Materials.—Lead tetraacetate was obtained from K and K Laboratories, Inc., dried by suction filtration with a rubber dam, and stored overnight in a vacuum desiccator over potassium hydroxide. β-Pinene (95–98% pure, $[\alpha]^{21.5}\text{D}$ −17.1°) was obtained by distillation of commercial β-pinene (K and K, 76%) through a 24-in. spinning-band column. Purity was determined by gas chromatographic analysis on didecyl phthalate.

Oxidation in Benzene.—β-Pinene (33.0 g., 0.242 mole) in dry benzene (300 ml.) was added to a stirred suspension of lead tetraacetate (106.0 g., 0.239 mole) in dry benzene (450 ml.) over a 30-min. period at room temperature. The reaction was carried out in the absence of direct light. After stirring for an additional hour, the lead diacetate precipitate was filtered. The filtrate was then mixed with water (600 ml.) and no lead dioxide was precipitated indicating total consumption of oxidant. The benzene layer was separated and washed with two 600-ml. portions of water. The benzene was distilled from the dried solution (magnesium sulfate), and the product mixture was fractionally distilled through a spinning-band column.

Unreacted β-pinene (4.6 g., 0.034 mole) was recovered by distillation at *ca.* 15 mm. Continued distillation gave a total of 23.0 g. (0.118 mole, 57% yield based on unrecovered β-pinene) of monoacetate, b.p. 47–55° at 0.30 mm. Gas chromatography of the several fractions obtained showed two major products: *trans*-pinocarvyl acetate (46%) and myrtenyl acetate (10.5%).

Collection of pure samples was achieved by gas chromatography of appropriate fractions. The infrared spectrum of *trans*-pinocarvyl acetate showed the expected bands for ester carbonyl (1745 cm.^{-1}) and disubstituted alkene (1658 and 905 cm.^{-1}). Myrtenyl acetate showed infrared absorption for ester carbonyl (1748 cm.^{-1}) and trisubstituted alkene (1661 and 800 cm.^{-1}).

***trans*-Pinocarveol and Myrtenol.**—Several acetate fractions obtained from lead tetraacetate oxidation of β-pinene in benzene were combined to give a mixture estimated to contain 87% *trans*-pinocarvyl acetate and 11% myrtenyl acetate. A solution of this mixture (24.5 g., 0.126 mole) and sodium (0.4 g.) in methanol (400 ml.) was heated to its boiling point. Methanol and the methyl acetate formed in the transesterification were then distilled from the solution, over a 6-hr. period, until a negative ester test was observed with ferric hydroxamate reagent[12]; about 250 ml. of distillate was obtained. The remaining solution was poured into water (400 ml.), and that mixture was then extracted with three 150-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate.

The ether was removed, and the mixture of alcohols was distilled *in vacuo* through a spinning-band column (18 in. long). Five fractions were obtained yielding a total of 17.2 g. (0.113 mole, 90%) of alcohols. Gas chromatographic analysis, on hyprose, of the fractions showed them to contain *trans*-pinocarveol (77%) and myrtenol (10%). Fractions 2, 3, and 4 (13.8 g.) each contained *trans*-pinocarveol of greater than 95% purity. Fraction 3 was pure *trans*-pinocarveol, b.p. 38° at 0.30 mm.; the *p*-nitrobenzoate derivative was recrystallized from methanol to give white platelets, m.p. 93–94°, lit. m.p. 91–92°,[3] 93.5–94.5°.[13] The infrared spectrum of this fraction showed O–H absorption at 3370 cm.^{-1} and typical disubstituted alkene absorption at 1650 and 893 cm.^{-1}. The spectrum was identical with the infrared spectrum of authentic *trans*-pinocarveol.[14] The gas chromatographic retention times of the two samples on hyprose and on didecyl phthalate were also identical. Optical rotation of the alcohol (fraction 3) was $[\alpha]^{22.5}\text{D}$ +64.9° (*c* 0.80, chloroform). The infrared spectrum and gas chromatographic retention times for fraction 3 differed considerably from those of *cis*-pinocarveol.[15]

The acetate prepared by acetylation of known *trans*-pinocarveol, using sodium acetate and acetic anhydride, and the major acetate product of lead tetraacetate oxidation of β-pinene were also shown to be identical by comparison of their infrared spectra and retention times on didecyl phthalate.

Gas chromatographic separation of fraction 5 gave a pure sample of the minor alcohol product of the transesterification. The infrared spectra and gas chromatographic retention times on hyprose and on didecyl phthalate of this alcohol and authentic myrtenol were identical. The infrared spectrum of myrtenol shows O–H absorption at 3330 cm.^{-1} and trisubstituted alkene absorption at 1661 and 800 cm.^{-1}.

Oxidation in Acetic Acid.—β-Pinene (27.7 g., 0.204 mole) in glacial acetic acid (50 ml.) was added dropwise for 1 hr. to a stirred suspension of lead tetraacetate (83.6 g., 0.189 mole) in glacial acetic acid (200 ml.) containing acetic anhydride (6 g.). During the addition the reaction mixture was kept at room temperature, and it gradually clarified to a yellow solution. Stirring was continued for an additional hour. The reaction solution was then poured into ether (800 ml.). The resulting precipitate dissolved in the following water wash (400 ml.); no lead dioxide was observed. Additional washings with two 200-ml. portions of water, six 200-ml. portions of 5% sodium bicarbonate, and two 250-ml. portions of water were employed. The ether solution was dried over magnesium sulfate.

The ether was removed and the remaining liquid was distilled through a spinning-band column (18 in.). An unreacted β-pinene fraction (4.71 g.) was obtained by distillation at *ca.* 15 mm. Distillation of the remainder at lower pressure yielded 10.55 g. of distillate, b.p. 49–73° at 0.40 mm. Gas chromatographic analysis on hyprose indicated that the yields of *trans*-pinocarvyl acetate and myrtenyl acetate were 10 and 12%, respectively (based on unrecovered β-pinene). The chromatograms also showed the presence of four other components in lesser amount.

The major monoacetate products were found to be *trans*-pinocarvyl acetate and myrtenyl acetate by transesterification, as described above, to the alcohols. Purification of these was carried out by preparative gas chromatography. Comparison of retention times on two columns and their infrared spectra with known samples confirmed them to be *trans*-pinocarveol and myrtenol.

A similar reaction carried out under a nitrogen stream with incorporation of ascarite tubes was found to yield no carbon dioxide.

Attempted Rearrangement of Acetates.—Two samples (each 0.50 g.) containing *trans*-pinocarvyl acetate (49%) and myrtenyl acetate (48%) were dissolved in glacial acetic acid (10 ml.) containing acetic anhydride (0.1 g.). These solutions were then heated at 60° for 1- and 4-hr. periods, respectively. The solutions were then cooled and worked up in the usual way. After removal of the ether, the acetates were subjected to the transesterification procedure. Ether solutions of the resulting alcohol mixtures were analyzed by gas chromatography. Two blanks were also analyzed; one of these had been carried through the entire procedure as the above samples (without heating), and the other had simply been deacetylated. All four samples contained the same relative amounts of *trans*-pinocarveol and myrtenol. A similar experiment with nearly pure *trans*-pinocarvyl acetate also showed no indication of rearrangement.

Acknowledgment.—The authors would like to express appreciation to Mr. G. S. Fisher of the Naval Stores Station, U. S. Department of Agriculture, for authentic samples of *trans*-pinocarveol and myrtenol. They also express their gratitude to Mr. L. O. Sell for the infrared spectra determinations and Mr. A. D. Darling for his assistance.

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(15) *cis*-Pinocarveol was prepared by aluminum isopropoxide reduction of pinocarvone[3]: m.p. 45–46° lit.[3]: m.p. 51°; *p*-nitrobenzoate, m.p. 103.5–104.5°, lit.[3] m.p. 104°.

The Reaction of Benzal Chloride with Lithium

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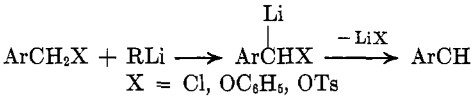
Recently several reports on the generation of phenylcarbenoids by α-elimination have appeared in which the type of mechanism shown could be applied.[1-3] In addition, the use of halogen–metal interchange[4,5] reactions and the reaction of chlorocarbene with phenyllithium[6] have been used to generate the carbenoid intermediate.

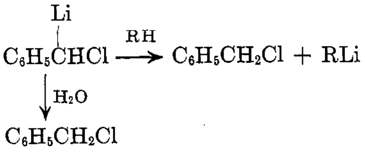


$$\mathrm{ArCH_2X + RLi \longrightarrow Ar\overset{Li}{\overset{|}{C}}HX \xrightarrow{-LiX} ArCH}$$
$$\mathrm{X = Cl,\ OC_6H_5,\ OTs}$$

There are few reports, however, on the generation of carbenes or carbene-like intermediates[7-12] by direct reaction of polyhalides with alkali metals. These generally involve the vapor-phase reaction of polyhalomethanes and the alkali metal.[9-12] Other metals, though, and the decomposition of some organometallic compounds have been shown to give carbenoid products.[13]

The reaction of lithium dispersion, benzal chloride, and cyclohexene in tetrahydrofuran gave the two 7-phenylnorcarane isomers and 3-benzylcyclohexene along with the expected 1,2-diphenylethane and stilbene.[14] A considerable amount of dark polymeric material was also formed presumably through a Wurtz type of reaction between the lithium and benzal chloride. Surprisingly no reaction occurred in ether. In a mixed solvent of 85% ether–15% tetrahydrofuran a slow reaction occurred giving trace amounts of products after 3 days at room temperature.

For comparison purposes the reaction described by Closs and Closs[1] using butyllithium, benzyl chloride, and cyclohexene was run. The product distribution reported by Closs and Closs[1] compares favorably with the product distribution obtained in the reaction of benzal chloride, lithium, and cyclohexene (see Table I). This strongly suggests that the same precursor was involved in both cases. In addition, the detection of benzyl chloride, in the benzal chloride reaction product, can be adequately accounted for on the basis of the following equations, both of which involve α-lithio-α-chlorotoluene.



$$\mathrm{C_6H_5\overset{Li}{\overset{|}{C}}HCl \xrightarrow{RH} C_6H_5CH_2Cl + RLi}$$
$$\mathrm{\downarrow{\scriptstyle H_2O}}$$
$$\mathrm{C_6H_5CH_2Cl}$$

On the information available[15] it is not possible to draw any definite conclusions as to whether the intermediate is a free carbene or an α-chloro-α-lithiotoluene that reacts with the olefin. However the fact that stilbene and 3-benzylcyclohexene were formed could be cited as evidence for carbene formation since the same products have been observed in the decomposition of phenyldiazomethane.[16] Work is now underway on this and other aspects of the reactions of alkali metals with polyhalides.

TABLE I

Products	% yield of product[a]	Li, $C_6H_5CHCl_2$, and C_6H_{10}, %[b]
7-Phenylnorcarane	14	20
1,2-Diphenylethane	14	26
3-Benzylcyclohexene	19	6
Stilbene	. . .	11

[a] Reported by Closs and Closs.[1] [b] Per cent in distillable portion of product by v.p.c. analysis.

Experimental

Lithium and Benzal Chloride in Tetrahydrofuran.—A lithium dispersion in mineral oil was prepared from 3.05 g. (0.44 g.-atom) of lithium. The mineral oil was drawn off and the lithium dispersion was washed twice with tetrahydrofuran. The flask was continuously flushed with nitrogen during this operation and a nitrogen atmosphere was maintained for the subsequent reaction. To the lithium dispersion was added 250 ml. of dry tetrahydrofuran and 32.6 g. (0.4 mole) of cyclohexene. Three drops of benzal chloride was added and high-speed stirring was employed to initiate the reaction. After 5–10 min., the mildly exothermic reaction started and the flask was cooled to 5° in an ice bath. The rest of the benzal chloride (32.2 g., 0.2 mole) in 50 ml. of dry tetrahydrofuran was added at such a rate that the temperature did not rise above 10°. The reaction mixture was stirred for an additional 2 hr. and then hydrolyzed by the careful addition of water. The organic layer was separated, washed with sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The solvent and unreacted cyclohexene were removed under reduced pressure. The reaction products (6.75 g.) with boiling points up to 170° (2 mm.) were collected. A dark residue (11.0 g.) remained in the distilling flask. The distillate was separated by v.p.c. on a 9-ft. SE-30 silicone column. 1,2-Diphenylethane (26%) and *trans*-stilbene (11%) were identified by comparing retention times and taking mixture melting points with authentic samples. The 7-phenylnorcaranes (20%) were identified by comparing retention times with the product of the *n*-butyllithium, benzyl chloride, and cyclohexene reaction described below, by the infrared spectra of the isolated samples (1030-cm.$^{-1}$ cyclopropyl band and absence of 1650-cm.$^{-1}$ olefinic bands), and by analysis.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.88; H, 9.22.

In addition to these products 3-benzylcyclohexene (6%), benzyl chloride (8%), and unreacted benzal chloride (9%) were identified by retention times. The product distribution varied somewhat with small changes in reaction conditions.

Partial Reduction of Reaction Product.—Partial hydrogenation of the distillate obtained above (5 hr. at 50-p.s.i. hydrogen pressure) with platinum oxide in 100 ml. of ethanol eliminated the v.p.c. peaks assigned to benzyl chloride, benzal chloride, and stilbene, decreased the peaks assigned to 3-benzylcyclohexene and the 7-phenylnorcaranes, and produced a correspondingly large new peak. This is consistent with the known reduction of these three isomers to produce benzylcyclohexane.[1,17]

Lithium and Benzal Chloride in Ether.—When ether was used in place of tetrahydrofuran no discernible reaction occurred. In 300 ml. of mixed solvent (85% ether–15% tetrahydrofuran) a slow reaction occurred and after stirring at room temperature for 3 days, the unreacted lithium was filtered off and the ether solution was hydrolyzed and dried over sodium sulfate. Distillation after removal of the solvent afforded 12.05 g. of volatile material (b.p. <170° at 2 mm.) and 4.9 g. of residue. Analysis by v.p.c. showed the distillate contained principally unreacted

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benzal chloride with small amounts of stilbene and diphenylethane and only traces of the $C_{13}H_{16}$ hydrocarbons.

n-**Butyllithium and Benzyl Chloride.**—The procedure used was based on the method outlined by Closs and Closs.[1] A butyllithium solution was prepared from 3.6 g. (0.54 g.-atom) of lithium, 34.25 g. (0.25 mole) of butyl bromide, and 150 ml of dry ether as described by Jones and Gilman.[18] The *n*-butyllithium solution was added slowly to a mixture of benzyl chloride (50.6 g., 0.4 mole) and cyclohexene (50 g., 0.6 mole) maintained at 10°. The reaction mixture was then hydrolyzed and the ether layer was separated and dried over sodium sulfate. The solvent was removed by distillation before evaluation of the product by v.p.c. In addition to the products reported by Closs and Closs[1] (14% 1,2-diphenylethane, 14% 7-phenylnorcarane, 19% 3-benzylcyclohexene, and 30% amylbenzene), a small amount of stilbene was detected.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Dithiolium Derivatives. VI. Reactions of Primary Amines and Ammonia with 2-Methylthio-1,3-dithiolium Perchlorate[1]

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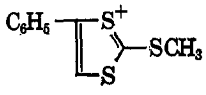
We have recently reported the facile nucleophilic attack on 2-methylthio-1,3-dithiolium salts by active methylene carbanions[3,4] and secondary amines.[5] Secondary amines have also been shown to react with 3-methylthio-5-phenyl-1,2-dithiolium perchlorate to form N,N-disubstituted 3-amino-5-phenyl-1,2-dithiolium perchlorates.[5] However, Olofson[6] has reported an excellent yield of 4-phenylisothiazole when a 4-phenyl-1,2-dithiolium salt was treated with ammonia in alcohol. While we have shown that aminodithiolium derivatives result from the reaction of dialkyl or alkylarylamines with 2-methylthio-1,3-dithiolium perchlorates, it is possible that reaction with primary amines or ammonia might lead to the more stable thiazole derivatives. Therefore the reaction of 4-phenyl-2-methylthio-1,3-dithiolium perchlorate (**1**) with several primary amines and with ammonia was investigated.

The reaction of **1** with aniline, *p*-bromoaniline, or cyclohexylamine in glacial acetic acid produced the neutral imino derivatives, **2**, in good yield. In trifluoroacetic acid these compounds are evidently protonated to the immonium derivatives **3**, since in this solvent they showed the characteristic aminodithiolium ultraviolet absorption band in the 315–345-mμ region,[7]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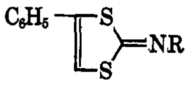
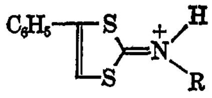

2a, R=C_6H_5
b, R=C_6H_4Br-*p*
c, R=C_6H_{11}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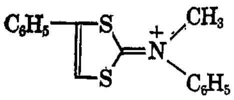
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as well as n.m.r. signals for the C-5 proton at τ 2.60–2.72, and a proton on nitrogen at 7.62–7.63. The n.m.r. spectrum of the neutral N-cyclohexyl-2-imino-4-phenyl-1,3-dithiole (**2c**), taken in carbon tetrachloride, shows the C-5 proton at τ 3.50, an upfield shift for this proton characteristic of such dithioles,[4] but no proton on nitrogen. The identity of the aniline derivative **2a** was further confirmed by methylation of the nitrogen atom to form the same methylanilinium salt (**4**) previously obtained from **1** and methylaniline.[5]

The reaction of ammonia with **1** under a variety of conditions was investigated, but only intractable tars were obtained. These conditions included ammonium acetate in acetic acid, ammonia in ethanol, acetonitrile, tetrahydrofuran, or water, and addition of **1** to liquid ammonia. Since 4-phenyl-2-methylthiothiazole is a stable derivative which forms high-melting salts,[8] one must conclude that little, if any, of this is present in the mixture produced by decomposition of **1** with ammonia.

Experimental[9]

N,4-Diphenyl-2-imino-1,3-dithiole (2a).—The procedure employed was that described by Schmidt, Lüttringhaus, and Hübinger.[10] To 3.24 g. (0.01 mole) of 2-methylthio-4-phenyl-1,3-dithiolium perchlorate (**1**) dissolved in 25 ml. of hot glacial acetic acid was added 1.86 g. (0.02 mole) of aniline. The solution was refluxed an additional 5 min., and then poured into 400 ml. of ice–water. This mixture was stirred several hours and the solid material which separated was collected and dried, yielding 2.25 g. (84%) of **2a**. Recrystallization twice from acetonitrile (Norit) afforded colorless needles which melted at 93–95°: $\lambda_{\max}^{CF_3CO_2H}$ 343 mμ (log ε 4.07); $\tau_{CF_3CO_2H}$ 2.38 (m, 5H), 2.47 (m, 5H), 2.63 (1H), and 7.63 (1H).

Anal. Calcd. for $C_{15}H_{11}NS_2$: C, 66.88; H, 4.12; S, 23.81. Found: C, 66.71; H, 4.35; S, 23.75.

A similar procedure was employed with *p*-bromoaniline to afford **N-*p*-bromophenyl-2-imino-4-phenyl-1,3-dithiole** (**2b**) in 95% yield. After two recrystallizations from acetonitrile, **2b** melted at 149–151°: $\tau_{CF_3CO_2H}$ 2.20 (d, 2H), 2.45 (m, 5H), 2.57 (d, 2H), 2.60 (1H), and 7.62 (1H).

Anal. Calcd. for $C_{15}H_{10}BrNS_2$: C, 51.73; H, 2.89; S, 18.41. Found: C, 51.69; H, 2.91; S, 18.19.

The dithiolium perchlorate **1** and cyclohexylamine treated similarly afforded **N-cyclohexyl-2-imino-4-phenyl-1,3-dithiole** (**2c**) in 71% yield. In this case, it was necessary to extract the aqueous solution with benzene and recover **2c** by evaporation. Two recrystallizations from hexane gave colorless plates which

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[2] Taken in part from the Ph.D. Thesis of R. D. Hamilton, submitted to Indiana University, June 1964.

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[9] All melting points were determined in soft glass capillaries using a Mel-Temp heated block and are corrected. Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Ultraviolet measurements were made with a Cary 14 spectrophotometer. Infrared spectra were recorded by a Perkins-Elmer Model 137 Infracord in potassium bromide mulls. All n.m.r. measurements were at concentrations between 6–10% w./v. at approximately 31°, using a Varian A-60 spectrometer operating at 60 Mc./sec. Chemical shifts are recorded on the frequency independent τ-scale relative to an internal TMS reference. For multiple signals the following abbreviations are used: d = doublet, m = multiplet.

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