and lithium (1.8 g., 0.26 g.-atom) as described above. The reaction mixture was poured onto Dry Ice. The mixture was hydrolyzed with dilute hydrochloric acid. The ether layer was extracted with 10% sodium carbonate solution. Acidification of the carbonate gave some acidic material. Recrystallization from chloroform and chromatography of this acidic material on alumina gave, besides benzoic acid, some 2-biphenylcarboxylic acid (0.63 g., 0.0032 mole, 13% yield), m.p. 111–113°, which was identified by an infrared spectra comparison and by a mixed melting point with an authentic sample.

Reaction of Phenyl Sulfoxide with a Phenyllithium–Lithium Thiophenoxide Mixture.—Thiophenol (3.2 g., 0.029 mole) in ethyl ether (5 ml.) was added dropwise over a 10-min. period with stirring to an ether solution of phenyllithium made from bromobenzene (20 g., 0.13 mole) and lithium (1.8 g., 0.26 g.-atom). After 10 additional minutes, phenyl sulfoxide (5.0 g., 0.025 mole) in ether was added dropwise over a 20-min. period. The reaction mixture was poured into water, acidified with dilute hydrochloric acid, and the organic layer removed and extracted with dilute sodium hydroxide to remove any thiophenol. Distillation of the organic layer gave a biphenyl–phenyl sulfide mixture (7.86 g.). Vapor phase chromatography indicated 73% of the distillate to be phenyl sulfide (5.7 g., 0.031 mole, 120% yield) and 27% to be biphenyl (2.1 g., 0.0014 mole, 56% yield).

Addition of an ethereal phenyllithium solution prepared from bromobenzene (39 g., 0.250 mole) and lithium (3.5 g., 0.50 g.-atom) to phenyl sulfoxide (5.0 g., 0.025 mole) and thiophenol (13.8 g., 0.125 mole) in ether over a 45-min. period with stirring gave upon working up the reaction phenyl sulfide (5.6 g., 0.030 mole, 120% yield) and biphenyl (1.8 g., 0.12 mole, 48% yield).

Reaction of Triphenylsulfonium Bromide with Phenyllithium.—Triphenylsulfonium bromide (2.8 g., 0.0082 mole) was added in one portion to an ethereal solution of phenyllithium prepared from bromobenzene (5.2 g., 0.033 mole) and lithium (0.46 g., 0.066 g. atom). After stirring for 4 hr. the reaction mixture was hydrolyzed. The ether layer was worked up as in the preceding reaction to give a biphenyl–phenyl sulfide mixture (1.01 g.). The yield of each component was determined by vapor phase chromatography: biphenyl (0.43 g., 0.0028 mole, 34% yield); phenyl sulfide (0.58 g., 0.0031 mole, 38% yield). Extraction of the aqueous layer with chloroform did not give any unchanged sulfonium salt.

Reaction of Triphenylsulfonium Bromide with a Phenyllithium–Lithium Thiophenoxide Mixture.—Thiophenol (1.0 g., 0.0091 mole) in ethyl ether (5 ml.) was added dropwise to an ethereal phenyllithium solution prepared from bromobenzene (2.8 g., 0.018 mole) and lithium (0.28 g., 0.040 g.-atom). Triphenylsulfonium bromide (1.5 g., 0.0044 mole) was added in one portion to the reaction mixture. After stirring for 15 min., the reaction mixture was hydrolyzed and the ether layer worked up as in the preceding reaction to give phenyl sulfide (0.20 g., 0.0011 mole, 25% yield) and biphenyl (0.05 g., 0.0003 mole, 7% yield). Extraction of the aqueous layer gave 0.09 g. of a white solid which was probably unreacted sulfonium salt.

Reaction of Triphenylsulfonium Chloride with Lithium Thiophenoxide.—Thiophenol (5.5 g., 0.050 mole) in ether was added dropwise to an ethereal phenyllithium solution prepared from bromobenzene (7.9 g., 0.050 mole) and lithium (0.76 g., 0.11 g.-atom). Triphenylsulfonium chloride (1.7 g., 0.0057 mole) was added all at once and the mixture stirred for 2.5 hr. The mixture was hydrolyzed with 10% hydrobromic acid (100 ml.). The aqueous layer was extracted with chloroform to give triphenylsulfonium bromide (1.54 g., 91% recovery).

Monomers and Polymers, A Synthesis of Vinyl Cyclopropane and Dicyclopropyl[1]

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Received October 11, 1962

During a recent search for a convenient route to vinylcyclopropane suitable for stereospecific polymerization, the Simmons–Smith[3] route to cyclopropane *via* addition of :CH_2 to a double bond was applied to butadiene. Since the behavior of this system with a conjugated diolefin has not been reported, we are describing the results here. Mass spectral fragmentation patterns of vinyl cyclopropane and dicyclopropyl are also presented.

Butadiene reacted with methylene iodide and a zinc–copper couple in *p*-dioxane at 60° in a closed reaction tube. Analysis of the reaction products by gas chromatography showed the presence of three compounds in addition to the starting butadiene and *p*-dioxane solvent. Concentration of these products by distillation followed by removal of *p*-dioxane on a polar gas chromatography column yielded a mixture of the three unknown compounds and some butadiene.

Removal of the butadiene and complete separation of the three compounds was accomplished on a nonpolar gas chromatography column. Mass spectrometry showed one of the components to be methyl iodide, arising from the hydrolysis of the iodomethylzinc component formed from the methylene iodide and zinc employed in the reaction. The other two pure components had a molecular weight of 68 and 82 and their fragmentation patterns (shown in Table I) indicated formulas of C_5H_8 and C_6H_{10}. An infrared spectrum on a mixture of the two compounds collected in 50% carbon tetrachloride at this point matched the published infrared spectra of vinylcyclopropane[4] and dicyclopropyl[5] in every detail, with no extraneous peaks

Table I

Mass Spectrometer Fragmentation of Vinyl Cyclopropane (A) and Dicyclopropyl (B)[a]

	Relative intensity			Relative intensity	
m/e	A	B	m/e	A	B
13	1.1	0.7	54		100.0
14	4.4	3.0	55	3.3	26.0
15	5.5	8.2	56	2.2	3.7
16	1.1	0.7	57	3.3	1.5
25	1.1		58		0.7
26	11.1	14.8	60	1.1	
27	40.9	58.8	61	2.2	0.7
29	17.7	13.3	62	3.3	1.5
30		1.5	63	5.0	4.5
31	2.2	0.7	64	1.1	1.5
36		0.7	65	10.0	11.9
37	7.6	5.9	66	7.6	5.6
38	18.3	14.8	67	100.0	96.3
39	75.5	92.0	68	91.3	
40	42.0	22.6	70		1.5
41	46.5	89.3	74		1.7
42	24.3	15.9	75		0.7
43	6.6	4.5	77		8.0
44	2.2	0.7	78		2.6
49	2.2	1.5	79		12.2
50	7.6	13.6	80		1.9
51	10.0	18.9	81		32.2
52	4.4	11.5	82		34.8
53	65.5	37.0			

[a] Electron energy 70, volts; trap current, 0.1 μ amp.; helium carrier gas.

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[1] This is the 24th in a series of papers concerned with new monomers and polymers; for the previous paper in this series see C. G. Overberger and J. J. Ferraro, *J. Org. Chem.*, **27**, 3539 (1962).

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[3] H. E. Simmons and R. D. Smith, (a) *J. Am. Chem. Soc.*, **81**, 4256 (1959); (b) **80**, 5323 (1958).

appearing. Subsequent chromatographic isolation and purification of the individual compounds showed them to have the correct boiling points and refractive indices for vinylcyclopropane[4] and dicyclopropyl.[5] During the identification work, products in addition to vinyl cyclopropane and dicyclopropyl that might also arise from the reaction[6] or subsequent work-up were carefully looked for, but none was found.

The results of five runs made at several conditions are listed in Table II. It is to be noted that the ratio of dicyclopropyl to vinylcyclopropane increased with an increase in the ratio of methylene iodide to butadiene.

TABLE II

REACTION OF BUTADIENE WITH METHYLENE IODIDE

Reactants	I-21[a]	I-25	I-31	I-35	I-50
Butadiene, moles	0.11	0.17	0.20	0.20	0.21
CH_2I_2	0.100	0.100	0.100	0.102	0.165
Zn(Cu), moles	0.15	0.15	0.15	0.15	0.25
Dioxane, ml.	90	90	90	90	90
Temperature, °C.	37	60	60	60	60
Time, hr.	5	72	72	48	42
Conversion, mole % based on CH_2I_2					
Vinylcyclopropane	0	[b]	[b]	26	26
Dicyclopropyl	0	[b]	[b]	7	23

[a] Run at atmospheric pressure in a 500-ml. round-bottomed flask fitted with a Dry Ice condenser and drying tube. [b] Not worked up quantitatively; both products formed at a total conversion of <30%, but the numerical ratios are not certain.

Experimental

Instrumental Analysis.—Gas phase chromatograms for analyses were carried out isothermally on a Perkin-Elmer Model 154 vapor fractometer using a 6-ft. column of polypropylene glycol packed on Haloport F support.

Chromatographic separations were run on an F and M-500 linear programmed gas chromatograph using a 6-ft. column of β,β'-oxydipropionitrile packed on Haloport F and an 8-ft. column of Dow-Corning silicone grease packed on Haloport F.

Infrared analyses were performed on a Perkin-Elmer Model 21 double beam instrument with a sodium chloride prism and a 0.1-mm. microcell of 0.005-ml. capacity.

Mass spectrometry was carried out in a Bendix Time of Flight spectrometer, Model 12-101.

Boiling points were measured by the Emich capillary technique on 2-3 μl. of sample. A National Bureau of Standards calibrated thermometer that could be read to the nearest 0.1° was used.

Refractive indices were read on a 5-decimal place Bausch and Lomb refractometer that would accept a 0.025-ml. sample.

Reaction of Butadiene with Methylene Iodide-Zinc (Cu) Couple.—The zinc-copper couple was prepared by the method of Shank and Shechter[7] from 2-mesh zinc shot (Matheson Coleman and Bell reagent).

To 90 ml. of *p*-dioxane (distilled and dried over Linde 5A sieves) in a 11 in. × 1.5 in. borosilicate glass reaction tube was added 10.8 g. (0.2 mole) of butadiene (MC and B instrument grade). An iodine crystal was added, followed by 26.8 g. (0.1 mole) of reagent grade methylene iodide. Then 9.6 g. (0.15 mole) of the zinc-copper couple was added and the tube was sealed with a metal bottle cap lined with Neoprene rubber and a Teflon gasket. The reaction tube was tumbled in a 60° oil bath for 48 hr. It was opened and its contents were decanted through glass wool. The sludge of zinc-copper and zinc iodide was washed twice with 10 ml. of dioxane and the washes were added to the filtrate which now amounted to 110 g. Analysis o a portion by gas chromatography (column of polypropylene glycol 40°, helium flow of 46 ml./min. at 10 p.s.i.g.) showed five peaks a the following retention times (minutes past the air peak) and percentages by weight: 0.70 (7.7%), 2.00 (0.22%), 2.52 (1.61%), 8.15 (0.26%), 11.36 (90.2%). The 0.70 and 11.36 retention time peaks were shown to be butadiene and *p*-dioxane by comparison with the original reagents employed. Subsequent identification work described below showed that the 2.00 peak was methyl iodide and that the 2.52-min. peak material was vinylcyclopropane and the 8.15-min. peak material was dicyclopropyl.

Isolation of Vinylcyclopropane and Dicyclopropyl.—The bulk of the butadiene was removed from the reaction solution by fractionation through a 3"×1/2" Heli-Pak packed micro column and the methyl iodide, vinylcyclopropane and dicyclopropyl distilled along with some *p*-dioxane. Gas chromatography analysis of the distillate showed its composition was 3% butadiene, 6% methyl iodide, 24% vinyl cyclopropane, 5% dicyclopropyl, and 62% *p*-dioxane.

The *p*-dioxane was removed by preparative gas chromatography on a 6 ft × 1/4 in. β,β'-oxydipropionitrile column maintained at 75° and using a helium flow of 40 ml./min. at 35 p.s.i.g., and a block and injection port temperature of 125°. The mixture was injected in 0.5-ml. slugs and the lower boiling materials collected in a 3-in. tapered test tube maintained at −20°. The exhaust from the column was led into and out of the collector by two 20-gauge hypo needles inserted through a rubber serum cap. The collected mixture of butadiene, methyl iodide, vinylcyclopropane, and dicyclopropyl was next separated as individual components by reinjection through a silicone grease column maintained at 25° (helium flow 30 ml./min. at 35 p.s.i.g., block and injection port maintained at 80°). Gas chromatography of these fractions showed only one peak.

Identification of Methyl Iodide, Vinylcyclopropane, and Dicyclopropyl.—A 10-microliter portion of a three-component mixture isolated from the β,β'-oxydipropionitrile column, consisting of 7% methyl iodide, 65% vinylcyclopropane, and 28% dicyclopropyl, was injected into an 8-ft. silicone grease column at 25° as described above. The individual pure components eluting from the column were fed into a Bendix Time of Flight mass spectrometer and analyzed (electron energy, 70 volts; trap current, 0.1 μamp.) The methyl iodide was identified by comparison with the mass spectrum of authentic methyl iodide. The mass spectra of known vinyl cyclopropane and dicyclopropyl were not available from any source so an identification could not be made by a comparison. However, the suspected vinylcyclopropane showed a molecular weight of 68 and the suspected dicyclopropyl showed a molecular weight of 82. The confirmation of the identity of these two compounds was accomplished on the basis of their infrared spectra, boiling points, and refractive indices.

A portion of distillate containing 88% vinylcyclopropane, 9% methyl iodide, and 2% butadiene was purified in the 8-ft silicone grease column at 25°. Gas chromatography of the collected vinylcyclopropane fraction showed only one peak; b.p. 40.2-40.6° (760) and $n^{25}\mathrm{D}$ 1.41133 [vinyl cyclopropane, b.p. 40.19° (760) $n^{20}\mathrm{D}$ 1.4138].[4] Another portion of distillate containing 92% dicyclopropyl, 4% vinylcyclopropane, and 4% dioxane was purified to give only one peak; b.p. 76.0° (760), $n^{23.6}\mathrm{D}$ 1.42201 [dicyclopropyl, b.p., 76.1° (760) and $n^{20}\mathrm{D}$ 1.4239][5]. An infrared spectrum of the two compounds in carbon tetrachloride was identical in every way with those published by Slabey[4,5] for vinylcyclopropane and dicyclopropyl.

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[4] V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4930 (1952).

[5] V. A. Slabey, *ibid.*, **74**, 4928 (1952).

[6] Particularly cyclopentene from 1,4-addition and dicyclo[3.1.0]hexane from subsequent reaction of cyclopentane [V. Franzen, *Ber.*, **95**, 571 (1962)]. W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958), found pentene and 2-methyl-2-butene among the expected cyclopropane products when methylene iodide and zinc-copper couple was added to *cis*- and to *trans*-butene-2.

[7] R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

Alkyl-(alkoxyalkyl-)hydrazones

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Received July 2, 1962

A recent report from this laboratory described the synthesis of methylhydrazine by the thermal decom-

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