containing a conjugated olefinic bond is a component of the distillate. The 920 $cm.^{-1}$ band in the infrared spectrum is indicative of a monosubstituted ethylene. From these data the unknown components were identified as 4,4-diphenyl-1-butene (77.5%) and 1,1-diphenylbutene (8.8%), and were satisfactorily compared (infrared, ultraviolet and gas–liquid chromatographical analyses) with authentic samples.

The specific rotation of the distillate was +15.81 ± 0.88° ($CHCl_3$, *c* 2.890). Based on the composition of the distillate, as determined by gas–liquid chromatography, the specific rotation of the 1-methyl-2,2-diphenylcyclopropane is +115 ± 4°.

(−)-S-2-Methyl-3,3-diphenylpropionic Acid.—The racemic acid was prepared by the method of Sykes and Walborsky.[39] Resolution of the racemic acid was accomplished by successive fractional crystallization of the quinine salt from acetone, ethyl acetate and benzene, to a constant melting point of 164–165°. Decomposition of this salt afforded the (−)-acid, m.p. 146.5–147.5°, $(\alpha)^{26.5}D$ −52.6 ± 1.7° ($CHCl_3$, *c* 1.578).

(+)-S-2-Methyl-3,3-diphenylpropanol.—(−)-2-Methyl-3,3-diphenylpropionic acid (1.5 g., $[\alpha]D$ −49.5°) in dry tetrahydrofuran (50 ml.) was added dropwise to a stirred solution of lithium aluminum hydride (0.35 g.) in anhydrous ether (50 ml.). The reaction mixture was refluxed for 4 hours, and then stirred at room temperature overnight. Hydrolysis of the reaction mixture with aqueous ammonium chloride, filtration of the precipitated inorganic salts, and evaporation of the filtrate to dryness gave the crude carbinol as a viscous liquid. The product was purified by elution from an alumina column, followed by distillation, to give 1.2 g. of (+)-2-methyl-3,3-diphenylpropanol; yield 85%, b.p. 115–120° (0.1 mm.), $(a)^{26}D$ +21.63 ± 2.2° ($CHCl_3$, *c* 0.897). The n.m.r. spectrum, although difficult to interpret, was not inconsistent with the assigned structure.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.90; H, 8.03. Found: C, 84.19; H, 8.10.

(+)-S-1-Chloro-2-methyl-3,3-diphenylpropane.—A stirred solution of pyridine (0.4 g.) and (+)-3,3-diphenyl-2-methylpropanol (1.2 g., $[\alpha]D$ + 21.6°) in benzene (25 ml.) was cooled to 0°, and 0.7 g. of thionyl chloride was added. The reaction mixture was then heated at reflux temperature, until evolution of sulfur dioxide had ceased (about 4 hours). The reaction mixture was diluted with ether, and successively washed with dilute hydrochloric acid, aqueous sodium bicarbonate and water. The ether was removed by distillation, and the product was purified by elution from an alumina column, followed by distillation, to give (+)-2-methyl-3,3-diphenylchloropropane, 0.97 g. (69%), b.p. 102–103° (0.1 mm.), $n^{28}D$ 1.5703, $(\alpha)^{27.5}D$ +27.96 ± 1.37° ($CHCl_3$, *c* 1.753).

Anal. Calcd. for $C_{16}H_{17}Cl$: C, 78.50; H, 7.15. Found: C, 78.67; H, 7.05.

(+)-S-2-Methyl-3,3-diphenylpropyl *p*-Toluenesulfonate.—2-Methyl-3,3-diphenylpropanol (2.8 g., $[\alpha]D$ +23.7°) in dry pyridine (25 ml.) was added to a solution of *p*-toluenesulfonyl chloride (7.0 g.) in dry pyridine (25 ml.) at 0°, and the combined solutions were refrigerated at this temperature for 48 hours. The crude tosylate was isolated as a white solid by pouring the pyridine solution onto crushed ice. Filtration, and crystallization of the crude solid from ether–petroleum ether, gave 4.0 g. (91%) of (+)-2-methyl-3,3-diphenylpropyl *p*-toluenesulfonate, m.p. 103.5–104.0°, $(\alpha)^{25.5}D$ +22.0 ± 2.8° ($CHCl_3$, *c* 1.174).

Anal. Calcd. for $C_{23}H_{24}O_3S$: C, 72.60; H, 6.36. Found: C, 72.91; H, 6.40.

Cyclization of 2-Methyl-3,3-diphenylpropyl *p*-Toluenesulfonate.—Treatment of 2.0 g. of the sulfonate ($[\alpha]D$ +22°) with sodium amide (3 mole equiv.) in liquid ammonia, following the procedure described above, gave 0.45 g. (41%) of the levorotatory isomer of 1-methyl-2,2-diphenylcyclopropane, b.p. 82–83° (0.1 mm.), $n^{27}D$ 1.5730, $(\alpha)^{25}D$ −125.6 ± 2.2° ($CHCl_3$, *c* 2.119). Gas–liquid chromatography indicated that the distillate was homogeneous, whereas the undistilled product contained less than 1% of hydrocarbons formed from competing elimination reactions.

Cyclization of 1-Chloro-2-methyl-3,3-diphenylpropane.—Following the procedure described previously, 1.4 g. of 1-chloro-2-methyl-3,3-diphenylpropane (0.0056 mole, $[\alpha]D$ −5.55°) in ether was added to a solution of sodium amide (2 equiv.) in liquid ammonia. On distillation of the products, a fraction (0.70 g.) with a boiling range of 85–90° (0.12 mm.) was collected. Gas–liquid chromatography of the distillate showed it to contain two components in the ratio of 62:38 (peak areas). The retention time of the smaller fraction indicated that it was 1-methyl-2,2-diphenylcyclopropane.

The mixture was separated by gas–liquid chromatography, passing it twice through a 8′ × 0.5″ DEGS column (temperature 180°, flow rate 160 ml./min., 20% substrate on 60–80 mesh Chromosorb W). The smaller component was confirmed by infrared analysis to be 1-methyl-2,2-diphenylcyclopropane, $n^{17}D$ 1.5778, $(\alpha)^{27}D$ +27.29 ± 3.0° ($CHCl_3$, *c* 0.850), optical purity 21.8 ± 2.9%.

The second component showed no characteristic bands in the infrared, but absorbed in the ultraviolet (maximum at 244 mμ, ε 12300). This compound was identified as 1,1-dimethyl-2,2-diphenylethylene, and was satisfactorily compared with an authentic sample (*vide infra*), $n^{23}D$ 1.5855. The optical purity of the 2-methyl-3,3-diphenylpropane was 19.2 ± 4.6%.

Isomerism of 3,3-Diphenyl-2-methylpropene.—3,3-Diphenyl-2-methylpropene (0.2 g.) in dry ether (30 ml.) was added to a solution of sodium amide (0.1 g. sodium) in liquid ammonia (50 ml.). A red coloration was immediately observed. The ammonia was allowed to evaporate (2 hours), and sodium amide was destroyed with ammonium chloride and water. The product was isolated by extraction with ether. After drying over sodium sulfate, the solvent was removed by distillation. The residue was analyzed by gas–liquid chromatography and infrared spectroscopy, and found to be greater than 90% 1,1-dimethyl-2,2-diphenylethylene.

(−)-S-3-Methyl-4,4-diphenyl-2-butanone.—To 2.88 g. of 2-methyl-3,3-diphenylpropionic acid (0.012 *M*, $[\alpha]D$ −52.6°) in anhydrous ether (100 ml.) was slowly added a solution of methyllithium (0.03 *M*) in anhydrous ether (60 ml.). After stirring for 2 hours at room temperature, the reaction mixture was hydrolyzed with dilute sulfuric acid,

(38) H. M. Walborsky and F. J. Impastato, *J. Am. Chem. Soc.*, **81**, 5835 (1959).

(39) H. M. Walborsky and M. Sykes, M. S. Dissertation, Florida State University (1958).

and the product was extracted with ether. The combined ether extracts were washed with dilute sulfuric acid, aqueous sodium hydroxide and water, and then dried over sodium sulfate. Unchanged acid (1.0 g.) was recovered from the alkaline extract. Removal of the solvent and fractional crystallization of the residue from petroleum ether gave 0.8 g. of (−)-3-methyl-4,4-diphenyl-2-butanone, m.p. 79–80°, $(\alpha)^{26}D$ −31.5 ± 2.2° ($CHCl_3$, *c* 1.170); λ_{max} (isoöctane) 286 mμ, ε 38.6; R.D. (*c* 0.54) in isoöctane: $(\alpha)_{700}$ +7°, $(\alpha)D$ +3°, $(\alpha)_{600}$ +1°, $(\alpha)_{350}$ +33°, $(\alpha)_{315}$ +215° (peak), $(\alpha)_{310}$ +166° (shoulder), $(\alpha)_{300}$ 0°, $(\alpha)_{290}$ −226°.

Only a plain dispersion curve was observed in methanol and in dioxane. The carbonyl absorption was observed as a shoulder on the larger benzenoid absorption (1st maximum 270 mμ). That this shoulder was actually the carbonyl absorption was demonstrated by observing the shifts of the absorption bands on changing the polarity of the solvent. In determining the maxima and extinction coefficients of the ketone and (−)-2-methyl-3,3-diphenylpropionaldehyde it was necessary to extrapolate the absorption curves.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.65; H, 7.61. Found: C, 85.71; H, 7.41.

(−)-S-2-Methyl-3,3-diphenylpropionaldehyde.—To a solution of 3.0 g. of chromic anhydride[40] in pyridine (30 ml.) was added 3.0 g. of 2-methyl-3,3-diphenylpropanol ($[\alpha]D$ +23.7°) in pyridine (30 ml.). The combined solutions were allowed to stand at room temperature for 22 hours, and then poured into an excess of water. The product was obtained by extraction with ether. The combined ether extracts were washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate and water, before drying over sodium sulfate. The residual oil, after removal of the solvent, was distilled to give 1.25 g. of the desired aldehyde, b.p. 113–114° (0.15 mm.), $(\alpha)^{26.5}D$ −14.3 ± 2.2° ($CHCl_3$, *c* 1.430); λ_{max} (isoöctane) 290 mμ, ε 50; R.D. (*c* 1.04) in isoöctane: $(\alpha)_{700}$ −38°, $(\alpha)D$ −46°, $(\alpha)_{400-390}$ −69° (plateau), $(\alpha)_{350}$ −50°, $(\alpha)_{340}$ −19° (peak), $(\alpha)_{335}$ −42°, $(\alpha)_{330}$ −65° (shoulder, $(\alpha)_{315}$ −194° (shoulder), $(\alpha)_{310}$ −218°. In the presence of air and light the aldehyde underwent rapid autoxidation, and it was necessary to use freshly prepared material for determination of physical constants.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.93; H, 7.32.

Morpholinothiocarbamide[41] of (−)-2-Methyl-3,3-diphenylpropionic Acid.—A mixture of thionyl chloride (2.2 g.) and (−)-2-methyl-3,3-diphenylpropionic acid (1.5 g., $[\alpha]D$ −52.6°) was allowed to stand at room temperature for 2 days. Excess of thionyl chloride was then distilled from the reaction product under reduced pressure. Without further purification the acyl chloride was dissolved in anhydrous acetone (40 ml.) and added to freshly dried potassium thiocyanate (0.6 g.). This mixture was refluxed for 1 hour, when 10 g. of dry morpholine was added. After refluxing for a further 10 minutes, the reaction mixture was allowed to stand overnight. The acetone was evaporated under reduced pressure, and the residue was dissolved in chloroform. The chloroform solution was washed with dilute hydrochloric acid and water, before drying over sodium sulfate. Removal of the solvent and crystallization of the solid residue from chloroform–petroleum ether gave 2.0 g. of the desired product, m.p. 171–172°, $(\alpha)^{26}D$ +36.1 ± 2.1° ($CHCl_3$, *c* 1.545); λ_{max} (MeOH) 275 and 342 mμ, log ε 4.15 and 2.61; R.D. in methanol (*c* 0.64): $(\alpha)_{700}$ +35°, $(\alpha)D$ +30°, $(\alpha)_{510}$ 0°, $(\alpha)_{400}$ −697°; (*c* 0.064): $(\alpha)_{380}$ −1820°, $(\alpha)_{372}$ −2100° (trough), $(\alpha)_{353}$ 0°, $(\alpha)_{320}$ +6060.

Anal. Calcd. for $C_{21}H_{24}O_2N_2S$: C, 86.44; H, 6.56. Found: C, 86.37; H, 6.75.

1,1-Dimethyl-2,2-diphenylethylene.—Triphenylisopropylphosphonium iodide[42] (10.8 g., 0.025 mole) was added to a solution of butyllithium (0.25 mole) in anhydrous ether (70 ml.) at 0° and under an atmosphere of nitrogen. The reaction mixture was stirred at this temperature for 2 hours and at room temperature for 4 hours. Benzophenone (6.0 g., 0.033 mole) was then added to the red colored solution and, after refluxing for 4 hours, the mixture was stirred overnight. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in petroleum ether, and again filtered. The precipitates were digested with hot petroleum ether and the washings were combined with the filtrate. Unreacted benzophenone was removed by elution of the petroleum ether solution from an alumina column; distillation of the partially purified product gave 2.8 g. (54%) of 1,1-diphenyl-2,2-dimethylethylene, b.p. 80° (0.08 mm.), $n^{21}D$ 1.5886; λ_{max} (95% ethanol) 244 mμ, ε 13000; reported for 1,1-diphenyl-2,2-dimethylethylene, $n^{23.5}D$ 1.586,[43] λ_{max} (heptane) 248 mμ, ε 11700.[44]

1,1-Diphenylbutene.—1,1-Diphenylbutene was prepared by the acid-catalyzed dehydration of 1,1-diphenylbutanol.[45] Gas–liquid chromatography showed that the product was homogeneous; b.p. 80–82° (0.1 mm.), $n^{20}D$ 1.5865°; λ_{max} (EtOH) 250 mμ, ε 12,700; reported[46] for 1,1-diphenylbutene, $n^{20}D$ 1.5898.

4,4-Diphenyl-1-butene.—Diphenylmethane (0.05 mole, 8.4 g.) in dry ether (100 ml.) was added to a solution of potassium amide (0.05 mole) in liquid ammonia (250 ml.). After stirring for 30 minutes, allyl chloride (0.05 mole, 4.0 g.) in dry ether (40 ml.) was added to the reaction mixture. The red color of the potassium diphenylmethide disappeared as the addition was completed. Excess of potassium amide was neutralized with ammonium chloride, and the ammonia was allowed to evaporate. The residual ether solution was filtered and, after removal of the solvent, was distilled under reduced pressure. The fraction b.p. 82–84° (0.12 mm.) was collected to yield 7.9 g. (76%), $n^{21.5}D$ 1.5739, infrared 995 and 920 $cm.^{-1}$ ($CH{=}CH_2$).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.74. Found: C, 92.16; H, 7.80.

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(41) C. Djerassi and K. Undheim, *ibid.*, **82**, 5755 (1959).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

Cyclopropanes. XIV. The Haller–Bauer Cleavage Reaction[1,2]

BY F. J. IMPASTATO AND H. M. WALBORSKY

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The cleavage of (−)-(R)-1-benzoyl-1-methyl-2,2-diphenylcyclopropane by sodium amide in toluene produced (+)-(S)-1-methyl-2,2-diphenylcyclopropane. Under these conditions the reaction proceeds with complete retention of activity and configuration. The mechanism of the reaction is discussed.

Introduction

Evidence for at least a certain lack of geometric stability for the cyclopropyl carbanion exists in the base-catalyzed *cis–trans* conversions of the isomers of 1-benzoyl-2-nitro-3-phenylcyclopropane.[3] A sim-

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(2) For a preliminary communication see H. M. Walborsky and F. J. Impastato, *Chemistry & Industry*, 1690 (1958); H. M. Walborsky, *Rec. Chem. Prog.*, **23**, 75 (1962).

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