very viscous sirup which hardened to a glass on cooling. This material had $[\alpha]_D$ +1.27° (c 5.3 in pentane). It was identified as disiloxane by its infrared spectrum as compared to authentic disiloxane.[1] The yield was 66%. Crystallization and recrystallization from pentane gave white crystals (0.31 g.), m.p. 96–98°. A mixture m.p. with authentic meso-R₃Si*OSi*R₃ showed no depression (authentic meso-disiloxane prepared from reaction of

(−)R₃Si*OK with (−)R₃Si*Cl). A 50–50 mixture of the reaction product and racemic (+)R₃Si*OSi*R₃ (racemic siloxane prepared by mixing equal amounts of (+)- and (−)-enantiomers) had m.p. 85–95°.

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

Cyclopropanes. XV. The Optical Stability of 1-Methyl-2,2-diphenylcyclopropyllithium[1]

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RECEIVED JANUARY 20, 1964

Halogen–lithium interchange between (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane and n-butyllithium produced 1-methyl-2,2-diphenylcyclopropyllithium which on treatment with carbon dioxide, bromine, and iodine yielded products in which the configuration as well as the optical activity had been completely retained. No effect on the optical results could be found on varying the temperature, solvent, or reaction time. The lithium derivative was found to react with solvent in the order 1,2-dimethoxyethane > tetrahydrofuran > diethyl ether.

Introduction

Previous studies on the optical stability of tetrahedrally (sp³) hybridized organolithium compounds have revealed that their stability is both temperature and solvent dependent. Letsinger[2] showed that halogen–metal interchange between (−)-(R)-2-octyl iodide and sec-butyllithium at −70° followed by carbonation gave (−)-(R)-2-methyloctanoic acid which was 80% racemized. It was also demonstrated that a small amount of diethyl ether (~6%) in the petroleum ether solvent was required for the halogen–metal interchange to occur and furthermore the optical purity decreased with increased temperature and time alloted for the exchange. The latter observations were also made by Curtin and Koehl[3] in their study on the exchange between (±)-2-octyllithium and di-(−)-(R)-sec-butylmercury which yields on carbonation (−)-(R)-2-methylbutyric acid. This exchange occurs in pentane solution and diethyl ether is not necessary to effect it. As a matter of fact when 6% of diethyl ether is added the product obtained is racemic whereas when pentane alone is the solvent the product is 20–30% optically pure. The effect of diethyl ether may well be to cause dissociation of the carbon–lithium bond which then results in racemization. This would be consistent with observations made on the amines which are isoelectronic with the tetrahedrally hybridized carbanions. In the case of amines there is no gegenion available and consequently there is a very rapid inversion of configuration.

Trigonally hybridized vinyllithium derivatives have been shown to retain their configuration to a much larger extent than tetrahedrally hybridized ones, although substituent, solvent, and temperature effects have also been observed.[3,4] Miller and Lee[5] have

established lower limits to the activation energy for the isomerization of vinyl carbanions formed from 1,2-dihaloethenes as 25–35 kcal./mole.

With trigonally hybridized nitrogen, stereoisomeric forms of oximes[6] and azomethines[7] have been isolated which demonstrate that the trigonally hybridized non-bonded pair of electrons is capable of maintaining its configuration. This is illustrated by the observation that the oxime of 4-ketocyclohexanecarboxylic acid could be resolved into its optically active enantiomers.[8] Curtin and Hausser[9] have recently studied the kinetics of cis–trans isomerization of a number of stereoisomeric imines and have found that, as in the case of vinyl anions, substituents capable of delocalizing a negative charge have a marked influence on the rate of isomerization.

The cyclopropane ring has been characterized as having a great deal of "double bond character."[10] The stereochemical fate of a pair of nonbonding electrons in an orbital which is part of a three-membered ring poses an interesting question. Would the cyclopropyl carbanion whose exocyclic orbitals are reported[11] to be sp²·²⁸ hybridized behave like the trigonally hybridized (sp²) vinyl carbanion or the tetrahedrally hybridized (sp³) carbanion? In an attempt to answer this question, optically active 2,2-diphenylcyclopropyl cyanide (I) was treated with lithium diisopropylamide in ether. Under these conditions racemization was rapid.[12] However, a comparison of the rate of racemization of I. by methoxide in methanol, with the acyclic analog 1-methyl-2,2-diphenylpropionitrile indicated that a barrier to inversion did exist since the latter racemized 1.2×10^3 faster than I.[13] The existence of this energy barrier to inversion was reinforced

(1) This work was supported by a grant from the National Science Foundation.

(2) R. L. Letsinger, J. Am. Chem. Soc., **72**, 4842 (1950).

(3) D. Y. Curtin and W. J. Koehl, Jr., ibid., **84**, 1967 (1962).

(4) E. A. Braude and J. A. Coles, J. Chem. Soc., 2078 (1951); A. S. Dreiding and R. J. Pratt, J. Am. Chem. Soc., **76**, 1902 (1954); F. G. Bordwell and P. S. Landis, ibid., **79**, 1593 (1957); D. Y. Curtin and J. W. Crump, ibid., **80**, 1922 (1958); D. Y. Curtin and E. E. Harris, ibid., **73**, 2716 (1951); A. N. Nesmayanov, A. E. Borisov, and N. A. Vol'kenau, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 992 (1954); A. N. Nesmayanov, A. E. Borisov, and N. V. Novikova, Dokl. Akad. Nauk SSSR, **119**, 712 (1958); D. Seyferth and L. G. Vaughan, J. Organometal. Chem., **1**, 201 (1963).

(5) S. I. Miller and W. G. Lee, J. Am. Chem. Soc., **81**, 6313 (1959).

(6) A. Hantzsch and A. Werner, Ber., **23**, 11 (1890).

(7) W. Manchot and J. R. Furlong, ibid., **42**, 3030 (1909).

(8) W. H. Mills and H. Schindler, J. Chem. Soc., 312 (1923), and references cited therein; R. E. Lyle and G. G. Lyle, J. Org. Chem., **22**, 856 (1957).

(9) D. Y. Curtin and J. W. Hausser, J. Am. Chem. Soc., **83**, 3474 (1961).

(10) For a recent review of the physical and chemical evidence upon which this characterization is based see M. Yu. Lukina, Russ. Chem. Rev. (Engl. Trans.), **31**, 419 (1962).

(11) L. L. Ingraham in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

(12) H. M. Walborsky and F. M. Hornyak, J. Am. Chem. Soc., **77**, 6026 (1955).

(13) H. M. Walborsky and F. M. Hornyak, ibid., **78**, 872 (1956).

by the observation that the rate of hydrogen–deuterium exchange was 8080 times faster than the rate of racemization.[14]

As in the case of cyclopropanes, the inversion of a nonbonded pair of electrons in a three-membered ring containing nitrogen (aziridines) has been shown to be slower than that of the corresponding tetrahedrally hybridized pair of electrons.[15] Reasonable suggestions have been made to account for the differences in stability of the tetrahedral, trigonal, and cyclopropyl carbanions.[16,17]

It was recognized that the cyano group in I was assisting in lowering the energy barrier for racemization. In an effort to obtain a cyclopropyl carbanion which was not adjacent to an unsaturated substituent the Haller–Bauer cleavage of 1-benzoyl-1-methyl-2,2-diphenylcyclopropane (II) was investigated.[18] When the (−)-(R)-II was cleaved with sodium amide in toluene the hydrocarbon (+)-(S)-1-methyl-2,2-diphenylcyclopropane was produced, presumably via the 1-methyl-2,2-diphenylcyclopropyl carbanion. The hydrocarbon was shown to have completely retained its optical activity as well as its configuration.

In order to gain some further insight into the stability of the 1-methyl-2,2-diphenylcyclopropyl carbanion the investigation of the halogen–metal interchange reaction between n-butyllithium and (+)-(S)-1-bromo-1-methyl-2.2-diphenylcyclopropane was undertaken.[19]

Results and Discussion

Syntheses and Configurational Relationships.—The preparation of (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane was accomplished by the reduction of (+)-(S)-1-bromo-2,2-diphenylcyclopropanecarboxylic acid[20] with lithium aluminum hydride to the corresponding (+)-(S)-1-bromo-2,2-diphenylcyclopropylcarbinol. The carbinol was converted to the (+)-(S)-p-toluenesulfonate ester which was reduced with lithium aluminum hydride to the desired starting material. (−)-(R)-1-Iodo-1-methyl-2,2-diphenylcyclopropane was prepared by the reaction of (−)-(R)-1-bromo-1-methyl-2,2-diphenylcyclopropane with n-butyllithium followed by the addition of iodine.

The absolute configuration of (+)-1-methyl-2,2-diphenylcyclopropane has been established as S by a direct chemical correlation with (+)-(R)-propylene oxide.[21] Since (+)-(S)-2,2-diphenylcyclopropanecarboxylic acid was chemically related to (+)-(S)-1-methyl-2,2-diphenylcyclopropane,[18] its absolute configuration is also established as are those of (−)-(S)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid and (−)-(R)-1-bromo-2,2-diphenylcyclopropanecarboxylic acid which have been related in configuration to (+)-(S)-2,2-diphenylcyclopropanecarboxylic acid by the method of quasiracemates.[20]

(14) H. M. Walborsky, A. A. Youssef, and J. M. Motes, J. Am. Chem. Soc., **84**, 2465 (1962).

(15) A. T. Bottini and J. D. Roberts, ibid., **80**, 5203 (1958).

(16) D. E. Applequist and A. H. Peterson, ibid., **83**, 862 (1961).

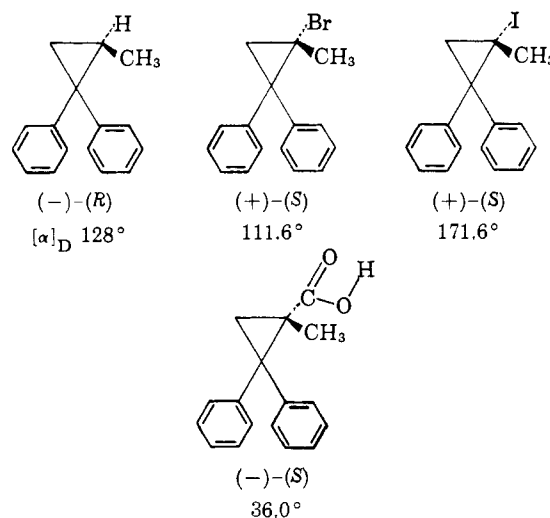(17) H. M. Walborsky, Record Chem. Progr., **23**, 75 (1962).

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

(19) For a preliminary communication see (a) H. M. Walborsky and F. J. Impastato, ibid., **81**, 5835 (1959); (b) H. M. Walborsky and A. E. Young, ibid., **83**, 2595 (1961); (c) ref. 17.

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

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

The relation between 1-iodo-1-methyl-2,2-diphenylcyclopropane and 1-bromo-1-methyl-2,2-diphenylcyclopropane was accomplished by a chemical correlation. Treatment of (−)-(R)-1-bromo-1-methyl-2,2-diphenylcyclopropane with n-butyllithium followed by iodine gave (−)-1-iodo-1-methyl-2,2-diphenylcyclopropane which was converted to (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid by further reaction with n-butyllithium and then carbon dioxide. It has previously been demonstrated, in the case of vinyl halides, that the sequence of reactions, halogen–metal interchange followed by carbonation, proceeds with over-all retention of configuration.[4,22] This has also been shown to be the case with 1-bromo-1-methyl-2,2-diphenylcyclopropane as will be seen later in the Discussion. On this basis the (−)-1-iodo-1-methyl-2,2-diphenylcyclopropane has been assigned the R-configuration. The following are the configurational relationships and specific rotations of the molecules that will be used in the subsequent discussion.
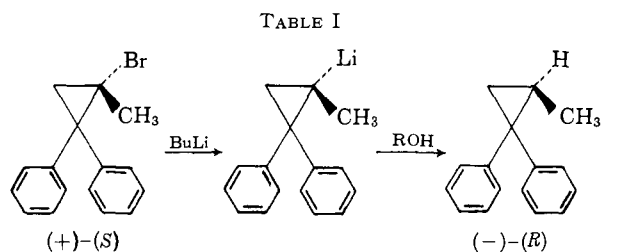

(−)-(R)   (+)-(S)   (+)-(S)

$[\alpha]_D$ 128°   111.6°   171.6°

(−)-(S)

36.0°

Optically Active 1-Methyl-2,2-diphenylcyclopropyllithium.—Treatment of (+)-(S)-1-bromo-2,2-diphenylcyclopropane with n-butyllithium followed by hydrolysis with methanol produced (−)-(R)-1-methyl-2,2-diphenylcyclopropane. The stereochemistry of the reaction is that of over-all retention of configuration. The results are summarized in Table I and the data clearly show that the reaction proceeds with a high degree of retention of optical activity as well as configuration. The optical purity of the hydrocarbon formed on hydrolysis ranged from 76–85%.

A possibility exists that the 1-methyl-2,2-diphenylcyclopropyllithium might undergo a rearrangement. Carbanionic rearrangements involving phenyl migration to the carbanion site have been observed in cases involving both tetrahedrally hybridized and trigonally hybridized carbanions. For example, 2,2,2-triphenylethyllithium rearranges to 1-lithio-1,1,2-triphenylethane,[23] and 2,2-diphenylpropyllithium[23,24] rearranges to 1,2-diphenyl-1-methyllithium presumably through a transition state or intermediate such as III. In the trigonally hybridized case it has been demonstrated

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(23) E. Grovenstein, Jr., and L. P. Williams, Jr., J. Am. Chem. Soc., **83**, 2537 (1961); E. Grovenstein, Jr., and G. Wentworth, ibid., **85**, 3305 (1963).
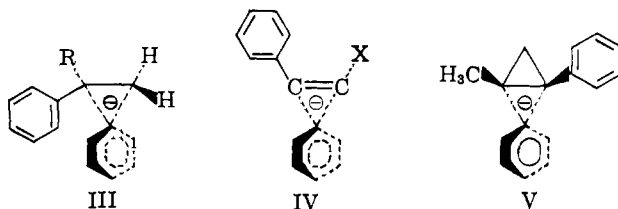
(24) H. E. Zimmerman and A. Zweig, ibid., **83**, 1197 (1961).

TABLE I

(+)-(S)   (−)-(R)

Run	$[\alpha]_D$ of bromide	Solvent	Temp., °C.	Time, min.	Yield, %	Optical purity,[a] %
1	106.0	Ether–benzene–petr.[d]	6	30	43	60[c]
2	106.2[b]	2:1:1	35	10	44	77
3	107.1	Ether	35	10	61	84
4	107.1	Ether	−3 to 0	30	73[e]	76
5	91.9	Petr–DME[f]	28–33	10	69	85

[a] The maximum rotation of the bromide is taken to be 111.6° and of the hydrocarbon[18] 128°. [b] Enantiomer used. [c] Low value[19] due to contamination with (+)-bromide. [d] Petroleum ether (30–60°). [e] Yield based on recovered bromide. [f] 1,2-Dimethoxyethane.

that 2-halo-1,1-diphenylethene rearranges[25−28] to tolan, possibly *via* IV. It was felt that 1-methyl-2,2-diphenylcyclopropyllithium might rearrange in a similar manner to yield 2-methyl-1,2-diphenylcyclopropyllithium, through a transition state or intermediate such as V. However, when the lithium

III   IV   V

was hydrolyzed with deuterium oxide, the mass spectral analysis showed[29] that the deuterium was incorporated in the 1-position of the 1-methyl-2,2-diphenylcyclopropane and therefore under the conditions employed very little, if any, rearrangement occurred.[30] The mass spectral analysis also showed that only 75% of the theoretical amount of deuterium was incorporated on hydrolysis. Since it is known that alkyllithium compounds readily cleave diethyl ether at room temperature,[31] the above result is not surprising.

The data in Table I, runs 1–4, indicate that the optical purity of the product is independent of the solvent, time, and the temperature. Zook and Russo[32] reported that 1,2-dimethoxyethane (DME) greatly increased the rates of alkylation of enolate anions by coordinating with the cation, thereby facilitating the dissociation of the carbon–metal bond. On the assumption that the solvents used in runs 1–4 were unable to affect dissociation of the carbon–lithium bond and therefore the retention of activity that is observed

is due to the covalent nature of the carbon–lithium bond, it was decided to use DME as the solvent (run 5, Table I). In contrast to the reaction in the other solvent systems, where the solution turned a bright yellow on the addition of *n*-butyllithium to the bromide, when DME was used the yellow color only made a transient appearance. In addition, carbonation of the reaction mixture failed to yield any 1-methyl-2,2-diphenylcyclopropanecarboxylic acid, the only product isolated being the hydrocarbon in 85% optical purity, a result not differing appreciably from the previous experiments. That the cyclopropyllithium did cleave DME to methyl vinyl ether was clearly demonstrated by passing the exit gases from the reaction through an acid solution of 2,4-dinitrophenylhydrazine and isolating the 2,4-dinitrophenylhydrazone of acetaldehyde, which is the hydrolysis product of methyl vinyl ether.

Although the carbanionic character of the carbon–lithium bond was enhanced, no effect was observed on the optical purity of the resulting hydrocarbon. The optical purities reported in Table I are minimum values due to the difficulty encountered in removal from the (−)-hydrocarbon all of the unreacted (+)-bromide. To circumvent this difficulty the carbonation of 1-methyl-2,2-diphenylcyclopropyllithium was undertaken (Table II).

TABLE II

Run	Solvent	Temp. °C.	Time, min.	Yield, %	Optical purity,[a] %
1	Ether	28	30	53	100[b]
2	Ether	28–29	10	52	100
3	Ether	−8 ± 2	30	49	100
4	THF	−8 ± 2	20	39	100

[a] The maximum rotation of the bromide is taken to be 111.6° and that of the acid as 36°. [b] Within experimental error.

As in the case of hydrolysis of 1-methyl-2,2-diphenylcyclopropyllithium, there is an apparent lack of temperature, solvent, or time dependence on the optical purity. It should be noted that the over-all reaction proceeds, within experimental error, with complete retention of optical activity as well as configuration. Furthermore, it is observed that THF reacts with the lithium reagent more readily than does diethyl ether.

Besides hydrolysis and carbonation, cyclopropyllithium was allowed to react with iodine and bromine.[33] Earlier in the Discussion the result from the addition of iodine to the lithium reagent was described and it was demonstrated that the reaction proceeded with complete retention of configuration and optical activity. That brominolysis gives comparable results was shown by converting (+)-(S)-1-iodo-1-methyl-2,2-diphenylcyclopropane to the corresponding lithium reagent and allowing this reagent to react with bromine. The bromide isolated was shown to be 95% optically pure and the configuration was the same as that of the

(25) J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, **64**, 1271 (1960); A. A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 3293 (1955).

(26) D. Y. Curtin and E. W. Flynn, *ibid.*, **81**, 4714 (1959), and earlier references described therein.

(27) S. J. Cristol and R. S. Bly, Jr., *ibid.*, **81**, 4714 (1959).

(28) W. M. Jones and R. Damico, *ibid.*, **85**, 2273 (1963).

(29) We are indebted to Dr. W. A. Bailey, Jr., Shell Oil Co., Houston, Texas, for the mass spectral analysis and interpretation.
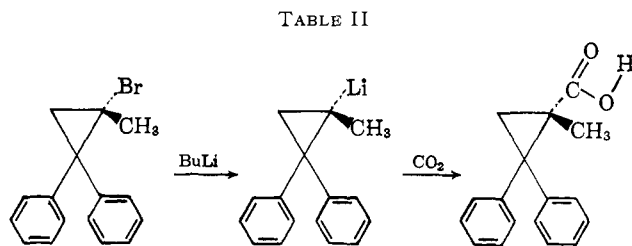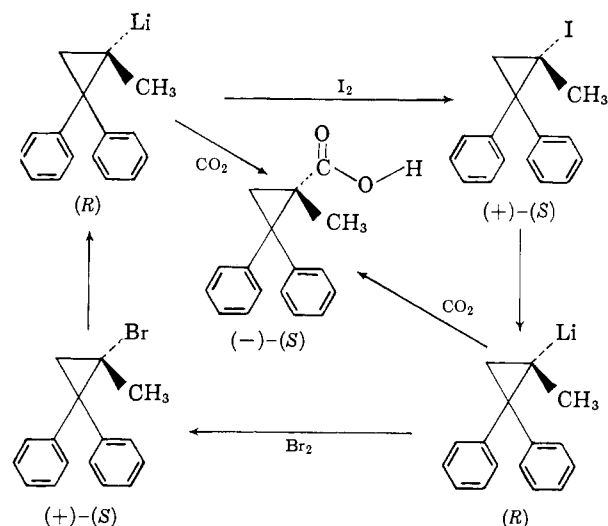
(30) We are currently exploring the conditions necessary to bring about such a rearrangement.

(31) R. G. Jones and H. Gilman in "Organic Reactions," Vol. 6, edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 351.

(32) H. D. Zook and T. J. Russo, *J. Am. Chem. Soc.*, **82**, 1258 (1960).

(33) We are indebted to M. S. Aronoff for performing this experiment.

starting iodide. The stereochemical results are summarized.

(R)   (+)-(S)

(−)-(S)

(+)-(S)   (R)

The cleavage of organomercury compounds with bromine or iodine has been shown to involve competing free-radical and polar processes and that by varying reaction conditions either process could be made to predominate.[34] It was also shown that in brominolysis the ionic process prevailed when polar solvents or sources of positive bromine were used and that under these conditions one obtains a high degree of retention of configuration.[34b,35] The brominolysis of cis- and trans-2-methylcyclopropyllithium has been reported to be highly stereospecific in pentane but much less so in pentane–ether mixtures.[16] The almost complete stereospecificity found in the brominolysis and iodinolysis of the 1-methyl-2.2-diphenylcyclopropyllithium in ether is in agreement with the previous observations made on the hydrolysis and carbonation of this reagent. The stereochemical results are consistent with an $S_{E}i$ or $S_{E}2$ mechanism[34a,36] for these reactions.

In summary, it has been demonstrated that 1-methyl-2,2-diphenylcyclopropyllithium is capable of maintaining its configuration, as judged by the optical purity of the products obtained, when allowed to react with methanol, water, carbon dioxide, bromine, and iodine. Moreover, solvent changes, temperature, and reaction time had very little, if any, effect on the optical purity. These results imply that the 1-methyl-2,2-diphenylcyclopropyllithium is configurationally more stable than alkyllithiums (sp^3) and stilbenyllithium (sp^2) which have been shown either to racemize or isomerize under comparable conditions. It is comparable in stability to alkyl-substituted vinyllithiums.[37]

Experimental[38]

Polarimetry.—The instrument used was a Bellingham and Stanley polarimeter equipped with a sodium vapor lamp. The instrument could be read to 0.01° and estimated to ±0.0025°.

(34) (a) S. Winstein and T. G. Traylor, J. Am. Chem. Soc., **78**, 2597 (1956); (b) F. R. Jensen and C. H. Gale, ibid., **82**, 148 (1960).

(35) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, ibid., **82**, 2466 (1960).

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

(37) D. E. Applequist and D. F. O'Brien, J. Am. Chem. Soc., **85**, 743 (1963).

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

A 1-dm. tube was used in all determinations using chloroform as the solvent.

(±)-1-Bromo-2,2-diphenylcyclopropanecarbinol.—A slurry of 196 g. (0.59 mole) of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate[20] in 400 ml. of dry tetrahydrofuran and 500 ml. of dry ether was added with stirring to 0.35 mole of lithium aluminum hydride in 250 ml. of dry ether and stirred for 3 hr. after addition. The excess hydride was decomposed by adding aqueous ammonium chloride and the ethereal solution was filtered, dried, and stripped to yield a yellow solid which on crystallization from aqueous methanol gave 120 g. (67%) of the desired product, m.p. 125–128°.

Anal. Calcd. for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99; Br, 26.35. Found: C, 63.58; H, 5.03; Br, 26.38.

(+)- and (−)-1-Bromo-2,2-diphenylcyclopropanecarbinol.—To a slurry of 3.5 g. (0.092 mole) of lithium aluminum hydride in 200 ml. of dry ether was added in a slurry 17.5 g. (0.055 mole) of 1-bromo-2,2-diphenylcyclopropanecarboxylic acid[20] ($[\alpha]^{24}D$ +111.6 ± 3.0°) in 250 ml. of dry ether. Stirring was continued for 2 hr. after addition. The excess hydride was decomposed using aqueous ammonium chloride, and the ethereal solution was filtered, dried, and stripped to give a white solid which on crystallization from aqueous methanol gave 13.2 g. (75%), m.p. 133–134° and $[\alpha]^{24}D$ +108.71 ± 5.0° (c 0.519).

Anal. Calcd. for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.64; H, 5.07.

The (−)-enantiomer was obtained in a similar manner from resolved acid having $[\alpha]^{23}D$ −109.8 ± 2.5° giving m.p. 130–131.5°, $[\alpha]^{23}D$ −108.1 ± 2.5° (c 1.013).

Anal. Calcd. for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.48; H, 5.14.

(±)-1-Bromo-2,2-diphenylcyclopropanecarbinol p-Toluenesulfonate.—A solution of 34.6 g. (0.11 mole) of 1-bromo-2,2-diphenylcyclopropanecarbinol in 100 ml. of dry pyridine was added to 43.4 g. (0.23 mole) of p-toluenesulfonyl chloride in 100 ml. of dry pyridine at 0°. The mixture was allowed to remain at 0° overnight, poured over ice giving a tan solid, which on crystallization from aqueous acetone yielded 45.7 g. (85%) of the desired tosylate, m.p. 118° dec. Further recrystallization from aqueous acetone gave the analytical sample, m.p. 121° dec.

Anal. Calcd. for $C_{23}H_{21}BrSO_3$: C, 60.26; H, 4.80. Found: C, 60.42; H, 4.62.

(+)- and (−)-1-Bromo-2,2-diphenylcyclopropanecarbinol p-Toluenesulfonate.—The optically active tosylates were prepared in an identical manner with that of the racemic material. From carbinol having $[\alpha]^{24}D$ +108.71 ± 5.0° was obtained (+)-1-bromo-2,2-diphenylcyclopropanecarbinol p-toluenesulfonate, m.p. 121° dec., $[\alpha]^{24}D$ +70.57 ± 1.9° (c 1.312).

Anal. Calcd. for $C_{23}H_{21}BrSO_3$: C, 60.26; H, 4.80; Br, 18.05; S, 7.12. Found: C, 60.49; H, 4.62; Br, 17.81; S, 6.94.

Carbinol having $[\alpha]^{23}D$ −108.16 ± 2.5° gave tosylate, m.p. 121° dec., $[\alpha]^{24}D$ −73.10 ± 2.6° (c 0.941).

Anal. Calcd. for $C_{23}H_{21}BrSO_3$: C, 60.26; H, 4.80; Br, 18.05; S, 7.12. Found: C, 60.44; H, 4.80; Br, 17.81; S, 7.32.

(±)-1-Bromo-1-methyl-2,2-diphenylcyclopropane.—To a slurry of 10 g. (0.38 mole) of lithium aluminum hydride in 500 ml. of dry ether was added 39.2 g. (0.086 mole) of racemic tosylate in 200 ml. of dry tetrahydrofuran. Stirring was continued for 3 hr. after the addition. The excess hydride was decomposed with aqueous ammonium chloride and the reaction mixture was filtered, dried, and the solvent stripped to give a yellowish solid which on crystallization from methanol gave 19.6 g. (80%) of the desired bromide, m.p. 80–82°. The analytical sample had m.p. 82–84°.

Anal. Calcd. for $C_{16}H_{15}Br$: C, 66.90; H, 5.23. Found: C, 66.72; H, 5.18.

(+)- and (−)-1-Bromo-1-methyl-2,2-diphenylcyclopropane.—Reduction of the optically active tosylates in a manner identical with that used for the racemic gave from tosylate having $[\alpha]^{24}D$ +70.57 ± 1.9°, 1-bromo-1-methyl-2,2-diphenylcyclopropane, m.p. 81–82°, $[\alpha]^{21.3}D$ +107.1 ± 2.2° (c 1.034). The highest rotation obtained was $[\alpha]^{25.5}D$ 111.59 ± 0.89°.

Anal. Calcd. for $C_{16}H_{15}Br$: C, 66.90; H, 5.23. Found: C, 66.71; H, 5.47.

From tosylate having $[\alpha]^{24}D$ −73.10 ± 2.6° was obtained the bromide, m.p. 82–83°, $[\alpha]^{23}D$ −106 ± 2.0° (c 1.024).

Anal. Calcd. for $C_{16}H_{15}Br$: C, 66.90; H, 5.23. Found: C, 66.77; H, 5.33.

(−)- and (±)-1-Methyl-1-iodo-2,2-diphenylcyclopropane.—To a solution of 1 g. (0.0034 mole) of (±)-1-methyl-1-bromo-2,2-di-

phenylcyclopropane in 20 ml. of anhydrous ether was added 25 ml. of a 1 M ethereal solution of n-butyllithium over a 5-min. period. A brilliant yellow solution resulted which after stirring for 5 additional min. was treated with small portions of iodine until the violet color persisted. The solution was washed with aqueous sodium thiosulfate, water, and dried. Removal of the solvent gave a viscous oil which after three recrystallizations from methanol gave 0.47 g. (41%) of the desired product, m.p. 86.5–88.0°.

Anal. Calcd. for $C_{16}H_{15}I$: C, 57.51; H, 4.53; I, 37.94. Found: C, 57.73; H, 4.71; I, 37.71.

Using a procedure similar to that used for the racemic iodide, 5 g. (0.016 mole) of (−)-1-methyl-1-bromo-2,2-diphenylcyclopropane, ($[\alpha]^{25.5}$D −111.59 ± 0.89°), when treated with 90 ml. of an ethereal solution of 1 M n-butyllithium, followed by the addition of iodine, gave 2.03 g. (37%) of (−)-1-methyl-1-iodo-2,2-diphenylcyclopropane, with $[\alpha]^{25}$D −171.62 ± 2.2° (c 1.075), m.p. 117–119°. The infrared spectrum was superimposable with a spectrum of racemic material.

Anal. Calcd. for $C_{16}H_{15}I$: C, 57.51; H, 4.53; I, 37.94. Found: C, 57.57; H, 4.67; I, 37.49.

Conversion of (−)-1-Methyl-1-iodo-2,2-diphenylcyclopropane to (+)-1-Methyl-2,2-diphenylcyclopropanecarboxylic Acid *via* Halogen–Metal Interchange with n-Butyllithium Followed by Carbonation.—Addition of 15 ml. of an ethereal solution of 1 M n-butyllithium over a period of 5 min. with stirring to 0.65 g. (0.0018 mole) of 1-methyl-1-iodo-2,2-diphenylcyclopropane ($[\alpha]^{25}$D −171.62 ± 2.2°) gave a yellow solution which was stirred an additional 5 min. with the temperature at 22–24°. The solution was poured onto a crushed Dry Ice–ether slurry with stirring, and the Dry Ice was allowed to evaporate. The ether was removed, and the salts were dissolved in 10% potassium hydroxide and extracted with ether. Acidification of the basic aqueous layer yielded the acid which was filtered and dried to give 0.279 g. (61%), m.p. 185–87.5°, $[\alpha]^{22.8}$D +34.57 ± 1.2° (c 2.123). The infrared spectrum of the acid was identical with that of an authentic sample.

Reaction of (−)-1-Methyl-1-bromo-2,2-diphenylcyclopropane with n-Butyllithium Followed by Hydrolysis with Methanol.—To a stirred solution of 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane, ($[\alpha]^{23}$D −106.19 ± 1.5°) in 1:1 petroleum ether (30–60°)–benzene was added over a 5-min. period 25 ml. of a 1 M ether solution of butyllithium. The solution turned a brilliant yellow and the solution was refluxed at 35–38°, after which it was cooled in a Dry Ice–acetone bath and hydrolyzed with methanol. The solution was filtered and concentrated to give a yellow liquid which on distillation gave 1-methyl-2,2-diphenylcyclopropane, 0.33 g. (44%), b.p. 75° at 0.04 mm., $[\alpha]^{23}$D +97.69 ± 0.86° (c 2.903).

Deuteration of (±)-1-Methyl-2,2-diphenylcyclopropyllithium. Addition of 30 ml. of a 1.7 M ether solution of n-butyllithium to 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane in 50 ml. of ether over a period of 5 min. at 29° gave a yellow solution. The reaction mixture was stirred an additional 5 min., cooled in an ice bath, and hydrolyzed with 1.40 g. (0.07 mole) of 99.5% deuterium oxide. The solution was filtered, dried over sodium sulfate, and distilled, b.p. 81–82° at 0.05 mm., to give 0.62 g. (77%) of hydrocarbon product which had a carbon–deuterium band at 4.5 μ in the infrared.[39] Mass spectral analysis[29] showed that the deuterium atom was substituted at carbon 1. The analysis gave the results: undeuterated, 21.9; dideuterated, 3.6; and higher, < 0.1.

Interchange of (+)-1-Methyl-1-bromo-2,2-diphenylcyclopropane with n-Butyllithium at 35° and Hydrolysis with Methanol.—To a stirred solution of 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{22.3}$D +107.10 ± 1.5°) in 50 ml. of ether was added dropwise 30 ml. of a 1.7 M ether solution of n-butyllithium. The solution turned yellow and was refluxed at 33–35° for 5 min. with continued stirring, cooled in Dry Ice–acetone, and hydrolyzed with methanol. The solution was washed with water, dried over calcium chloride, and concentrated to give a yellow oil which was distilled, b.p. 80.5° at 0.06 mm., to give 0.49 g. of hydrocarbon (61%), $[\alpha]^{23.6}$D −105.80 ± 0.85° (c 2.975, CHCl₃), infrared spectrum identical with that of an authentic sample of the hydrocarbon.

Reaction of (−)-1-Methyl-1-bromo-2,2-diphenylcyclopropane with n-Butyllithium at 0° followed by Hydrolysis with Methanol.—A solution of 30 ml. of 1.7 M n-butyllithium in ether was added

to 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{22.3}$D +107.10 ± 1.50°) in 50 ml. of ether cooled to −3.5 to 0° by an ice–hydrochloric acid bath over a period of 15 min. The yellow solution was stirred an additional 15 min., cooled in a Dry Ice–acetone bath, and hydrolyzed with methanol. The solution was washed with water, dried over calcium chloride, and concentrated to give a viscous oil which crystallized on cooling. The hydrocarbon was separated from the bromide by leaching with petroleum ether (30–60°) while cooling the mixture in a Dry Ice–acetone bath, and distilled, b.p. 74–75° at 0.05 mm., to give 0.275 g. (73% based on recovered bromide), $[\alpha]^{25}$D −96.40 ± 1.9° (c 1.410). The infrared spectrum was identical with that of an authentic sample of hydrocarbon. The recovered bromide, 0.607 g., had $[\alpha]^{24}$D +105.13°.

Reaction of (+)-1-Methyl-1-bromo-2,2-diphenylcyclopropane with n-Butyllithium in Ethylene Glycol Dimethyl Ether (DME).—To a solution of 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{24.8}$D +91.86 ± 2.0°, 82% optically pure) in 50 ml. of DME was added dropwise with stirring over a 5-min. period a 1.7 M pentane solution of n-butyllithium. Only a transient yellow color was observed and the temperature rose from 28 to 33°. After an additional 5 min. of stirring while cooling in a water bath at 30–32° the solution containing a flocculent precipitate was poured onto crushed Dry Ice covered with ether, and after evaporation of the carbon dioxide the solution was washed with dilute sodium hydroxide and then water. Acidification of the basic extracts with hydrochloric acid failed to yield any 1-methyl-2,2-diphenylcyclopropanecarboxylic acid. The ether layer was dried over sodium sulfate, then concentrated to give a yellow oil which on distillation, b.p. 77–80° at 0.05 mm., gave 0.553 g. (69%) of the desired hydrocarbon. Redistillation gave a sample with $[\alpha]^{21.5}$D −95.05 ± 2.2° (c 1.071), and an infrared spectrum identical with that of an authentic sample. In another experiment the exit gases were bubbled through 2,4-DNPN solution, and 0.25 g. of derivative was collected. Recrystallization of the product from aqueous ethanol gave a m.p. 148–149.5° which corresponds to the 2,4-DNPH derivative of acetaldehyde. A mixture melting point of this sample with an authentic sample of the 2,4-DNPH of acetaldehyde was undepressed.

Carbonation of the Product from the Reaction of n-Butyllithium with (+)-1-Methyl-1-bromo-2,2-diphenylcyclopropane at Room Temperature in Ether for 10 Min.—To a solution of 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{22.3}$D +107.10 ± 1.5°) in 50 ml. of ether was added 30 ml. of a 1.7 M ether solution of n-butyllithium over a 5-min. period with stirring. The solution turned yellow and the temperature rose to 28–29°. After an additional 5 min. of stirring, the solution was poured onto a crushed Dry Ice–THF slurry with stirring. The carbon dioxide was allowed to evaporate and the ether solution was acidified, washed with water, and extracted with dilute aqueous potassium hydroxide. Acidification of the basic layer yielded the solid acid which was collected and dried to give 0.51 g. (52.5%), m.p. 186.5–188.5°, $[\alpha]^{20.8}$D −35.41 ± 1.2° (c 2.126), which had an infrared spectrum identical with that of an authentic sample.

When bromide having $[\alpha]^{24.8}$D +91.86 ± 2.0° (82% optically pure) was used under conditions identical with those of the previous experiment, a 51.5% yield of acid was obtained, m.p. 174–184°, $[\alpha]^{24.2}$D −29.57 ± 1.2° (c 2.012).

Carbonation of the Product of the Reaction between n-Butyllithium and (+)-1-Methyl-1-bromo-2,2-diphenylcyclopropane at −8 ± 2° in Ether for 30 Min.—A solution of 1.4 M n-butyllithium in 25 ml. of ether was added dropwise with stirring over a period of 15 min. to a solution of 1.10 g. (0.0038 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane ($[\alpha]^{24.5}$D +91.86 ± 2.0° (82% optically pure)) in 50 ml. of ether cooled to −7 ± 2° by an ice–hydrochloric acid bath. The solution turned yellow and was stirred an additional 15 min., then poured onto a crushed Dry Ice–ether slurry with stirring. The carbon dioxide was allowed to evaporate, and the ether solution 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 aqueous extracts with hydrochloric acid yielded the solid acid which was collected and dried to give 0.154 g. (45.4% based on recovered bromide), m.p. 173–184.5°, $[\alpha]^{23.4}$D −27.51° ± 1.2° (c 1.443), infrared spectrum identical with that of an authentic sample.

The neutral ether layer was dried over calcium chloride and concentrated to give a viscous oil which was dissolved in methanol

(39) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3244 (1961).

and yielded 0.715 g. of starting bromide, $[\alpha]^{24}$D $+95.90°$ (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 ($[\alpha]^{25.5}$D $− 111.59 \pm 0.8°$) 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°, $[\alpha]^{26}$D $+35.26 \pm 1.2°$ (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 ± 2° 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 ($[\alpha]^{28}$D $− 107.53 \pm 1.5°$) in 50 ml. of THF over a period of 10 min. with the temperature held at $−8 \pm 2°$ 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°, $[\alpha]^{26.5}$D $+34.71 \pm 1.3°$ (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, $[\alpha]^{23}$D $− 163.6°$ (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 element. The solid fractions were combined to yield 0.097 g. (17%), m.p. 78–82°, $[\alpha]$D $− 103.4°$ (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.

Cyclopropanes. XVI. An Optically Active Grignard Reagent and the Mechanism of Grignard Formation[1,2]

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RECEIVED JANUARY 20, 1964

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 ± 2% optical purity) and (−)-(R)-1-methyl-2,2-diphenylcyclopropane (10 ± 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 bromide[5] 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 Pauling[7] 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 Jaffé[9] 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 paper[10] 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).

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