Pyrolysis of Sultine 6.—Cyclic sulfinate 6 (0.61 g, 1.71 × 10^{-3} mol) was placed in a 100-ml, three-necked, round-bottomed flask with a gas inlet and outlet stopcock in the side necks of the flask, and a standard taper stopper in the center neck. The flask was flushed with Linde high-purity dry nitrogen as it was heated up to 360°. The nitrogen flow was reduced to a slight positive pressure (the outlet may be connected to a mercury-filled bubbler) and the metal bath heated to 360–400° for 5 min. At about 375–380° [temperature measured with a partial (76 mm) immersion thermometer] a sudden evolution of gas was observed, and the compound became dark red. An analysis of the gases was not done. The pyrolyzed compound was cooled in a nitrogen atmosphere, dissolved in a minimum amount of carbon tetrachloride, and separated on a column (2 × 47 cm) of Woelm acidic alumina, activity grade I. Elution with ethanol-carbon tetrachloride (1:9) and with carbon tetrachloride alone gave fluorenone 2 (122 mg, 3.63 × 10^{-4} mol, 21.2% yield) and fluorene 3 (43 mg, 1.34 × 10^{-4} mol, 7.8% yield), identified by comparison of their ultraviolet and infrared spectra with those of 2 and 3 produced in the normal pyrolysis of naphthothiete sulfone 1.

Registry No.—1, 979-37-3; 2, 19639-51-1; 3, 19639-52-2; 4, 19639-53-3; 4 (dithioketal), 19639-54-4; 6, 19639-55-5; reduction product of 6 ($C_{23}H_{16}OS$), 19639-56-6; 5-phenylbenzo[*b*]naphtho[1,2-*d*]thiophene, 19639-57-7.

The Reaction of Phenyllithium with 1-Halo-2-butenes[1]

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Received November 12, 1968

Phenyllithium reacted with *cis*- and *trans*-1-chloro-2-butene and *trans*-1-bromo-2-butene and gave a mixture of 3-phenyl-1-butene, *cis*- and *trans*-1-phenyl-2-butene, and *cis*- and *trans*-1-methyl-2-phenylcyclopropane. The ratio of the isomeric cyclopropanes was similar to that obtained from the addition of phenyllithium to 3-methylcyclopropene and confirmed the formation of this compound in the reaction. Phenylsodium and phenylmagnesium bromide in their reactions with the 1-halo-2-butenes gave only the three olefins.

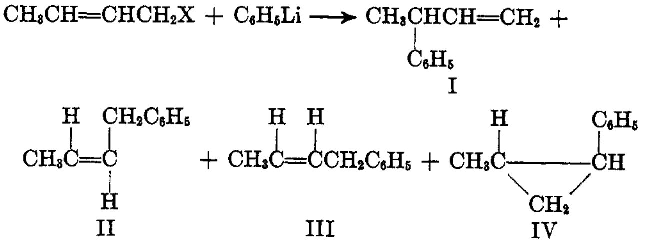
Two mechanisms have been offered for the formation of cyclopropanes in the reaction of phenyllithium with allylic halides. The first of these suggested an attack of the phenyl carbanion on the β-carbon atom of the halide followed by an intramolecular cyclization to the cyclopropane.[2] The second one suggested the formation of a carbene followed by cyclization to a cyclopropene which reacts with phenyllithium and forms the cyclopropane.[3] Results with deuterated allyl chloride and allyl-1-^{14}C chloride[4] have confirmed the second mechanism for the formation of the cyclopropane.

In this paper studies are reported on the course of the reaction between phenyllithium and 1-halo-2-butenes and the stereochemistry of the cyclopropane produced. The first mechanism would be expected to produce only *trans*-1-methyl-2-phenylcyclopropane and the second offers the possibility of a mixture of *cis* and *trans* isomers.

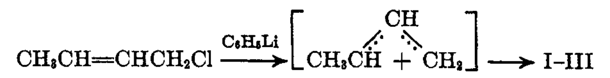
The results obtained for the reaction of phenyllithium with *cis*- and *trans*-1-chloro-2-butene and *trans*-1-bromo-2-butene, and of phenylsodium with *trans*-1-chloro-2-butene are listed in Table I.

Examination of the results in Table I indicates that *cis*- and *trans*-1-methyl-2-phenylcyclopropane (IV) are formed together with 3-phenyl-1-butene (I), *trans*-1-phenyl-2-butene (II), and *cis*-1-phenyl-2-butene (III) in the reaction of phenyllithium with 1-halo-2-butenes (Scheme I). Phenylsodium in the same reaction did not form any detectable cyclopropane. The cyclopropane formed varied in yield with the conditions used and was by vpc analysis better than 93.9% *trans;* the *cis* compound was present in amounts of 6.1% or less. The high ratio of *trans* to *cis* isomers would suggest that the first mechanism was operating but a study of the reaction of 3-methylcyclopropene with phenyllithium found the same ratio of isomeric cyclopropanes. The results therefore confirm the second mechanism for the formation of the cyclopropanes and are in agreement with the results of Magid and Welch.[4]

SCHEME I



An interesting sidelight on the reaction was the formation of a small percentage of *cis*-1-phenyl-2-butene (III) in the reaction of phenyllithium with *trans*-1-chloro-2-butene and a small amount of the corresponding *trans* olefin in the reaction involving *cis*-1-chloro-2-butene. A similar behavior was found with phenylsodium and *trans*-1-chloro-2-butene. This isomerization is consistent with the ionization mechanism proposed for the reaction of phenyllithium and 1-chloro-2-butene.[5] The stereochemistry of the allylic



$$CH_3CH{=}CHCH_2Cl \xrightarrow{C_6H_5Li} \left[CH_3\overset{CH}{CH} + CH_2\right] \longrightarrow \text{I-III}$$

cation could be altered by an internal return of the halide ion to form the 3-halo-1-butene followed by ionization of this halide.

The effect of solvents on the ratio of the products obtained indicates that a complex between the phenyl-

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[1] Abstracted in part from the Ph.D. Theses of B. J. Studnicka, 1966, and A. R. Zigman, 1968.

[2] (a) S. Wawzonek, B. J. Studnicka, H. J. Bluhm, and R. E. Kallio, *J. Amer. Chem. Soc.*, **87**, 2069 (1965); (b) S. Wawzonek, H. J. Bluhm, B. J. Studnicka, R. E. Kallio, and E. J. McKenna, *J. Org. Chem.*, **30**, 3028 (1965).

[3] (a) R. M. Magid and J. G. Welch, *J. Amer. Chem. Soc.*, **88**, 5681 (1966); (b) J. G. Welch and R. M. Magid, *ibid.*, **89**, 5300 (1967).

[4] R. M. Magid and J. G. Welch, *ibid.*, **90**, 5211 (1968).

[5] S. J. Cristol, W. C. Overhults, and J. S. Meek, *ibid.*, **73**, 813 (1951).

TABLE I

REACTION OF PHENYLLITHIUM AND PHENYLSODIUM WITH 1-HALO-2-BUTENES

$CH_3CH{=}CHCH_2X$	Solvent	Addn[b] temp, °C	Reaction time, hr	Total[c] yield, %	Isolated[d] yield, %	Product distribution[e] I	II	III	IV
C_6H_5Li[a]									
trans chloride	Ether	Reflux	2.25	79	66	18	54	16	11 (0.54)
trans chloride[f]	Ether	Reflux	3.25	78	49	28	56	5	12 (0.67)
trans chloride	Benzene[g]	Reflux	2.5	98	64	49	31	8	2 (0.06)
trans chloride	THF[g]	10–15	2.5	61	44	2	77	17	3 (0.20)
cis chloride[h]	Ether	Reflux	2.25		40	23	7	67	3 (0.10)
trans bromide[i]	Ether	Reflux	2.25	43	14	11	79	8	2
C_6H_5Na[j]									
trans chloride	Pentane	Reflux	2.25		39	10	70	20	0

[a] 1-Halo-2-butene (0.111 mol) was added to phenyllithium (0.222 mol) unless otherwise noted. [b] Initial addition temperature of the reaction. [c] The total yield of compounds I–IV was determined by vpc analysis. Thermal conductivity corrections were not made for the products. [d] Total yield of compounds I–IV by vpc analysis after distillation. [e] Product distribution of compounds I–IV was determined from the total isolated yield. The total amount of cyclopropanes is listed under IV. The amount of *cis*-1-methyl-2-phenylcyclopropane is given in parentheses. The yield from the *trans* bromide was too small to evaluate. [f] The phenyllithium solution was added to the ether solution of the halide. [g] The phenyllithium was first prepared in ether and the ether was replaced by benzene or tetrahydrofuran. [h] The reaction was carried out using 0.0308 mol of the chloride and 0.0555 mol of phenyllithium. [i] The reaction was carried out using 0.0667 mol of the bromide and 0.222 mol of phenyllithium. The bromide consisted of 23.7% 3-bromo-1-butene and 76.3% *trans*-1-bromo-2-butene. [j] Phenylsodium (0.2 mol) was coupled with the halide (0.111 mol).

TABLE II

REACTION OF PHENYLMAGNESIUM BROMIDE[a] WITH 1-HALO-2-BUTENES

$CH_3CH{=}CHCH_2X$	Solvent	Addn[b] temp, °C	Reaction time, hr	Total yield,[b] %	Isolated yield,[b] %	Product distribution[b] I	II	III
trans chloride	Ether	Reflux	8.25[c]	73	64	44	52	5
trans chloride[d]	Ether	Reflux	1.25[e]	96	81	39	54	7
trans chloride	Ether	0	2.5[f]	71	66	37	57	6
trans chloride	Benzene[b]	Reflux	8.25[c]	90	85	20	69	11
trans chloride	THF[b]	Reflux	3.5[g]	73	67	11	79	10
trans bromide[b]	Ether	Reflux	8.25[c]	68	50	55	41	4
cis chloride[h]	Ether	Reflux	8.25[c]		53	49	14	38

[a] Phenylmagnesium bromide (0.222 mol) was treated with 1-halo-2-butene (0.111 mol) unless noted otherwise. [b] Same as Table I. [c] The addition of the allylic halide required 15 min and the reaction was refluxed for an additional 8 hr. [d] The phenylmagnesium halide solution was added to the allylic halide. [e] The addition required 15 min and the solution was refluxed for 1 hr and allowed to stand at room temperature for 30 hr. [f] The addition process was completed in 30 min at 0° and the solution was stirred at 0° for 2 hr and allowed to stand at room temperature for 6 hr. [g] The addition process was completed in 30 min and the solution was stirred under reflux for an additional 3 hr. [h] *cis*-1-Chloro-2-butene (0.0308 mol) was added to phenylmagnesium bromide (0.0555 mol).

lithium and the halide, similar to that postulated in the metalation reaction of aromatic compounds,[6] is formed with a stability dependent upon the solvent involved. Further evidence for such a complex is the formation of similar olefinic products with the exception of the cyclopropene in the reaction of phenylmagnesium bromide with 1-halo-2-butenes. The results obtained under varying conditions are given in Table II.

The effects of the solvents on the ratio of the products using the Grignard reagent is the same as that with the phenyllithium with the exception of benzene. The most polar solvent, tetrahydrofuran, gives the smallest amount of the SN2′ product.

Experimental Section[7]

Coupling of Phenyllithium with *trans*-1-Chloro-2-butene.—To a stirred phenyllithium (0.222 mol) solution in ether (90 ml) under nitrogen was added dropwise *trans*-1-chloro-2-butene (10 g) in anhydrous ether (20 ml) over a period of 15 min at the reflux temperature of the solution. The reaction mixture was refluxed with stirring for an additional 2 hr. The resulting reaction mixture was cooled and treated with water and the ether layer obtained was washed with 2 *N* sodium hydroxide and water, and dried over anhydrous potassium carbonate.

Removal of the ether gave an oil (15.9 g) which by vpc analysis on an 8 ft × 0.25 in. column (A) packed with Carbowax 20M (0.2 g) on Chromsorb P (19.8 g) contained the coupled products (79%). The retention times for bromobenzene, 3-phenyl-1-butene, *trans*-1-phenyl-2-butene, *cis*-1-phenyl-2-butene, *trans*-1-methyl-2-phenylcyclopropane, and biphenyl were 1.07, 1.24, 1.80, 1.80, 1.80, and 22.0 min, respectively.

The experimental conditions were as follows: detector temperature, 290°; injection port temperature, 330°; column temperature, 100°; helium pressure, 30 psi; helium flow rate, 150 ml/min.

The crude product was distilled through a zigzag column rated at six theoretical plates and a fraction distilling at 85–100° (50 mm) was collected. Vpc analysis using a 50 ft × 0.25 in. column (B) packed with XF-1150 (16.0 g) (nitrile silicon polymer liquid) on Chromosorb P (15.0 g) (35/80 mesh) showed a 65.5% yield of hydrocarbons with a relative product distribution of 3-phenyl-1-butene, *trans*-1-phenyl-2-butene, *cis*-1-methyl-2-phenylcyclopropane, *cis*-1-phenyl-2-butene, and *trans*-1-methyl-2-phenylcyclopropane of 18.0, 54.0, 0.54, 16.3, and 10.46%, respectively. Retention times for the above compounds were 62.7, 87.8, 90.1, 103.2, and 106.5 min, respectively.

For the examples containing 3.3% or less cyclopropanes the ratio of the cyclopropanes, was difficult to evaluate in the mixture directly by vpc. These mixtures were therefore oxidized with potassium permanganate in acetone as described under *trans*-1-methyl-2-phenylcyclopropane and the product was evaluated on column B.

Experimental conditions were as follows: detector temperature, 300°; injection port temperature, 295°; column temperature, 105°; helium pressure, 40 psi; helium flow rate, 67 ml/min.

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[6] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

[7] Boiling points are not corrected. Infrared spectra were obtained using films of undetermined thickness between sodium chloride windows and a Perkin-Elmer 21 double-beam recording spectrophotometer. Nmr spectra were measured with a Varian A-60 nuclear magnetic resonance spectrometer using tetramethylsilane as an internal standard. The samples were analyzed either neat or in carbon tetrachloride.

Preparative vpc on a 10 ft × 3/8 in. column (C) packed with polydiethanolamine succinate polyester (45.0 g) on Chromosorb P_1 (125 g) (80/100 mesh) gave pure samples of 3-phenyl-1-butene, *trans*-1-phenyl-2-butene, and a sample containing a mixture of *cis*-1-phenyl-2-butene and *trans*-1-methyl-2-phenylcyclopropane.

Experimental conditions were as follows: detector temperature, 200°; injection port temperature, 210°; column temperature, 150°; helium pressure, 30 psi; helium flow rate, 100 ml/min.

The infrared spectrum of 3-phenyl-1-butene was identical with Sadtler No. 1616; nmr (CCl_4) δ 1.37 doublet (CH_3), 3.44 multiplet (3-H), 5.00 multiplet ($=CH_2$), 6.00 multiplet (2-H), 7.17 singlet (aromatic); relative ratio 3:1:2:1:5.

The infrared spectrum of *trans*-1-phenyl-2-butene was identical with Sadtler No. 7852; nmr (CCl_4) δ 1.68 doublet (CH_3), 3.27 doublet (CH_2), 5.56 triplet ($CH{=}CH$), 7.11 singlet (aromatic); relative ratio of 3:2:2:5.

The nmr spectrum of the third fraction (CCl_4) was a composite of the spectra of *trans*-1-methyl-2-phenylcyclopropane and *cis*-1-phenyl-2-butene. The migration times of all the components of the reaction mixture agreed with those of authentic samples. Variation in conditions for other runs are given in Table I.

***trans*-1-Methyl-2-phenylcyclopropane.**—The mixture of coupling products (10.0 g) was refluxed in acetone (200 ml) with potassium permanganate (50 g) for 2 days. After this period an additional 50 g of permanganate was added and the refluxing continued for 2 days. Removal of the manganese dioxide was followed by the addition of more permanganate (30 g) and allowing the mixture to stand for 1 day at room temperature. Permanganate (20 g) was added and the solution was refluxed for an additional 3 days. Removal of the manganese dioxide and acetone gave an oil which was taken up in pentane and chromatographed through 8 in. × 0.75 in. alumina column. The product (0.8 g) when purified by preparative vpc on column C gave *trans*-1-methyl-2-phenylcyclopropane which agreed in properties with a sample prepared by the reaction of *trans*-1-phenyl-1-propene with methylene iodide and zinc–copper couple.[8]

Coupling of Phenylmagnesium Bromide with *trans*-1-Chloro-2-butene.—To a stirred and refluxing solution of phenylmagnesium bromide (0.222 mol) in ether (90 ml), *trans*-1-chloro-2-butene (10 g, 0.111 mol) was added over a period of 15 min and the resulting reaction mixture was refluxed for an additional 8 hr. The reaction mixture was treated with saturated ammonium chloride (40 ml) and the ether layer after washing with water and sodium hydroxide solution and drying gave 14.68 g of crude product. Analysis by vpc on column A indicated a 73% yield of coupled products.

Fractional distillation gave 9.43 g of product, bp 84–102° (50 mm). Vpc analysis on an 8 × 0.25 in. column (D) packed with diisodecyl phthalate (1.0 g) on Gas Chrom P (19.0 g) showed that the product consisted of 3-phenyl-1-butene, *trans*-1-phenyl-2-butene, and *cis*-1-phenyl-2-butene in a ratio of 43.6:51.5:4.9, respectively. The retention times were 13.8, 21.8, and 22.8 min, respectively.

Experimental conditions were as follows: detector temperature, 200°; injection port temperature, 215°; column temperature, 100°; helium pressure, 40 psi; helium flow rate, 105 ml/min. Vpc analysis of the distillate on column B indicated the absence of *cis*- and *trans*-1-methyl-2-phenylcyclopropane. Variations in this procedure are reported in Table II.

Addition of Phenyllithium to 3-Methyl-1-cyclopropene.—3-Methyl-1-cyclopropene was prepared by the addition of *trans*-1-chloro-2-butene (90 g) to a refluxing slurry of sodium amide (50 g) in tetrahydrofuran (250 ml). The 3-methyl-1-cyclopropene was displaced by a stream of nitrogen through a trap containing 2 *N* sulfuric acid, dried with Drierite, and collected in a Dry Ice trap. Four bulb-to-bulb distillations gave a liquid (3 g) which by nmr analysis[9] consisted of 3-methyl-1-cyclopropene (0.8 g) and tetrahydrofuran. This liquid in ether (10 ml) was treated with 25 ml of 1 *M* phenyllithium solution in ether in a Dry Ice bath. The resulting solution when treated with water gave 2.85 g of a liquid which by vpc analysis on a 10 ft × 0.25 in. column packed with Carbowax 20M (10%) on Gas Chrom P (100/120 mesh) contained 30.5% 1-methyl-2-phenylcyclopropane. Vpc analysis indicated a mixture of 94.5% *trans*- and 5.5% *cis*-1-methyl-2-phenylcyclopropane.

Experimental conditions were as follows: detector temperature, 300°; injection port temperature, 270°; column temperature, 150°; helium pressure, 30 psi; helium flow rate, 60 ml/min, retention time, 8.7 min.

Starting Materials and Authentic Samples.—*trans*-1-Chloro-2-butene (Aldrich) was used directly as purchased. Analysis by vpc using column D indicated that this compound was 98.6–99.1% pure. The impurity was probably 3-chloro-1-butene. Retention times were 3.3 and 1.7 min, respectively, using a column temperature of 60°; detector block, 150°; injection port temperature, 150°; helium pressure, 30 psi; helium flow rate, 133 ml/min.

***trans*-1-Bromo-2-butene.**—The commercial sample (Aldrich) was washed with cold water and 3% sodium carbonate solution and distilled at atmospheric pressure using a spinning-band column rated at 40 theoretical plates. The fraction boiling at 97–98°, n^{20}_{D} 1.4808 (lit.[10] n^{25}_{D} 1.4795), and corresponding to the primary bromide showed by vpc analysis on a 6-ft diisodecylphthalate column (F&M Scientific Corp.) a mixture of 23.7% 3-bromo-1-butene and 76.3% *trans*-1-bromo-2-butene with retention times of 3.9 and 8.3 min using a column temperature of 70°; detector block, 125°; injection port temperature, 105°; helium pressure, 30 psi; helium flow rate, 200 ml/min. The liquid did not change in composition after standing for 4 days at room temperature and was used as such in the reaction with phenyllithium and phenylmagnesium bromide.

Isomeric 1-Phenyl-2-butenes.—The coupling between 1-chloro-2-butyne and phenylmagnesium bromide was carried out using the directions given for the coupling with the bromo compound.[11] The yield of product distilling at 72–84° (16 mm) was 23.6% [lit.[11] bp 70–82° (13 mm)]. Vpc analysis on column C showed two components in the ratio of 31:69 with retention times of 36.0 and 48.1 min, respectively. Experimental conditions were as follows: detector temperature, 245°; injection port temperature, 255°; column temperature, 150°; helium pressure, 40 psi; helium flow rate, 158 ml/min.

The same reaction with phenyllithium in place of the Grignard reagent gave no volatile hydrocarbon.

The mixture of hydrocarbons from the Grignard reaction was not separated further but was hydrogenated in methanol using 5% palladium on barium sulfate as the catalyst at room temperature with a hydrogen pressure of 40 psi. The product obtained from vpc analysis on column C contained a mixture of *trans*- and *cis*-1-phenyl-2-butene (36%) with a distribution of 46–54% and retention times of 18.7 and 21.1 min, respectively. Experimental conditions were similar to the above.

Preparative vpc gave pure samples of the two isomers. The infrared spectrum of *cis*-1-phenyl-2-butene showed medium-to-strong bands at 3.32, 3.43, 6.03, 6.22, 6.68, 6.68, 6.87, 7.15, 7.31, 9.35, 9.72, 10.08, 10.62, 12.15, 12.43, 13.55, and 14.37 μ; nmr (CCl_4) δ 1.71 doublet (CH_3), 3.37 doublet (CH_2), 5.57 multiplet ($CH{=}CH$), 7.12 singlet (aromatic); relative ratios 3:2:2:2:5.

***cis*-1-Chloro-2-butene**[12] by vpc analysis on column D was 98% pure and had a retention time of 3 min using a column temperature of 60°; detector temperature, 150°; injection port temperature, 155°; helium pressure, 30 psi; helium flow rate, 133 ml/min. The nmr spectrum (heat) showed δ 1.68 multiplet (CH_3), 4.07 multiplet (CH_2), 5.63 multiplet ($CH{=}CH$); relative ratio of 3:2:2, respectively.

***cis*-1-Methyl-2-phenylcyclopropane** was prepared by the reaction of *cis*-1-phenyl-1-propene with methylene iodide and zinc copper couple.[8]

Registry No.—Phenyllithium, 591-51-5; I, 934-10-1; II, 935-00-2; III, 15324-90-0.

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[12] L. F. Hatch and S. S. Nesbitt, *J. Amer. Chem. Soc.*, **72**, 727 (1950).