

and yielded 0.715 g. of starting bromide, $[\alpha]^{24D} +95.90^\circ$ (c 1.683), on cooling in a Dry Ice-acetone bath.

Carbonation of the Product from the Reaction of *n*-Butyllithium with (–)-1-Methyl-1-bromo-2,2-diphenylcyclopropane at Room Temperature in Ether for 30 Min.—To a solution of 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{26.5D} -111.59 \pm 0.8^\circ$) in 50 ml. of ether was added 25 ml. of a 1.7 *M* *n*-butyllithium in ether over a period of 15 min. with stirring. The solution turned yellow and the temperature was maintained at 26°. After stirring an additional 15 min. the solution was poured onto crushed Dry Ice-ether slurry with stirring. The carbon dioxide was allowed to evaporate, after which the ether solution was acidified with dilute hydrochloric acid, washed with water, and extracted with aqueous potassium hydroxide. Acidification of the basic extracts with hydrochloric acid yielded the solid acid, which was collected and dried to give 0.550 g. (53%), m.p. 182–184°, $[\alpha]^{26D} +35.26 \pm 1.2^\circ$ (c 2.110), infrared spectrum identical with that of an authentic sample of acid.

Carbonation of the Product of the Reaction between *n*-Butyllithium and (–)-1-Methyl-1-bromo-2,2-diphenylcyclopropane at $-8 \pm 2^\circ$ in THF for 20 Min.—A solution of 1.7 *M* *n*-butyllithium in 25 ml. of ether was added with stirring to 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{26D} -107.53 \pm 1.5^\circ$) in 50 ml. of THF over a period of 10 min. with the temperature held at $-8 \pm 2^\circ$ by an ice-hydrochloric acid bath. The solution was stirred an additional 10 min., during which time it developed an intense orange color, and was poured onto a crushed Dry Ice-ether slurry with stirring. The carbon dioxide was allowed to evaporate, after which the ether solution was acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification

of the basic extracts gave the solid acid which was collected and dried to give 0.381 g. (37%), m.p. 183–185°, $[\alpha]^{26.5D} +34.71 \pm 1.3^\circ$ (c 1.904), an infrared spectrum identical with that of an authentic sample of acid.

Brominolysis of the Lithium Reagent from (–)-1-Iodo-1-methyl-2,2-diphenylcyclopropane.—The apparatus used was a 3-necked flask which had a stopcock at the bottom. This flask was connected by the joint attached to the stopcock, to another 3-necked flask equipped with thermometer, gas inlet tube, condenser, and magnetic stirring bar. The reaction was carried out under an atmosphere of dry nitrogen.

In the upper flask a solution of 0.650 g. (0.002 mole) of (–)-1-iodo-1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{23D} -163.6^\circ$ (c 2.31), in 40 ml. of anhydrous ether, was allowed to react with an excess of *n*-butyllithium dissolved in ether. After 10 min. at room temperature the upper flask was cooled with a Dry Ice bath and its contents was slowly added to the lower flask which contained 2 ml. of bromine (0.04 mole) dissolved in 40 ml. of ether. The lower flask was covered with an aluminum foil and immersed in a Dry Ice bath. The addition took 5 min. and the temperature never rose above -40° . The solution was allowed to stir for an additional 15 min. Any unreacted lithium reagent was destroyed by the addition of 1.5 ml. of methanol. The solution was allowed to warm to -15° and an aqueous solution of sodium hydroxide was added. The ether layer was washed until neutral, dried, and stripped and the residue chromatographed on alumina. Petroleum ether (30–60°) was used as the eluent. The solid fractions were combined to yield 0.097 g. (17%), m.p. 78–82°, $[\alpha]^{26D} -103.4^\circ$ (c 0.970), 95% optically pure. It was shown by a control experiment in which an optically impure bromide was chromatographed that, within experimental error, no change in optical purity occurred.

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

Cyclopropanes. XVI. An Optically Active Grignard Reagent and the Mechanism of Grignard Formation^{1,2}

BY H. M. WALBORSKY AND A. E. YOUNG

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The reaction of (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane with magnesium leads to the formation of an optically active Grignard reagent since on carbonation (–)-(*S*)-1-methyl-2,2-diphenylcyclopropane-carboxylic acid ($12 \pm 2\%$ optical purity) and (–)-(*R*)-1-methyl-2,2-diphenylcyclopropane ($10 \pm 2\%$ optical purity) are isolated. Evidence is presented to show that the extensive racemization observed in the products occurs in the Grignard formation step and not after the Grignard reagent is formed. A mechanism for Grignard formation, which is consistent with the stereochemical observations, is suggested.

Introduction

There have been many attempts to prepare an optically active Grignard reagent from an optically active halide in which the halogen is directly attached to the asymmetric center. All such endeavors have failed. Acyclic halides such as (–)-2-iodobutane,³ (+)-2-bromooctane,^{4,5} and optically active 1-phenylethyl bromide⁵ have been shown to give rise to optically inactive products. A Grignard reagent prepared from a cyclic halide, (–)-3,3-dimethylcyclohexyl chloride, is also reported to yield racemic acid on carbonation.⁶

The carbon-magnesium bond has been described as being largely covalent. Using the electronegativity values of Pauling⁷ in conjunction with the Hannay and

Smyth equation,⁸ the percentage ionic character of the carbon-magnesium bond is calculated to be 27%. Using the orbital electronegativity values of Hinze and Jaffé⁹ in place of Pauling's electronegativity values one obtains the higher value of 35% ionic character for the bond between a tetrahedrally hybridized carbon and a tetrahedrally hybridized magnesium. For the trigonally hybridized carbon and a tetrahedrally hybridized magnesium bond the percentage ionic character of the bond is calculated to be 41% and a cyclopropyl ($sp^{2.28}$) to magnesium (sp^3) bond is found to be approximately 38% ionic in character. In an analogous manner the percentage ionic character of the carbon-lithium bond for a tetrahedral, trigonal, and cyclopropyl carbon is found to be 36, 42, and 39%, respectively.

In the preceding paper¹⁰ the geometric and optical stability of the carbon-lithium bond has been discussed. On the basis of ionic character alone one would expect a comparable stability for the carbon-magnesium bond.

(1) The support of this work by the Petroleum Research Fund and the National Science Foundation is gratefully acknowledged.

(2) For a preliminary report of this work see (a) H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **83**, 2595 (1961); (b) H. M. Walborsky, *Record Chem. Progr.*, **23**, 75 (1962).

(3) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

(4) A. M. Schwartz and J. R. Johnson, *J. Am. Chem. Soc.*, **53**, 1063 (1931).

(5) C. W. Porter, *ibid.*, **57**, 1436 (1935).

(6) H. L. Goering and F. M. McCarron, *ibid.*, **80**, 2287 (1958).

(7) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.

(8) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 171 (1946).

(9) J. Hinze and H. H. Jaffé, *ibid.*, **84**, 540 (1962).

(10) H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, **85**, 3283 (1964).

However, it should be recognized that the percentage of ionic character is calculated for molecules in the gas phase and that solvation energies will play an important role. That this may well be the case is indicated by the observation that in ether triethylmagnesium is highly colored¹¹ whereas ditriethylmagnesium is reported to be colorless,¹² indicating that the former is more highly dissociated in solution. This is also consistent with the observations of Grovenstein and Williams¹³ and Zimmerman, Smentowski, and Zweig¹⁴ who showed that 2,2,2-triphenylethyllithium and 2,2-diphenylpropyllithium undergo facile rearrangement to 1,1,2-triphenylethyllithium and 1-methyl-1,2-diphenylethyllithium, respectively. In contrast, the 2,2-diphenylpropyl Grignard reagent was shown not to rearrange even under more drastic conditions.¹⁴ The situation is by no means clear-cut since several workers^{15,16} on the basis of n.m.r. studies of primary Grignard reagents concluded that the carbon-magnesium bond either undergoes dissociation and the resulting carbanion inverts very rapidly¹⁶ or there is a rapid inversion at this site.¹⁵ It was also reported¹⁶ that methylmagnesium, dimethylmagnesium, and methyl Grignard have virtually identical n.m.r. spectra, indicating the similarity between the carbon-lithium and carbon-magnesium bonds. Similar conclusions were reached from the n.m.r. investigation of the allyllithium¹⁷ and allyl Grignard¹⁸ reagents. On the other hand, trigonally hybridized vinylmagnesium^{10,17} reagents^{16,19} appear to be configurationally more stable than the corresponding tetrahedrally hybridized reagents.

It has been demonstrated that 1-methyl-2,2-diphenylcyclopropyllithium is capable of maintaining its configuration as well as its optical activity. Based on this observation it was hopefully anticipated that using this system one might obtain the heretofore elusive optically active Grignard reagent. This article describes the successful preparation of this latter reagent.

Results

Syntheses and Configurational Relationships.—The cyclopropane derivatives used in this investigation were optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane, 1-chloro-1-methyl-2,2-diphenylcyclopropane, and 1-iodo-1-methyl-2,2-diphenylcyclopropane. The preparation of the bromo and iodo derivatives have been previously described^{10,20} and the chloro compound was prepared in an analogous manner to that described for the bromide²⁰ (see Experimental).

In order to ascertain the stereochemistry of the reaction of the different halides with magnesium it is

(11) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

(12) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 82.

(13) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957); E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 412 (1961); **83**, 2537 (1961).

(14) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957); H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(15) G. W. Whitesides, F. Kaplan, and J. D. Roberts, *ibid.*, **85**, 2167 (1963).

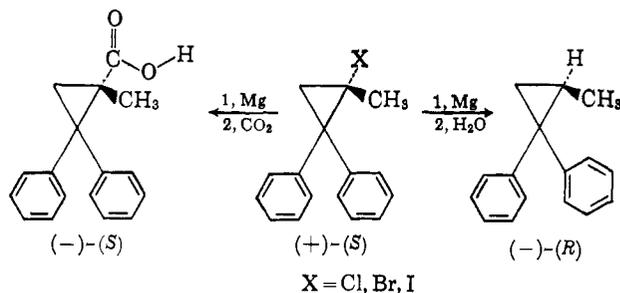
(16) G. Fraenkel, D. G. Adams, and J. Williams, *Tetrahedron Letters*, 767 (1963).

(17) C. S. Johnson, Jr., M. A. Weiner, J. S. Waugh, and D. Seyferth, *J. Am. Chem. Soc.*, **83**, 1306 (1961).

(18) J. E. Norlander and J. D. Roberts, *ibid.*, **81**, 1769 (1959); G. M. Whiteside, J. E. Norlander, and J. D. Roberts, *ibid.*, **84**, 2010 (1962).

(19) H. Normant and P. Maitte, *Bull. soc. chim. France*, 1439 (1956).

(20) F. J. Impastato and H. M. Walborsky, *J. Am. Chem. Soc.*, **84**, 4838 (1962).



necessary to relate the configurations of the halides to 1-methyl-2,2-diphenylcyclopropanecarboxylic acid, the product of carbonation, and 1-methyl-2,2-diphenylcyclopropane, the hydrolysis product of the Grignard reagents. With the exception of the chloro derivative the relative^{10,21} and absolute configurations²² of these molecules have been established. The iodide and bromide having the (+)-(S) configuration are related to the (-)-(R)-1-methyl-2,2-diphenylcyclopropane and (-)-(S)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid.

Of the many methods available for relating configurations²¹ one of the most convenient is the infrared analysis of quasiracemates.^{21,23} Since the absolute configuration of 1-bromo-2,2-diphenylcyclopropanecarboxylic acid is known, the infrared study of its quasiracemate formation with 1-chloro-2,2-diphenylcyclopropanecarboxylic acid was undertaken. The results are given in Table I. The solid state (KBr disks) spectrum of the equimolar mixture of the (-)-chloro acid and the (-)-bromo acid is shown to be similar to the spectrum of the (-)-chloro acid itself. On the other hand, the spectrum of the (-)-chloro and (+)-bromo acid mixture was like that of the (±)-chloro acid which is a racemic compound. On the basis of these results it can be concluded with confidence that the acids of like sign of rotation and consequently the hydrocarbons of like sign, 1-chloro-1-methyl-2,2-diphenylcyclopropane and 1-bromo-1-methyl-2,2-diphenylcyclopropane, that are derived from these acids possess the same configuration. The (S)-absolute configuration is heretofore assigned to all dextrorotatory 1-halo-1-methyl-2,2-diphenylcyclopropane derivatives (X = Cl, Br, and I).

TABLE I
THE INFRARED ABSORPTION BANDS (CM.⁻¹) ASSOCIATED WITH CARBOXYL GROUP^a

Compound ^b	COOH		Carbonyl stretching	Broad in-plane C-OH	Broad out-of-plane C-OH
	Bonded OH	dimer, submaxima			
(-)-A	3200	—, —, —	1725, 1687	1180	—, 820
(±)-A	—	2800-2500	1685	—	920, —
(+)-B	3210	—, —, —	1728, 1711	1243, 1219	—, 875
(±)-B	—	2750-2500	1688	—	932, —
(+)-B (-)-A	—	2800-2500	1690	—	925, —
(-)-B (-)-A	3200	—, —, —	1720, 1685	1175	—, 830, 810

^a The complete spectra can be found in the Ph.D. Dissertation of A. E. Young, Florida State University, 1963. ^b A = 1-chloro-2,2-diphenylcyclopropanecarboxylic acid. B = 1-bromo-2,2-diphenylcyclopropanecarboxylic acid.

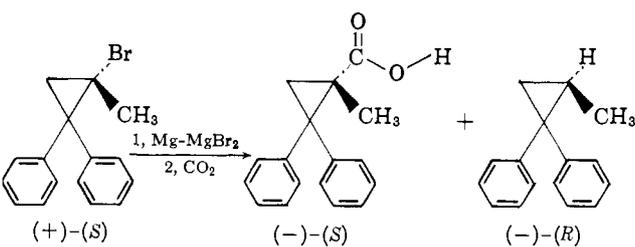
An Optically Active Grignard Reagent.—Encouraged by the very high configurational stability of 1-methyl-2,2-diphenylcyclopropyllithium,¹⁰ it was speculated that the corresponding optically active Grignard reagent

(21) H. M. Walborsky, L. Barasch, A. E. Young, and F. J. Impastato, *ibid.*, **83**, 2517 (1961).

(22) H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).

(23) A. Rosenberg and L. Schotte, *Arkiv. Kemi*, **7**, 347 (1954).

TABLE II



	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
$[\alpha]_D$ of RBr ^a	+106.5°	+106.5°	-109.1°	-111.6°	-111.6°	-111.6°
Optical purity, ^b %	96	96	98	100	100	100
Solvent	THF ^c	THF	Ether	THF ^d	THF	THF
Temp., °C.	65	25-27.5	35	65	65	65
Time, min.	20	40	20	30	30	180
Yield RH, ^e %	38	36	59	44	20	32
$[\alpha]_D$ RH ^e	-14.13°	-12.40°	+12.40°	+15.86°	+17.05°	+16.13°
Optical purity ^f RH, %	11.5	10.15	9.6	12.3	13.7	12.6
Yield RCOOH, ^g %	38	45	8.3	32	66	41
$[\alpha]_D$ RCOOH	-5.25°	-4.24°	+5.11°	+5.32°	+5.58°	+5.52°
Optical purity RCOOH, ^h %	15.2	12.6	14.5	14.8	15.5	15.3

^a R = 1-methyl-2,2-diphenylcyclopropyl. ^b Maximum rotation of RBr taken as 111.6°. ^c Ethylene dibromide added to bromide and magnesium. ^d No MgBr₂ added. ^e Maximum rotation of R-H taken as 128°. ^f Maximum rotation of RCOOH taken as 36°.

might also be prepared. When (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane was treated with a powdered magnesium-magnesium bromide mixture in refluxing tetrahydrofuran (THF) and the reaction mixture carbonated, the resulting products (-)-(S)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid and (-)-(R)-1-methyl-2,2-diphenylcyclopropane were found to be optically active with predominant retention of configuration. This represents the *first example of an optically active Grignard reagent* where magnesium is bonded to the dissymmetric site of a molecule with only one asymmetric carbon atom.²⁴ The results are summarized in Table II.

It should be noted that, as in the case of the corresponding lithium reagent,¹⁰ there is neither an effect of solvent (ether *vs.* THF),²⁵ temperature, nor of time on the optical purities of the products. It is clear, however, that the products are *largely racemized* and this contrasts with the results obtained with the lithium reagent. The question that needs to be answered is, *at which stage of the reaction does the racemization occur?*

The possibility exists that the preformed magnesium bromide or the magnesium bromide formed during the reaction caused racemization of the starting bromide. This was clearly shown not to be the case. A sample of (-)-(R)-1-bromo-1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{25}_D -107.5^\circ$, was treated with anhydrous magnesium bromide in refluxing THF for 70 min. and the recovered starting material, $[\alpha]^{25}_D -104^\circ$, was obtained essentially unchanged. In another experiment an excess of the bromide was treated with magnesium and then carbonated. Isolation of the unreacted bromide showed that it was not racemized.

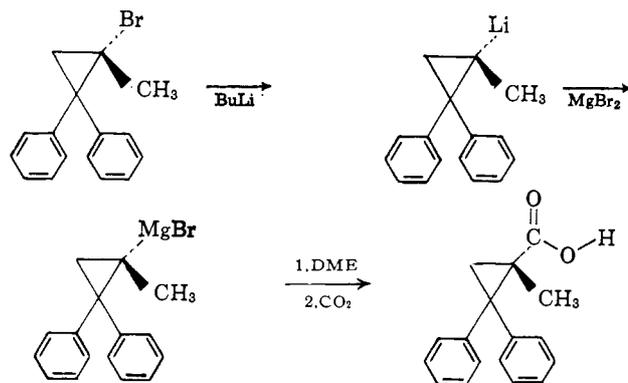
(24) After our original report,²⁴ O. A. Reutov, *Bull. soc. chim. France*, 1383 (1963), has made the claim that the Grignard reagent formed by treating (\pm)-1,4-dimethylpentylmagnesium bromide with optically active di-1,4-dimethylpentylmercury, when carbonated, resulted in the formation of 2,5-dimethylcaproic acid with "weak optical activity."

For an example of an asymmetric synthesis in the carbonation of a Grignard reagent dissolved in an optically active solvent, see H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 432 (1953).

(25) However, a solvent effect has been reported in the formation of the Grignard reagent from *trans*- β -bromostyrene. See T. Yoshino and Y. Manabe, *J. Am. Chem. Soc.*, **85**, 2860 (1963).

Another possibility was that racemization occurred *after* the Grignard reagent was formed. In order to test this point a method was sought in which the carbon-magnesium bond is formed without the use of metallic magnesium. A procedure similar to that of Ziegler and Dersch,²⁶ who reported the exchange of benzylmagnesium chloride and phenyllithium, was initially used. The optically active bromide was treated with butyllithium to produce 1-methyl-2,2-diphenylcyclopropyllithium, a reaction which has previously been shown to occur with complete retention of configuration.¹⁰ To this solution was added methylmagnesium bromide. Subsequent carbonation yielded the corresponding acid with complete retention of optical activity. The above experiment, however, suffered from the fact that one was unable to say with absolute assurance that the lithium-Grignard exchange had occurred.

It has previously been shown¹⁰ that 1-methyl-2,2-diphenylcyclopropyllithium is very rapidly decomposed by 1,2-dimethoxyethane (DME). The corresponding Grignard reagent, however, is stable in this solvent. Based on these observations the following experiment was performed.



When 1-methyl-2,2-diphenylcyclopropyllithium was added to an ethereal solution of anhydrous magnesium bromide, the intense yellow color characteristic of the

(26) K. Ziegler and F. Dersch, *Ber.*, **64**, 448 (1931).

lithium reagent rapidly disappeared. Carbonation of the reaction mixture yielded optically pure 1-methyl-2,2-diphenylcyclopropanecarboxylic acid, $[\alpha]_D^{25} -34^\circ$. This method for the preparation of Grignard reagents from the corresponding lithium reagent²⁷⁻²⁹ was repeated and this time DME was added to the Grignard solution in order to decompose any lithium reagent that might still be present. Carbonation of the reaction mixture again produced the corresponding acid with complete retention of optical activity and configuration. The results of these experiments clearly demonstrate that, once formed, the 1-methyl-2,2-diphenylcyclopropyl Grignard reagent is optically stable. This is further borne out by the data in Table II, runs 5 and 6, which show that the same stereochemical results are obtained whether the reaction is run for 30 or 180 min. Moreover, when THF is replaced by di-*n*-butyl ether and the Grignard solution is heated to reflux (*ca.* 120°) for over 30 min. the optical purities of the products are similar to those found when the reaction was performed in refluxing THF. Based on the above observations it is concluded that *the racemization must be occurring in the Grignard formation step.*

Effect of Halogen.—In order to gain some insight into the mechanism of Grignard formation, the 1-methyl-2,2-diphenylcyclopropyl chloride, bromide, and iodide were converted to their corresponding Grignard reagents and carbonated. The results are shown in Table III.

TABLE III

	Run 1 Cl	Run 2 Br	Run 3 I
$[\alpha]_D$	-65.4°	-111.6	-171.6
Temp., °C.	65	65	65
Time, min.	30	30	30
Yield RCOOH, %	53	63	40
$[\alpha]_D$ RCOOH	+9.86°	+5.58	+2.03
Optical purity RCOOH, ^a %	25	15	6
Yield R-H, %	...	20	21
$[\alpha]_D$ R-H	+32.63	+17.05	+6.09
Optical purity R-H, ^b %	26	13	5

^a Maximum rotation of RCOOH taken as 36°. ^b Maximum rotation of R-H taken as 128°.

It is readily apparent from Table III that the halogen atom has a pronounced effect on the stereochemical consequences of Grignard reagent formation. Although the reaction still occurs with predominant retention of configuration the halide does affect the optical purity of the product. As one goes from chloride to bromide to iodide, the optical purity of the products diminishes.

Solvent Cleavage in Grignard Reagent Formation.—From Table II, runs 2 and 3, it can be seen that the yield of acid resulting from Grignard formation in diethyl ether is greatly diminished (8.3%) in compari-

son of the yield obtained in THF (45%). This led to an investigation of whether or not there was reaction with the solvent during Grignard formation. The results of this study are summarized in Table IV.

TABLE IV

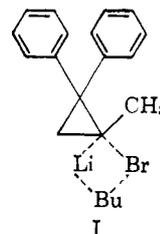
Solvent	Catalyst	Temp., °C.	Time, min.	Yield, %	Yield, % RH	Yield, % RD ^a
THF	MgBr ₂	65	30	76	20 ± 2	80 ± 2
THF	65	30	82	24 ± 2	76 ± 2
Ether	MgBr ₂	35	30	67	48 ± 1	52 ± 1

^a For method of analysis see Experimental.

The data clearly show that reaction with solvent in the Grignard formation step does occur and that diethyl ether is cleaved to a greater extent than THF. Furthermore, preformed magnesium bromide has no effect on the amount of cleavage of the THF.

Discussion

The results obtained in this work on the stability of optically active 1-methyl-2,2-diphenylcyclopropyllithium demonstrated that a cyclopropyllithium bond is an optically stable species.¹⁰ However, the reaction used to form the lithium reagent was that of halogen-metal interchange which is in all probability an *Sei* reaction involving a four-centered transition state (I) and would be expected to lead to retention of optical activity as well as configuration.³⁰⁻³² In the case of the Grignard reagent one is dealing with a completely



different situation since the formation of a Grignard reagent is not a halogen-metal interchange as described above but a surface reaction involving an elemental metal which is oxidized.

A great deal of evidence can be cited to support the thesis that Grignard formation occurs by a free radical surface mechanism³³ and we subscribe to this view. It is felt that the extensive racemization observed in the reaction of 1-halo-1-methyl-2,2-diphenylcyclopropane with magnesium is due to the radical nature of the Grignard formation step giving rise to the 1-methyl-2,2-diphenylcyclopropyl radical. It has been shown that the cyclopropyl radical does not maintain its configuration or its optical activity.^{2b} Treatment of (-)-2,2-diphenylcyclopropanecarboxylic acid, using the

(30) S. Winstein and T. G. Traylor, *J. Am. Chem. Soc.*, **78**, 2597 (1956).

(31) H. B. Charman, E. D. Hughes, C. Ingold, and F. G. Thorpe, *J. Chem. Soc.*, 1121 (1961), and references cited therein.

(32) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *J. Am. Chem. Soc.*, **82**, 2466 (1960).

(33) For a review of this evidence, see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954.

(27) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

(28) S. Gronowitz, *Arkiv. Kemi*, **16**, 363 (1960).

(29) H. J. S. Winkler and G. Wittig, *J. Org. Chem.*, **28**, 1733 (1963).

cyclopropyl Grignard reagent, if a Schlenk equilibrium exists ($2R_2MgX \rightleftharpoons [R_2Mg \cdot MgX_2] \rightleftharpoons R_2Mg + MgX_2$), the exchange of alkyl groups must be occurring with complete retention of configuration.^{41a} This has also been found to be the case for the exchange of alkyl groups in alkylmercuric halides.^{41b}

There is a possibility that the optically active Grignard reagent was formed by a route that does not involve direct reaction with metallic magnesium. It has been reported⁴² that a Grignard reagent can undergo exchange with a perfluorinated alkyl iodide. When *n*-heptafluoropropyl iodide is treated with phenylmagnesium bromide followed by the addition of acetone, a good yield of *n*-heptafluoropropyldimethylcarbinol is obtained. If halogen-Grignard reagent exchange was occurring in the case of the cyclopropyl system, using the analogy of halogen-lithium exchange,¹⁰ one would expect that the reaction would proceed with retention of configuration and this could account for the formation of optically active 1-methyl-2,2-diphenylcyclopropylmagnesium bromide. That this type of exchange could not be the reason for obtaining an optically active Grignard reagent can be seen from the results in Table III. Since the ease of halogen-metal exchange occurs in the order $I > Br > Cl$, one would expect that the optical purity of the product would also diminish in that order. It can be seen that this is in exact opposition to the results obtained. A free radical exchange mechanism⁴³ is also unlikely since complete racemization would be expected and since metal halides which catalyze this reaction were not present to any appreciable extent.⁴⁴

Experimental⁴⁵

All optical rotations were taken on a Bellingham and Stanley polarimeter equipped with a sodium vapor lamp. The instrument could be read to 0.01° and estimated to $\pm 0.0025^\circ$. A 1-dm. tube was used in all determinations using chloroform as the solvent. A Cary 14 recording ultraviolet spectrometer was used to obtain the ultraviolet spectra using 1-cm. quartz cells. Infrared spectra were obtained with a Perkin-Elmer infrared spectrophotometer 137. The potassium bromide disks were prepared by standard procedures²³ and solution spectra were run in either chloroform or carbon tetrachloride. A Varian 60 Mc. high resolution n.m.r. spectrometer was used to obtain spectra using carbon tetrachloride as a solvent and tetramethylsilane as an internal standard. An F and M Model 500 temperature programmed gas chromatograph with a thermistor detector equipped with a disk integrator was used to analyze the samples of 1-methyl-2,2-diphenylcyclopropane. Helium was used as the carrier gas and analytical determinations were carried out at 150° using a 2 ft. \times 0.25 in. o.d. copper column, packed with 20% diethylene glycol succinate on Chromosorb W. Preparative separation was carried out at 200° using a 5 ft. \times $\frac{3}{8}$ in. o.d. copper column packed with 20% SF-96 on Chromosorb W.

All halogen-lithium interchange and Grignard reactions were run under dry, oxygen-free nitrogen or argon. The solvents used

(41) (a) The nature of the Grignard reagent is an open question. See R. E. Dessy, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 3476 (1957); E. C. Ashby and W. E. Becker, *ibid.*, **85**, 118 (1963); G. D. Studky and R. E. Rundle, *ibid.*, **85**, 1002 (1963); R. M. Salinger and H. S. Mosher, *ibid.*, **86**, 1782 (1964). (b) O. A. Reutov, *Angew. Chem.*, **72**, 202 (1960); H. B. Charman, E. D. Hughes, and C. Ingold, *J. Chem. Soc.*, 2530 (1959); F. R. Jensen, *J. Am. Chem. Soc.*, **82**, 2469 (1960). For a review see G. Kobrich, *Angew. Chem. Intern. Ed. Engl.*, **1**, 382 (1962).

(42) R. Pierce, A. F. Meiners, and E. T. McBee, *J. Am. Chem. Soc.*, **75**, 2516 (1953).

(43) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944); R. T. Morrison, N. P. Loire, and F. L. Bach, Jr., Abstracts, 136th National Meeting of the American Chemical Society, Cleveland, Ohio, April 5-14, 1960, p. 20.

(44) See Experimental for analysis of trace metals in the magnesium used.

(45) All melting points and boiling points are uncorrected. Elemental analyses were performed by E. Thommen, Basel, Switzerland.

for these reactions were dried by distillation from lithium aluminum hydride. Spectroscopic analysis of the magnesium powder used in the Grignard reactions was shown to contain the following percentages of trace elements: Al, 0.006; Ca, 0.01; Cu, 0.001; Fe, 0.0043; Mn, 0.005; Ni, 0.0005; Pb, 0.006; Si, 0.005; Sn, 0.01; Zn, 0.002.⁴⁶

(\pm)-Methyl 1-Chloro-2,2-diphenylcyclopropanecarboxylate.—To a refluxing solution of 137 g. (1.14 moles) of methyl α -chloroacrylate⁴⁷ was added 200 ml. of a petroleum ether (30–60 $^\circ$) solution of 39 g. (0.20 mole, theoretical) of diphenyldiazomethane. Heating was continued until the solution decolorized. The solvent was stripped to give a pale yellow solid which after crystallization from methanol gave 39.5 g. (69%) of ester, m.p. 98–100 $^\circ$. The analytical sample had m.p. 99–100.3 $^\circ$.

Anal. Calcd. for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27. Found: C, 71.33; H, 5.12.

(\pm)-1-Chloro-2,2-diphenylcyclopropanecarboxylic Acid.—The reaction between methyl α -chloroacrylate (126 g., 0.12 mole) and 0.75 mole (theoretical) of diphenyldiazomethane was carried out as previously described. The solvent was removed and the ester, which was not isolated, was saponified by heating to reflux in a solution consisting of 1 l. of methanol, 200 ml. of water, and 84 g. (1.5 moles) of potassium hydroxide for 10 hr. The methanol was removed under vacuum, the residue dissolved in water, and extracted with ether. The aqueous layer was acidified and the crude acid collected by filtration and dried to yield 150 g. (73%) of product, m.p. 169–171 $^\circ$, which after one crystallization from an aqueous methanol solution gave m.p. 172.5–173.5 $^\circ$.

Anal. Calcd. for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80. Found: C, 70.57; H, 4.90.

(–)-1-Chloro-2,2-diphenylcyclopropanecarboxylic Acid.—The (–)-enantiomer was obtained from its quinine salt by fractional recrystallization from *N,N*-dimethylformamide, after obtaining the salt from a methanol solution. The analytical sample had m.p. 193–194 $^\circ$, $[\alpha]_D^{21.5} - 77.6 \pm 2.1^\circ$ (c 1.074).

Anal. Calcd. for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80; Cl, 13.00. Found: C, 70.21; H, 4.90; Cl, 12.78.

(\pm)-1-Chloro-2,2-diphenylcyclopropanecarbinol.—To a slurry of 6 g. (0.158 mole) of lithium aluminum hydride in 250 ml. of dry ether was added a solution of 35 g. (0.128 mole) of racemic acid in 250 ml. of dry ether, and the mixture was stirred for 6 hr. after addition was completed. The excess hydride was decomposed using aqueous ammonium chloride, the solution filtered, dried over sodium sulfate, and the solvent stripped to give a white solid which after crystallization from petroleum ether (60–110 $^\circ$) gave 31 g. (8%) of product which had m.p. 98–99.5 $^\circ$; analytical sample, m.p. 101.5–102.5 $^\circ$.

Anal. Calcd. for $C_{16}H_{15}ClO$: C, 74.27; H, 5.84. Found: C, 74.27; H, 5.83.

(–)-1-Chloro-2,2-diphenylcyclopropanecarbinol.—Lithium aluminum hydride reduction of the optically active acid ($[\alpha]_D^{21.5} - 77.6 \pm 2.1^\circ$) gave (–)-1-chloro-2,2-diphenylcyclopropanecarbinol, m.p. 110–111 $^\circ$, $[\alpha]_D^{20.2} - 58.2 \pm 1.7^\circ$ (c 1.325).

Anal. Calcd. for $C_{16}H_{15}ClO$: C, 74.27; H, 5.84; Cl, 13.72. Found: C, 74.22; H, 6.00; Cl, 13.45.

(\pm)-1-Chloro-2,2-diphenylcyclopropanecarbinyl *p*-Toluenesulfonate.—To a solution of 38.1 g. (0.20 mole) of *p*-toluenesulfonyl chloride in 100 ml. of dry pyridine at 0 $^\circ$ was added a solution of 25.5 g. (0.099 mole) of racemic carbinol in 50 ml. of dry pyridine. The solution was allowed to stand at 0 $^\circ$ for 3 hr. and then for 2 hr. at room temperature. The mixture was poured over ice giving a tan solid, which on crystallization from aqueous acetone gave 28 g. (71%), m.p. 120–121 $^\circ$ dec.

Anal. Calcd. for $C_{23}H_{21}ClSO_3$: C, 66.82; H, 5.14; S, 7.78; Cl, 8.61. Found: C, 67.08; H, 5.26; S, 7.92; Cl, 8.66.

(–)-1-Chloro-2,2-diphenylcyclopropanecarbinyl *p*-Toluenesulfonate.—The optically active tosylate was prepared in an identical manner with that of the racemic compound using carbinol with $[\alpha]_D^{20.2} - 68.2 \pm 1.7^\circ$ which after crystallization from aqueous acetone gave m.p. 123 $^\circ$ dec., $[\alpha]_D^{24} - 43.4 \pm 3.3^\circ$ (c 0.746).

Anal. Calcd. for $C_{23}H_{21}ClSO_3$: C, 66.82; H, 5.14; S, 7.78; Cl, 8.61. Found: C, 67.09; H, 5.24; S, 7.99; Cl, 8.75.

(\pm)-1-Chloro-1-methyl-2,2-diphenylcyclopropane.—A solution of 28 g. (0.070 mole) of racemic tosylate in 150 ml. of dry THF

(46) Kindly carried out by Dr. J. F. Pashak, Dow Chemical Co., Midland, Mich.

(47) C. S. Marvel, J. Dec, H. G. Cooke, and J. L. Cowan, *J. Am. Chem. Soc.*, **61**, 3156 (1939).

was added dropwise to a slurry of 6 g. (0.158 mole) of lithium aluminum hydride in 250 ml. of dry ether, and stirred for 7 hr. after addition. The excess hydride was decomposed with aqueous ammonium chloride, the ethereal solution dried, then stripped to give a white solid which after crystallization from methanol gave 13 g. (76%) of the desired chloride, m.p. 68.3–70°; analytical sample, m.p. 71.5–72.5°.

Anal. Calcd. for $C_{16}H_{15}Cl$: C, 79.16; H, 6.23. Found: C, 79.45; H, 6.25.

(-)-1-Chloro-1-methyl-2,2-diphenylcyclopropane.—The optically active chloride was prepared in a similar manner to that for the racemic compound using tosylate having $[\alpha]^{25D} - 43.4 \pm 3.3^\circ$ and giving the chloride, m.p. 66.5–67.5°, $[\alpha]^{26.5D} - 64.08 \pm 1.5^\circ$ (c 1.576).

Anal. Calcd. for $C_{16}H_{15}Cl$: C, 79.16; H, 6.23. Found: C, 78.94; H, 6.33.

Preparation of Optically Active 1-Methyl-2,2-diphenylcyclopropylmagnesium Bromide with Metallic Magnesium Followed by Carbonation. A. Reaction Run by Adding Ethylene Dibromide to (+)-1-Methyl-1-bromo-2,2-diphenylcyclopropane and Magnesium in Refluxing THF.—To a stirred solution of 2.30 g. (0.0080 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane¹⁰ ($[\alpha]^{27.5D} + 106.5 \pm 1.5^\circ$), 0.50 g. (0.020 mole) of magnesium powder, and a crystal of iodine in 12 ml. of refluxing THF was added, dropwise, a solution of 0.5 ml. of ethylene dibromide in 2.5 ml. of THF over a period of 5 min. After the addition was complete, the reaction mixture was stirred an additional 10 min. at reflux and then at room temperature for 5 more min. The greenish gray suspension was poured onto a crushed Dry Ice–ether slurry with stirring and the carbon dioxide was allowed to evaporate. The remaining solution was diluted with 100 ml. of ether, acidified with dilute hydrochloric acid, and washed with water. Extraction of the ethereal solution with dilute aqueous potassium hydroxide followed by acidification of the basic washings with hydrochloric acid gave the solid acid which was collected and dried to give 0.766 g. (38%), m.p. 176–181.5°, $[\alpha]^{29D} - 5.25 \pm 1.1^\circ$ (c 2.173), and an infrared spectrum identical with that of an authentic sample of acid.

The ether layer was dried over sodium sulfate, and the solvent removed to give a yellow oil which was distilled, b.p. 83° at 0.1 mm., to give 0.624 g. (38%), $[\alpha]^{21.5D} - 14.13 \pm 1.20^\circ$ (c 2.137), and an infrared spectrum identical with that of an authentic sample of the hydrocarbon.

B. Preparation of the Grignard Reagent at Room Temperature.—To a mixture of 0.50 g. (0.020 mole) of magnesium powder and a crystal of iodine was added dropwise with stirring 0.5 ml. of ethylene dibromide in 2.5 ml. of THF. After completion of this reaction the temperature was allowed to come to 24°, after which 2.30 g. (0.0080 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{27.5D} + 106.5 \pm 1.5^\circ$) in 12 ml. of THF was added dropwise. In a short time (10 min.) the temperature started to rise, and an ice bath was required to regulate the temperature between 25–27.5° over the 40 min. required for the addition, after which the greenish gray solution was stirred an additional 10 min., and poured onto a crushed Dry Ice–ether slurry with stirring. After evaporation of the carbon dioxide, the remaining slurry was diluted with ether and acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic extracts gave the solid acid which was collected and dried to give 0.908 g. (45%), m.p. 178–183°, $[\alpha]^{22D} - 4.24 \pm 1.100^\circ$ (c 2.238), infrared spectrum identical with that of an authentic sample of acid.

The ether layer was dried over calcium chloride; removal of the solvent gave a yellow liquid which on distillation, b.p. 88–91° at 0.20–0.25 mm., gave 0.588 g. (36%) of the hydrocarbon. Purification of this sample proved difficult and after two more distillations, a sample was obtained with a constant rotation $[\alpha]^{21.7} - 12.40 \pm 1.6^\circ$ (c 1.460). Gas-liquid chromatography showed less than 2% of an impurity present.

C. Formation of the Optically Active Grignard Reagent in Refluxing Diethyl Ether.—A solution of 0.5 ml. of ethylene dibromide in 5 ml. of ether was added to 0.50 g. (0.020 mole) of magnesium powder and an immediate evolution of ethylene was observed after which the solution was stirred for an additional 15 min. to ensure completion of the reaction. To this refluxing mixture was added a solution of 2.15 g. (0.0075 mole) 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{27.5D} - 109.1 \pm 1.3^\circ$) in 12 ml. of ether over a 10-min. period, after which stirring and heating were continued for an additional 10 min. The green solution was

poured onto a crushed Dry Ice–ether slurry with stirring. After the carbon dioxide had evaporated, the remaining slurry was diluted with ether, acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic extracts with hydrochloric acid gave the solid acid which was collected and dried to give 0.156 g. (8.3%), m.p. 174–180°, $[\alpha]^{26D} + 5.11 \pm 1.60^\circ$ (c 1.563), and an infrared spectrum identical with that of an authentic sample of acid.

The ethereal solution was dried over sodium sulfate then concentrated to give a yellow liquid which was distilled, b.p. 83–85° at 0.05 mm., to give 0.920 g. (59%) of the desired hydrocarbon, $[\alpha]^{26D} + 12.04 \pm 1.0^\circ$ (c 2.980).

D. Formation of the Optically Active Grignard Reagent without the Use of Preformed Magnesium Bromide in THF.—To 0.50 g. (0.020 mole) of magnesium powder in 2.5 ml. of THF, which was stirred and refluxed, was added a solution of 2.30 g. (0.0080 mole) of (-)-1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{25.5D} - 111.6 \pm 0.9^\circ$) in 10 ml. of THF over a 10-min. period. There was approximately a 15-min. induction period and stirring and heating were continued an additional 30 min. The green solution was poured onto a crushed Dry Ice–ether slurry with stirring and the carbon dioxide was allowed to evaporate. The remaining solvent was diluted with ether, acidified with dilute hydrochloric acid, and washed with water and dilute potassium hydroxide. Acidification of the basic washings with hydrochloric acid gave the solid acid which was collected and dried to give 0.640 g. (39%), m.p. 175–181°, $[\alpha]^{26.5D} + 5.32 \pm 0.85^\circ$ (c 2.873), and an infrared spectrum identical with that of an authentic sample of acid. The neutral ether layer was dried over magnesium sulfate and concentrated to give an oil which was distilled, b.p. 80° at 0.08 mm., to yield 0.730 g. (45%), $[\alpha]^{25D} + 15.86 \pm 0.7^\circ$ (c 3.657), and an infrared spectrum identical with that of an authentic sample of hydrocarbon.

E. Formation of the Optically Active Grignard Reagent by Adding the Bromide to Preformed Magnesium Bromide in Refluxing THF.—To 0.50 g. (0.020 mole) of magnesium powder in 2 ml. of the refluxing THF was added a solution of 0.5 ml. of ethylene dibromide in 2 ml. of THF and stirred for 15 min. after the evolution of ethylene was complete. To this stirred, refluxing slurry was added a solution of 2.30 g. (0.0080 mole) of (-)-1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{25.5D} - 111.6 \pm 0.9^\circ$) over an interval of 10 min., with an additional 20 min. of stirring and refluxing. The solution was poured onto a crushed Dry Ice–ether slurry with stirring and the carbon dioxide was allowed to evaporate. The residual solution was diluted with ether, acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic washings with hydrochloric acid gave the solid acid which was collected and dried to give 1.08 g. (66%), m.p. 173–182°, and $[\alpha]^{26D} + 5.58 \pm 0.90^\circ$ (c 2.953), and an infrared spectrum identical with that of an authentic sample of acid.

The neutral ether solution was dried over magnesium sulfate, then concentrated to give a yellow oil which was distilled using a molecular still, with the pot temperature at $42 \pm 2^\circ$ and a pressure of 0.05 mm., to yield 0.330 g. (20%), $[\alpha]^{26.5D} + 15.29 \pm 0.5^\circ$ (c 5.250). Gas-liquid chromatography showed the presence of a small shoulder which was removed by preparative gas-liquid chromatography to give a sample with $[\alpha]^{26D} + 17.05 \pm 0.7^\circ$ (c 3.465).

F. Preparation of the Optically Active Grignard Reagent in Refluxing THF for 180 Min.—To 0.50 g. (0.020 mole) of magnesium powder in 2 ml. of refluxing THF was added with stirring 0.5 ml. of ethylene dibromide in 2 ml. of THF. Stirring was continued for 10 min. after the evolution of ethylene had been completed and then a solution of 2.30 g. (0.0080 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{25.5D} - 111.6 \pm 0.9^\circ$) in 10 ml. of THF was added over an interval of 10 min. Stirring and heating were continued for 3 hr. after which the solution was poured onto a crushed Dry Ice–ether slurry with stirring. The carbon dioxide was allowed to evaporate and the remaining solution was diluted with ether, acidified with dilute hydrochloric acid, washed with water, and extracted with dilute potassium hydroxide. Acidification of the basic washings gave the solid acid which was collected and dried to give 0.67 g. (41%), m.p. 173.5–181°, $[\alpha]^{29D} + 5.52 \pm 0.94^\circ$ (c 2.553), and an infrared spectrum identical with that of an authentic sample of acid.

The neutral ether layer was dried over magnesium sulfate and concentrated to give a yellow oil which on distillation using a

molecular still with the pot temperature at $42 \pm 2^\circ$ and a pressure of 0.05 mm. gave 0.530 g. (32%) of hydrocarbon, $[\alpha]^{25D} + 15.16 \pm 0.2^\circ$ (c 11.610). This sample was shown to contain a maximum of 4% of an impurity. Preparative gas-liquid chromatography gave a sample, $[\alpha]^{25D} + 16.13 \pm 0.7^\circ$ (c 3.360), which gave only one peak in the gas-liquid chromatogram.

Preparation of the Optically Pure Grignard Reagent. A. Reaction of Optically Active 1-Methyl-2,2-diphenylcyclopropylithium with Magnesium Bromide Followed by Carbon Dioxide.—A solution of 1 *M* *n*-butyllithium in 20 ml. of ether was added over a 5-min. interval with stirring to 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{27.5} + 1.06.5 \pm 1.5^\circ$) in 25 ml. of ether with the temperature rising to 27° . The yellow solution was stirred an additional 5 min. after which 0.025 mole of methylmagnesium bromide in 25 ml. of ether was added over a 10-min. period. The stirring was continued an additional 15 min. and the reaction mixture was poured onto a crushed Dry Ice-ether slurry with stirring. After evaporation of the carbon dioxide, the ether solution was acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic fraction with hydrochloric acid gave the solid acid which was collected and dried to give 0.310 g. (32%), m.p. $185.5-187.5^\circ$, $[\alpha]^{21.4D} - 35.5 \pm 1.2^\circ$ (c 2.052), and an infrared spectrum identical with that of an authentic sample of acid.

B. Reaction of Optically Active 1-Methyl-2,2-diphenylcyclopropylithium with Magnesium Bromide Followed by Carbon Dioxide.—To 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{27.5D} + 106.5 \pm 1.5^\circ$) in 25 ml. of ether was added dropwise over a 5-min. interval 25 ml. of a 1.3 *M* solution of *n*-butyllithium in ether. Stirring was continued for 5 min. and the yellow solution was added to magnesium bromide in 30 ml. of ether prepared from 9.40 g. (0.050 mole) of ethylene dibromide, and 1.43 g. (0.059 mole) of magnesium powder. The ether was observed to reflux on the addition and stirring was continued an additional 30 min. during which the intense yellow color characteristic of the lithium reagent was seen to disappear. The solution was poured onto a crushed Dry Ice-ether slurry and after evaporation of the carbon dioxide the ethereal solution was acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic solution with hydrochloric acid yielded the solid acid which was collected and dried to give 0.290 g. (30%), m.p. $185-188.5^\circ$, $[\alpha]^{27.5D} - 34.2 \pm 1.1^\circ$ (c 2.206), and an infrared spectrum identical with that of an authentic sample of acid.

C. Reaction of Optically Active 1-Methyl-2,2-diphenylcyclopropylithium with Magnesium Bromide and DME followed by Carbonation.—To 2.00 g. (0.0070 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{27.5D} + 106.5 \pm 1.5^\circ$) in 35 ml. of ether was added dropwise over a 5-min. interval 25 ml. of a 1.3 *M* solution of *n*-butyllithium in ether. After stirring an additional 5 min. the bright yellow solution was added dropwise over a 5-min. period to magnesium bromide in 30 ml. of ether prepared from 9.40 g. (0.050 mole) of ethylene dibromide and 1.34 g. (0.059 mole) of magnesium powder. The ether was observed to reflux on the addition and stirring was continued for 15 min. during which the temperature dropped from 35 to 28° and the intense yellow color characteristic of the lithium reagent disappeared. To this mixture was added 7 ml. of DME, and an immediate precipitate of magnesium salts formed⁴⁸ with the temperature rising to 33° . After stirring for 15 more min. the reaction mixture was poured onto a crushed Dry Ice-ether slurry with stirring. The carbon dioxide was allowed to evaporate and the solution was acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic extracts gave the solid acid which was collected and dried to give 0.700 g. (40%), m.p. $183-187.5^\circ$, $[\alpha]^{28.2D} - 33.0 \pm 1.2^\circ$ (c 2.136), and an infrared spectrum identical with that of an authentic sample of acid.

Formation of the Optically Active Grignard Reagent from (-)-1-Methyl-1-chloro-2,2-diphenylcyclopropane and Metallic Magnesium in THF Followed by Carbonation.—To a refluxing slurry of preformed magnesium bromide prepared from 0.5 ml. of ethylene dibromide, 0.50 g. (0.020 mole) of magnesium powder, and 4 ml. of THF was added dropwise with stirring a solution of 2.00 g. (0.0083 mole) of 1-methyl-1-chloro-2,2-diphenylcyclopropane ($[\alpha]^{26.1D} - 65.4 \pm 1.5^\circ$) in 10 ml. of THF over a 10-min. period.

Following the addition, stirring and heating were continued for an additional 20 min. after which the reaction mixture was poured onto a crushed Dry Ice-ether slurry with stirring. The carbon dioxide was allowed to evaporate and the remaining slurry was diluted with water and extracted with dilute aqueous potassium hydroxide. Acidification of the basic solution gave the solid acid which was collected and dried to give 1.10 g. (53%), m.p. $176-182^\circ$, and $[\alpha]^{25D} + 9.86 \pm 0.75^\circ$ (c 3.314). An analogous experiment with chloride having $[\alpha]^{25.5D} - 64.1 \pm 1.5^\circ$ gave the corresponding acid, m.p. $172.5-180.5^\circ$, $[\alpha]^{26D} + 9.44 \pm 0.82^\circ$ (c 3.039), and an infrared spectrum identical with that of an authentic sample of acid.

The hydrocarbon could not be separated from the chloride by conventional distillation. Preparative gas-liquid chromatography gave a sample of pure hydrocarbon, with $[\alpha]^{26.5D} + 32.63 \pm 0.8^\circ$ (c 2.865).

Formation of the Optically Active Grignard Reagent from (-)-1-Methyl-1-iodo-2,2-diphenylcyclopropane and Metallic Magnesium in THF Followed by Carbonation.—To a refluxing slurry of preformed magnesium bromide from the reaction of 0.5 ml. of ethylene dibromide, 0.50 g. (0.020 mole) of magnesium powder, and 4 ml. of THF was added dropwise with stirring 1.55 g. (0.0046 mole) of 1-methyl-1-iodo-2,2-diphenylcyclopropane¹⁰ ($[\alpha]^{25D} - 171.6 \pm 2.2^\circ$) in 10 ml. of THF over a period of 10 min. Stirring was continued an additional 20 min. after completion of the addition, and the mixture was poured onto a crushed Dry Ice-ether slurry with stirring. After allowing the carbon dioxide to evaporate, the residue was diluted with ether, acidified with dilute hydrochloric acid, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic washings with hydrochloric acid gave the solid acid which was collected and dried to give 0.46 g. (39%), m.p. $173-183^\circ$, $[\alpha]^{27D} + 2.03 \pm 0.67^\circ$ (c 3.246), and in infrared spectrum identical with that of an authentic sample of acid.

The ethereal layer was dried over magnesium sulfate and concentrated to give a yellow oil which was distilled, b.p. $82.5-87.5^\circ$ at 0.07 mm., to give 0.214 g. (21%), $[\alpha]^{25D} + 5.21 \pm 0.30^\circ$ (c 9.305). Preparative gas-liquid chromatography gave a sample, $[\alpha]^{25D} + 6.09 \pm 0.73^\circ$ (c 3.525).

Experiment to Show that No Resolution Was Occurring in the Work-up of the Acidic Product.—An experiment showing that resolution of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid does not occur on the work-up of the reaction mixtures resulting from carbonation of the lithium or Grignard reagents was carried out in the following manner. A sample of 0.2564 g. of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid, $[\alpha]^{26D} + 21.56^\circ$ (c 2.564), was dissolved in dilute aqueous potassium hydroxide, acidified with hydrochloric acid, and extracted with ether. The ether layer was extracted with dilute aqueous potassium hydroxide and acidified with hydrochloric acid to give the solid acid which was collected and dried, giving the rotation $[\alpha]^{26D} + 21.81^\circ$ (c 2.307). This work-up was identical with that used in the preceding experiments and indicates that resolution was not occurring.

Check on the Stability of the Optically Active Bromide and Iodide toward Magnesium Bromide in Refluxing THF.—The reaction of 1.0 g. (0.041 mole) of coarse magnesium turnings with 1.0 ml. of ethylene dibromide in 15 ml. of THF was used to prepare anhydrous magnesium bromide. The solution of magnesium bromide in THF was filtered under dry argon into a flask containing 1.00 g. of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{25D} - 107.5 \pm 1.0^\circ$ (c 2.628)), and this solution which became homogeneous on heating was stirred and heated for 70 min. The mixture was poured into water, extracted with petroleum ether ($30-60^\circ$), dried over magnesium sulfate, and concentrated to give 0.952 g. of recovered bromide, $[\alpha]^{25.2D} - 104.4 \pm 1.0^\circ$ (c 2.272).

A similar amount of magnesium bromide was prepared as in the previous experiment using 10 ml. of THF. This slurry was heated with 0.350 g. of 1-methyl-1-iodo-2,2-diphenylcyclopropane, $[\alpha]^{25D} - 162.0$ (c 1.400), for 60 min. and then poured into water, extracted with petroleum ether ($30-60^\circ$), and dried over magnesium sulfate. Concentration of the ether solution gave 0.310 g. of recovered iodide with $[\alpha]^{26D} - 159.8^\circ$ (c 0.860).

Hydrolysis of 1-Methyl-2,2-diphenylcyclopropylmagnesium Bromide with Deuterium Oxide. A. Grignard Reagent Prepared in the Presence of Preformed Magnesium Bromide in THF.—To a refluxing solution of preformed magnesium bromide prepared from 0.50 g. (0.010 mole) of magnesium powder and 0.5 ml. of ethylene dibromide in 4 ml. of THF was added a solution

of 2.30 g. (0.008 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane in 10 ml. of THF over a 10-min. period with stirring. After stirring an additional 20 min., the reaction mixture was hydrolyzed using 99.5% D₂O. The solution was diluted with water, extracted with petroleum ether (30–60°), and dried over magnesium sulfate. Removal of the solvent gave a pale yellow oil which was distilled, b.p. 103–104° at 0.45 mm., to give 1.24 g. (74%) of the desired hydrocarbon. A peak height analysis of the n.m.r. spectra showed that 79.8 ± 1% incorporation of deuterium had occurred.

B. Grignard Reagent Prepared in Ether with Preformed Magnesium Bromide Present.—To a refluxing slurry of preformed magnesium bromide prepared from 0.50 g. (0.020 mole) of magnesium powder, 0.5 ml. of ethylene dibromide, and 4 ml. of ether was added dropwise 2.30 g. (0.0080 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane in 10 ml. of ether over a 10-min. period. Stirring was continued for an additional 20 min. after the addition and the reaction mixture hydrolyzed using 99.5% deuterium oxide. The solution was diluted with water, extracted with petroleum ether (30–60°), and dried over magnesium sulfate. Removal of the solvent gave a yellow oil which was distilled, b.p. 100–101° at 0.32 mm., to give 11.1 g. (66%) of the hydrocarbon. A peak height analysis of the n.m.r. spectra showed that 52 ± 1% incorporation of deuterium had occurred.

N.m.r. Analysis of Deuterium Incorporated into 1-Methyl-2,2-diphenylcyclopropane on Hydrolysis of the Grignard Reagent with Deuterium Oxide.—The 60 Mc. n.m.r. spectrum of 1,1-diphenyl-2-methylcyclopropane is very complex, consisting of a broad phenyl doublet, sixteen distinguishable methylene peaks,

and a sharp methyl doublet. The components of the methyl doublet were separated by 6 c.p.s. and deuteration showed that the chemical shift between the α -H and the methyl doublet was about 40 c.p.s. Therefore it was possible to determine the extent of deuteration by comparing the relative peak heights of the α -H methyl doublet with the α -D methyl singlet.^{49,50} Analysis for deuterium was also carried out by measuring the areas under each peak after extrapolation and the results were in good agreement. The n.m.r. data was also in agreement with the results of an analysis obtained from the mass spectrum of a sample.

Thermal Stability of Grignard Reagent.—The Grignard reagent was prepared in the usual manner using 0.5 g. of magnesium, 0.5 ml. of 1,2-dibromoethane, and 4 ml. of THF. To this mixture was added a solution of 2.3 g. of (–)-1-bromo-1-methyl-2,2-diphenylcyclopropane, [α]_D²⁵ – 111°, dissolved in 10 ml. of THF. The reaction mixture was stirred for 20 min. and 25 ml. of di-*n*-butyl ether was added and the reaction flask heated to distil off the THF. After ca. 15 ml. of distillate was collected and the pot temperature reached 128–129° (15 min.) the reaction mixture was kept at reflux temperature for an additional 30 min., cooled, and poured onto Dry Ice.

The reaction products were worked up as previously described to yield 0.50 g. of (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, m.p. 174–181°, [α]_D²⁵ + 5.51° (*c* 3.6), 15% optical purity, and 0.65 g. of (+)-1-methyl-2,2-diphenylcyclopropane, [α]_D²⁵ + 15.0° (*c* 12.12), 11% optical purity.

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Mechanisms of α -Elimination. Nitrobenzylsulfonium, -ammonium, and -phosphonium Ions Reacting with Aqueous Hydroxide¹⁻³

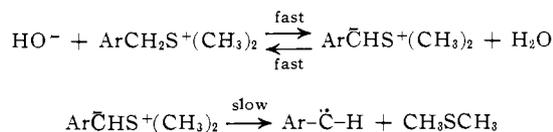
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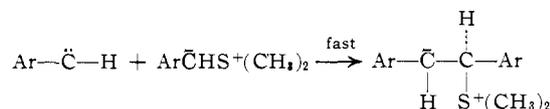
p-Nitrobenzyltrimethylsulfonium *p*-toluenesulfonate reacts with aqueous sodium hydroxide to give a quantitative yield of *p,p'*-dinitrostilbene, the methylene protons being rapidly and reversibly removed in D₂O–DO[–], according to n.m.r. *m*-Nitrobenzyltrimethylsulfonium bromide reacts with aqueous sodium hydroxide to give a 41% yield of *m,m'*-dinitrostilbene oxide and a 5% yield of *m*-nitrobenzyl alcohol, essentially the same result being obtained under nitrogen. *p*-Nitrobenzyltrimethylammonium bromide is nearly inert to refluxing aqueous sodium hydroxide. *p*-Nitrobenzyltriphenylphosphonium bromide reacts with aqueous sodium hydroxide to give largely triphenylphosphine oxide and *p*-nitrotoluene. The natures of the leaving group and the ring substituent appear to be critical for stilbene formation by α -elimination.

Many cases of α -elimination to form divalent carbon intermediates have been reported.⁴ In most of those carried out in aqueous base a number of products form. It was therefore of considerable interest that *p*-nitrobenzyl chloride in 50% aqueous dioxane⁵ and *p*-nitrobenzyltrimethylsulfonium tosylate (*p*-toluenesulfonate) in water⁶ react with dissolved sodium hydroxide to give quantitative yields of *p,p'*-dinitrostilbene. Kinetic studies showed that these reactions are first order in *p*-nitrobenzyl compound and first order in sodium hydroxide, yet cannot involve rate-determining proton removal because infrared spectra of recovered reactant after partial reaction in D₂O–DO[–]

showed substantial replacement of C–H by C–D bonds. The only reasonable mechanism seemed to involve rate-determining formation of a divalent carbon intermediate (carbene) followed by rapid reaction of the carbene to form *p,p'*-dinitrostilbene.^{5,6} Rapid, reversible removal of the proton followed by rate-determining attack of the intermediate on another substrate molecule would require kinetics second order in *p*-nitrobenzyl compound. The scheme proposed for the *p*-nitrobenzyltrimethylsulfonium ion⁶ is (where Ar = *p*-nitrophenyl)



followed by



(1) Previous paper (preliminary communication): I. Rothberg and E. R. Thornton, *J. Am. Chem. Soc.*, **85**, 1704 (1963).

(2) Acknowledgment is made to Smith Kline and French Laboratories for a fellowship to I. R. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(3) For further details cf. I. Rothberg, Ph.D. dissertation in chemistry, University of Pennsylvania, 1963.

(4) For reviews, see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 24; E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).

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