K & K Laboratories. The (−)-β-pinene was distilled under a N_2 atmosphere through a Widmer column before use.

Method of Isomerization.—No attempt has been made to optimize yields, as both reagents are relatively inexpensive.

Into a 3-l., three-neck flask equipped with a magnetic stirrer, condenser, and two septa was placed 780 g (5.73 mol) of freshly distilled (−)-β-pinene, $[\alpha]^{25}\mathrm{D}$ −20.32°. The system was evacuated and N_2 was passed through a T-joint at the top of the condenser. This procedure was repeated several times to ensure a N_2 atmosphere. The liquid was heated to near 150°, and 225 g (115 ml, 1.15 mol, 20 mol %) of iron pentacarbonyl was added *via* a syringe. The temperature of the stirring mixture dropped to 120° owing to the $Fe(CO)_5$ addition and gradually rose; when the solution attained 135° the temperature was held constant. Samples were taken by syringe through a septum and analyzed. After 32 hr [as in the case of 20 mol % $Fe(CO)_5$], the reaction was complete. The black mixture was cooled and volatile material was removed by vacuum distillation using a CO_2-acetone-cooled receiver. The trapped material was then distilled through a Vigreaux column, collecting the 154–157° fraction at atmospheric pressure. Generally, this crude α-pinene occurred in 50–60% yield. Finally, careful fractionation yielded 340.5 g (43.5%) of (−)-α-pinene: bp 155–156°; $n^{25}\mathrm{D}$ 1.4640 (lit.[2] bp 155.9°; $n^{25}\mathrm{D}$ 1.4631); $[\alpha]^{26}\mathrm{D}$ −44.45° (neat).

(+)-Isopinocamphenol.—Hydroboration of the (−)-α-pinene from the isomerization as described by Brown[1] with subsequent oxidation yielded crude (+)-isopinocampheol. The alcohol was recrystallized from a small amount of petroleum ether (bp 60–90°), dried under low vacuum, and sublimed under high vacuum at 30°, giving pure (+)-isopinocampheol: mp 55–55.5°; $[\alpha]^{24}\mathrm{D}$ +28.5° (*c* 3.15, benzene); 88% optical purity [lit.[11] for (−)-isopinocampheol, mp 54–56°; $[\alpha]\mathrm{D}$ −32.4° (*c* 4, benzene)].

Registry No.—I, 7785-26-4; II, 18172-67-3.

Acknowledgment.—The authors are grateful to the National Science Foundation for partial financial support of this work.

[11] H. Schmidt, *Chem. Ber.*, **77**, 544 (1944).

An Unusual Condensation. Ring-Closure Reaction[1]

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Contribution No. 2380 from the Department of Chemistry, The University of California at Los Angeles, Los Angeles, California

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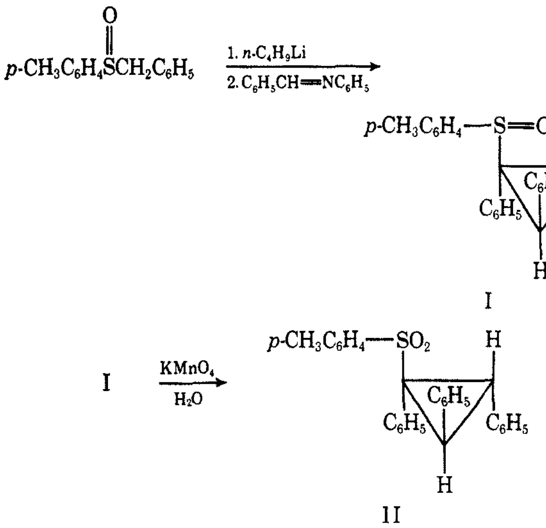
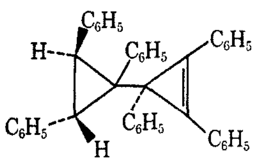
Treatment of benzyl *p*-tolyl sulfoxide with 1 mol of *n*-butyllithium followed by 1 mol of benzalaniline gave a 56% yield of 1,2,3-triphenylcyclopropyl *p*-tolyl sulfoxide (I). The gross and partial configurational structure of I was demonstrated by analytical, nmr, and mass-spectral analysis of I and of its corresponding sulfone, 1,2,3-triphenylcyclopropyl *p*-tolyl sulfone (II). The most prominent peak observed in the mass spectrum of I at 70 eV occurred at *m/e* 191, which is attributed to the 1,2-diphenylcyclopropenium cation fragment.

The stereospecific conversion of phosphine oxides to phosphinamides[3a] was used to complete a cycle of transformations that established the stereochemical course of ester–amide interchanges with phosphinate ester as starting material.[3b] In an attempt to complete a similar cycle applied to sulfinate ester–amide interchange, benzyl *p*-tolyl sulfoxide was treated with 1 mol of *n*-butyllithium followed by 1 mol of benzalaniline in tetrahydrofuran. Instead of the anticipated N-phenyl-*p*-toluenesulfinamide, a 56% yield (based on benzalaniline) of a single racemate of I was produced, along with small amounts of hydrazobenzene. Oxidation of sulfoxide I gave sulfone II.



Evidence for the structure of I was obtained from analytical, nmr, and mass-spectral analysis. Elemental analysis of I and II coupled with a parent peak at *m/e* 408 (70 eV) in the mass spectrum of I established the molecular formula of I. The molecular formulas of I and II demonstrate the presence of a ring in addition to the aryl groups in each of these compounds. The nmr spectrum of I in deuteriochloroform exhibited a singlet at τ 7.78 (3 H) attributed to the methyl group, an AB quartet centered at τ 6.22 (2 H, J_{AB} = 8.0 cps, Δ_{AB} = 0.66 ppm) assigned to the *trans* hydrogens on a saturated cyclopropane ring,[4] a doublet centered at τ 3.62 (2 H), and a multiplet centered at τ 2.9 (17 H) assigned to the other aromatic protons. The nmr spectrum of II in deuteriochloroform gave a singlet at τ 7.62 (3 H), an AB quartet centered at τ 6.1 (2 H, J_{AB} = 9.0 cps, Δ_{AB} = 0.83 ppm), and a multiplet centered at τ 2.9 (19 H). The AB quartet in both of these spectra (2 H) and the chemical shift of the two hydrogens resemble those of the *trans* hydrogens on the cyclopropane compound,[4] III. Sulfone II has the same symmetry properties as III, but sulfoxide I has the additional sulfoxide group as an asymmetric element, and therefore can exist in principle as two racemates, only one of which was obtained. The fact that the two cyclopropane hydrogens split each other in II demonstrates that they possess a *trans* rather than a *cis* arrangement. The sharp



III

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[1] This investigation was supported by U. S. Public Health Service Research Grant GM 12640-04 from the Department of Health, Education and Welfare.

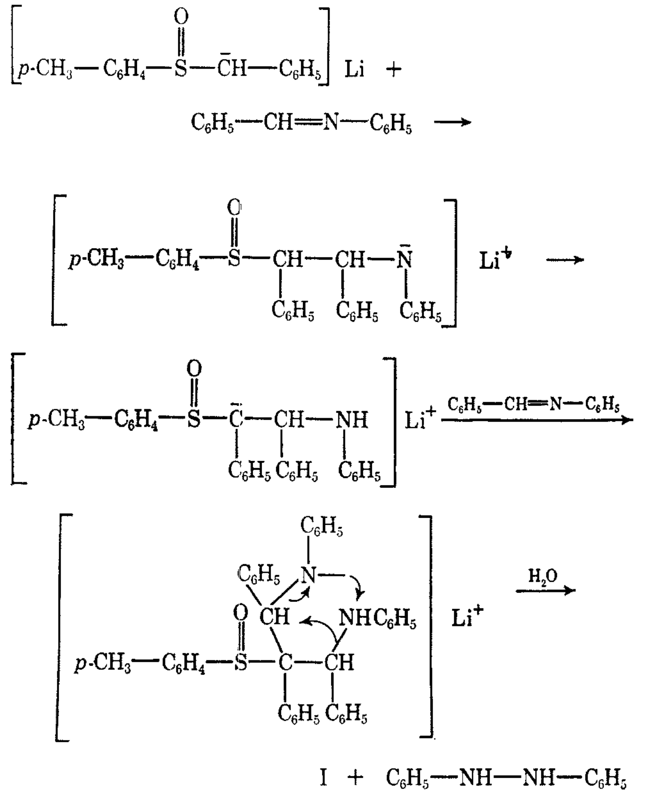
[2] This author wishes to acknowledge gratefully nonresident tuition grants from Dow Chemical Co. and U. S. Rubber Co.

[3] (a) L. Horner and H. Winkler, *Tetrahedron Lett.*, **44**, 3265 (1964); (b) A. Nudelman and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 3869 (1968).

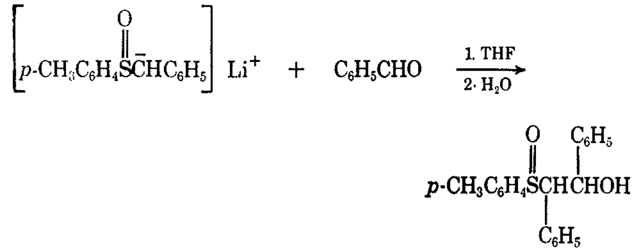
[4] R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963).

melting points coupled with the high symmetry of the AB quartets of I and II demonstrate that pure compounds rather than diastereomeric mixtures were obtained. The environment of the hydrogen *cis* to the sulfoxide group in I depends on the relative configuration of the sulfoxide group, and the diastereomers which differed only in their configurations at sulfur would be expected to have slightly different nmr spectra.

The following possible mechanistic sequence accounts for the formation of compound I and hydrazobenzene.

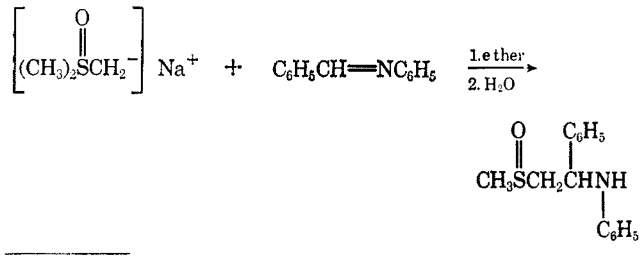


When benzaldehyde was substituted for benzalaniline in the above reaction, the more usual[5] product, III, was obtained.

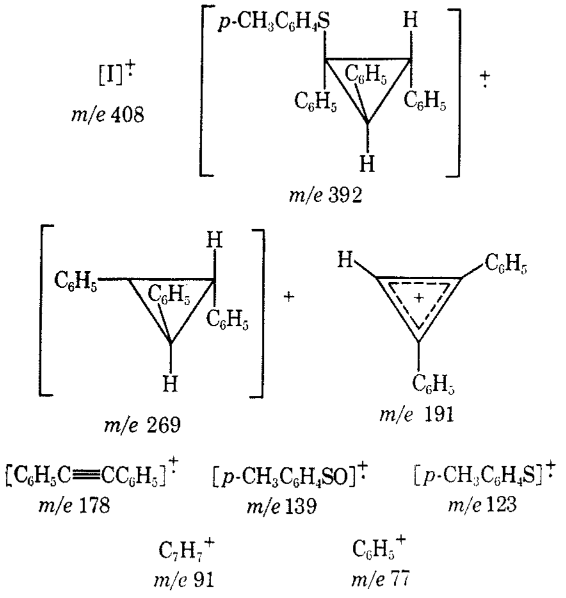


III

Others have reported the formation of cyclopropanes in γ-elimination reactions of sulfoxides,[6] as well as the addition of a sulfur ylide to benzalaniline.



The mass spectrum of cyclopropane derivative I was taken at 70 eV (AE 1 Model MS-9) by direct insertion. The parent peak at m/e 408 appeared in relatively low abundance. The structures of the major peaks were assigned as formulated.



The presence of the highly stable fragment ion m/e 191 (most intense peak in the spectrum) can be accounted for in part as a decomposition product of ion m/e 269. It is known[7a] that the product ion, m_2, from the m/e decomposition of a precursor ion, m_1, is most likely to be found at a mass m^*, where $m^* = m_2^2/m_1$. Thus, m^* should be the m/e of the center of the roughly Gaussian peak distribution of ions of the metastable peak. The only metastable peak observed in the spectrum occurred at m/e 135.6, which equals $191^2/269$. These facts support the structural assignments made to the fragments. Exact mass measurements of peaks m/e 392 and 191 were found to be 392.15840 and 191.08617, which correspond[7b] to elemental compositions $C_{28}H_{24}S$ and $C_{15}H_{11}$, respectively.

Experimental Section

1,2,3-Triphenylcyclopropyl *p*-Tolyl Sulfoxide (I).—To a solution of benzyl *p*-tolyl sulfoxide (1 g, 4.35 mmol) in 20 ml of dry tetrahydrofuran was added 2.72 ml (4.35 mmol) of a 1.6 *M* solution of *n*-butyllithium in hexane. The resulting bright yellow solution was stirred at 25° for 30 min, and a solution of 0.787 g (4.35 mmol) of benzalaniline in 20 ml of anhydrous tetrahydrofuran was added. After 3 hr of reflux, the solution was cooled and quenched with a mixture of dichloromethane and saturated aqueous ammonium chloride. The organic phase was separated, dried, and flash evaporated. The yellow residue (1.5 g) was chromatographed on 35 g of silica gel and eluted with 8:2 pentane–ether. Ten 200-ml fractions were collected. The first two fractions yielded *ca.* 0.25 g of hydrazobenzene, whose infrared spectrum and glpc retention times were identical with those of an authentic sample. Fractions 5–9, when combined, gave 0.5 g (56% yield based on benzalaniline) of sulfoxide I, which was recrystallized from ether; mp 171–173°.

Anal. Calcd for $C_{28}H_{24}OS$: C, 82.35; H, 5.88; S, 7.84. Found: C, 82.33; H, 5.94; S, 7.93.

1,2,3-Triphenylcyclopropyl *p*-Tolyl Sulfone (II).—To a solution of 83.1 mg (0.204 mmol) of sulfoxide I in 5 ml of glacial acetic acid was added 2 ml of a 3% aqueous solution of potassium per-

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[5] (a) M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963); (b) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

[6] R. Barker and M. J. Spillet, *Chem. Commun.*, 757 (1966).

[7] F. W. McLafferty, Ed., "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1967: (a) p 65; (b) p 15.

manganate. The purple color faded rapidly at the beginning of the addition with the formation of a brown precipitate, but remained at the end. After a few minutes of stirring, a small amount of sodium bisulfite was added until the color faded. Ice was added, and the precipitate was filtered and recrystallized from ethanol to give 44 mg (50% yield) of II, mp 178–179°.

Anal. Calcd for $C_{23}H_{24}O_2S$: C, 79.24; H, 5.66. Found: C, 79.21; H, 5.59.

1,2-Diphenyl-2-hydroxyethyl *p*-Tolyl Sulfoxide (III).—The procedure followed resembled that for preparation of I except that benzaldehyde was substituted for benzalaniline. The reaction product was isolated without chromatography by recrystallization of the reaction residue from ether; yield 40%, mp 176.5–178.5°.

Anal. Calcd for $C_{21}H_{20}O_2S$: C, 75.00; H, 5.95. Found: C, 75.15; H, 5.88.

Registry No.—I, 21473-30-3; II, 21473-31-4; III, 21473-32-5.

Heterocyclic Ring-Closure Reactions. III. 5-Aminoimidazoles from Azomethines[1a,b]

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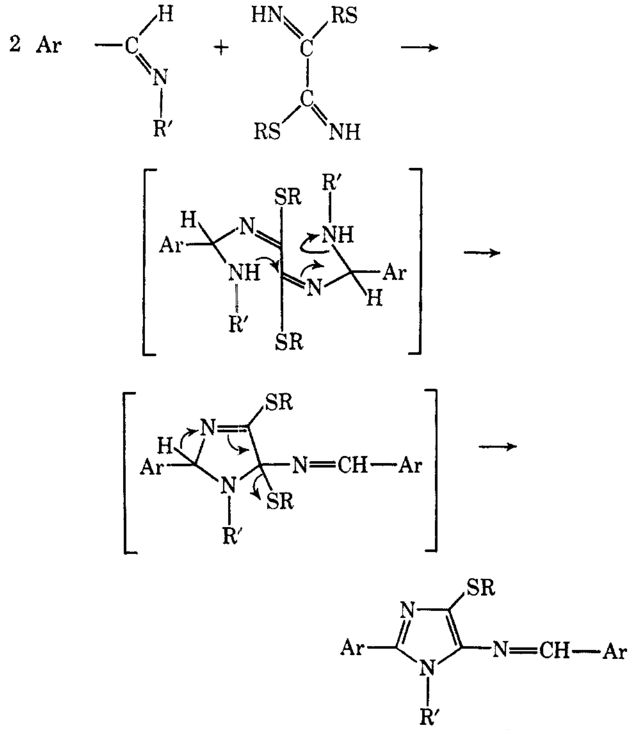
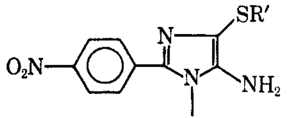
Received May 5, 1969

The thermal condensation of dithiooxamide with aromatic aldehydes has been shown to afford symmetrical, fully aromatized diarylthiazolothiazoles.[2] Aromatic aldehydes react with S,S′-disubstituted dithiooxaldiimidates to give 5-benzalamino-4-aryl- or alkylmercapto-2-aryloxazoles.[3] It was of interest to see if azomethines, the nitrogen analogs of aldehydes, would react with S,S′-disubstituted dithiooxaldiimidates in an analogous manner and thereby provide a route to imidazoles (1).[4]



Reaction of benzalmethylamine with S,S′-dibenzyl dithiooxaldiimidate gave the expected imidazole Schiff base (1). The destruction of the original chromophore by acid is similar to that observed in the oxazole series.[3] However, in the imidazole case no characterizable hydrolysis product was isolated. Reaction of Schiff bases of *p*-nitrobenzaldehyde with dialkyl or diaryl dithiooxaldiimidates afforded aminoimidazoles (2) in good yields.



2

The reaction between Schiff bases of aromatic aldehydes and S,S′-disubstituted dithiooxaldiimidates seems to be general and to give better yields than obtained in the oxazole synthesis from the aromatic aldehydes.[3]

Experimental Section[5]

Azomethines.—The procedures used for solids were those recommended by Vogel[6] whereas for liquids equimolar amounts of primary amine and aromatic aldehyde were allowed to react in benzene in the presence of Linde molecular sieve No. 3A. The mixture was stirred for 4 hr at room temperature. The reaction mixture was filtered, the solvent removed, and the residue distilled under reduced pressure.

S,S′-Dialkyl or Diaryl Dithiooxaldiimidates.—The procedure used was that of Woodburn and Sroog[7] as modified by Martin and Ketcham.[3]

Schiff Bases of Aminoimidazoles.—The following synthetic procedures are representative of the compounds listed in Table I.

Method A. 5-Benzalamino-4-benzylmercapto-1-methyl-2-phenylimidazole (1a).—A solution of 3.8 g (0.032 mol) of benzalmethylamine and 6 g (0.02 mol) of S,S′-dibenzyl dithiooxaldiimidate in 50 ml of absolute ethanol was refluxed for 2 hr. The volume of the resulting solution was reduced to about 25 ml and set aside for crystallization. It afforded yellow needles, mp 140–142°. Two recrystallizations from methanol yielded 5.9 g (80%) of yellow needles: mp 143–144°; λ_{max} 374 (ϵ 12,100) and 252 mμ (18,400) and irreversibly, in acid 273 (11,800) and 224 mμ (17,200); ν 3050 (aromatic CH), 2940 (CH_2), 1600

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[1] (a) Paper No. II. Previous paper: S. C. Mutha and R. Ketcham, *J. Org. Chem.*, **34**, 2053 (1969). (b) Supported by National Institute of Mental Health, Grant MH 08787. (c) Abstracted in part from the Ph.D. thesis of S. C. Mutha. (d) To whom inquiries should be sent.

[2] J. R. Johnson and R. G. Ketcham, *J. Amer. Chem. Soc.*, **82**, 2719 (1960).

[3] A. R. Martin and R. Ketcham, *J. Org. Chem.*, **31**, 3612 (1966).

[4] If dithiooxamide were to react with Schiff bases by loss of an amine, then the same diarylthiazolothiazole[2] would be formed. However, there appeared to be the possibility of loss of hydrogen sulfide rather than an amine, thereby affording a tetrasubstituted imidazoimidazole. The only product isolated from Schiff bases of benzaldehyde was the previously described[2] diphenylthiazolothiazole.

[5] Melting points were determined on a Thomas-Hoover capillary melting point apparatus, and are corrected. Elemental analyses were carried out by the microanalytical laboratory of the University of California at Berkeley. The uv spectra were determined in 95% ethanol, using a Cary Model 11 spectrophotometer. Absorptions are reported in millimicrons, intensities as molar extinction coefficient (ϵ). The ir spectra were run on a Perkin-Elmer 337 spectrophotometer. Potassium bromide was used for solids. The nmr spectra were taken in deuteriochloroform, unless otherwise indicated, with tetramethylsilane as the internal standard, using a Varian A-60A spectrometer. Chemical shifts are reported as δ values (parts per million) and coupling constants (J values) are given in cycles per second (hertz).

[6] A. I. Vogel in "A Textbook of Practical Organic Chemistry," Longmans Green and Co., London, 1956, pp 653–654.

[7] H. M. Woodburn and C. E. Sroog, *J. Org. Chem.*, **17**, 371 (1952).