

TABLE I
REACTION OF 5-CHLORO-2-PENTANONE WITH
VARIOUS BASE-SOLVENT SYSTEMS

Base-solvent	Yield ^{a,b} of cyclo- propyl methyl ketone, %	Base-solvent	Yield ^{a,b} of cyclo- propyl methyl ketone, %
NaOH ^{c,d}	85	<i>t</i> -BuOK-DMSO ^e	84
NaOH-H ₂ O ^{d,e}	98	<i>t</i> -BuOK-Et ₂ O ^{d,e}	100
NaOH-(50% DMSO-50% H ₂ O) ^e	96	PhOK-MeOH ^f	40
MeOK-MeOH ^e	93	K ₂ CO ₃ -H ₂ O ^{d,e}	7
EtOK-EtOH ^e	100	NaOAc-MeOH ^g	0
<i>t</i> -BuOK- <i>t</i> -BuOH ^e	98	Et ₃ N-C ₆ H ₆ ^e	0

^a Measured by glpc. ^b Estimated uncertainty $\pm 2\%$. ^c No solvent. Conditions: 120 min at 100°. ^d Heterogeneous. ^e Conditions: 15 min at 30°. ^f Conditions: 15 min at 25°. ^g Conditions: 120 min at reflux.

assessment of the relative importance of stabilizing conjugation of the carbonyl group with the developing three-membered ring,⁸ transition state entropy effects, or other factors which might be responsible for preferential cyclization to cyclopropyl methyl ketone.

Experimental Section

The base (3 mmol) in 10 ml of solvent was added to 5-chloro-2-pentanone³ (2 mmol) and isobutylbenzene (Ethyl Corp., internal standard), and the reaction mixture was magnetically stirred for the desired reaction time. A 1- μ l sample was injected directly⁹ into a Varian Aerograph flame ionization gas chromatograph using a 20 ft \times 1/8 in. column of 20% XF-1150 on Chromosorb P operated at 150°. When the solvent was water or 50% DMSO-50% H₂O, 20 ml of *t*-butyl alcohol was added to make the reaction mixture homogeneous before injection. Peak areas were measured with a Disc integrator.

Registry No.—5-Chloro-2-pentanone, 5891-21-4.

- (8) A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc., B*, 808 (1967).
(9) A glass insert filled with glass wool prevented column contamination.

Reduction and Elimination as Side Reactions in the Replacement of Vinyllic Bromine Atoms by Means of Lithium-Copper Organometallics

ALLAN T. WORM AND JAMES H. BREWSTER

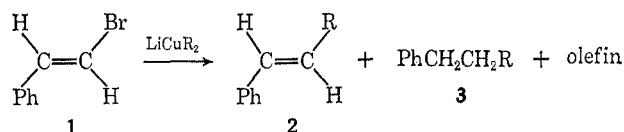
Department of Chemistry, Purdue University,
Lafayette, Indiana 47907

Received July 28, 1969

The reaction of vinyl halides with lithium dialkylcopper compounds¹⁻³ appeared promising as a method for the stereochemical correlation of certain chiral olefins. A pilot study with β -bromostyrene (90% *trans*, 10% *cis*) (1) has shown that the bromine atom

- (1) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968).
(2) H. O. House, W. L. Respass, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).
(3) G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

can be replaced by secondary, tertiary, and phenyl groups by this method. Several side reactions, of potential mechanistic interest, were noted. Thus, when the R group was isopropyl, the reduced compound (3, R = *i*-C₃H₇) was obtained as 40% of the C₁₁ product. With R as *t*-butyl, half of the C₁₂ product was 3, R = *t*-C₄H₉; isobutylene, recovered and identified as the dibromo derivative, was formed during the reaction in this case. Another reduction product, styrene, was always obtained, often as a major by-product. Reaction of the pure stereoisomers of 1 with lithium diphenylcopper gave much biphenyl and styrene. Stilbenes were formed in small amounts, with predominating, but not exclusive, retention of configuration, *trans*-1 giving 18% *cis*- and 84% *trans*-2, and *cis*-1 giving 70% *cis*- and 30% *trans*-2.



Experimental Section⁴

Reaction of Lithium Diisopropylcopper with β -Bromostyrene.—To a suspension of 7.6 g (0.04 mol) of cuprous iodide in 20 ml of ether at -15° was added 0.40 ml (0.076 mol) of commercial 1.9 *M* isopropyllithium in pentane.⁵ The solution was cooled to -78° , and 1.5 g (0.008 mol) of β -bromostyrene⁶ in 10 ml of ether was added. The mixture was stirred at -78° for 1 hr, warmed to about -15° , and worked up as above to give 0.8 g of a mixture containing (vpc isolation) styrene (trace), 1-phenyl-3-methylbutane (40%), and *trans*-1-phenyl-3-methylbutene (60%). The 1-phenyl-3-methylbutane had nmr (CDCl₃) δ 0.95 (d, 6, *J* = 5 cps, CH₃), 1.50 (m, 3, -CH₂CH-), 2.60 (m, 2, ArCH₂), and 7.17 (m, 5, phenyl); mass spectrum (75 eV) *m/e* (relative intensity) 148 (19) (C₁₁H₁₆⁺), 92 (100) (C₇H₈⁺), 91 (64). *trans*-1-Phenyl-3-methylbutene had nmr (CDCl₃) δ 1.06 (d, 6, *J* = 6 cps, CH₃), 2.41 (m, 1, >CH), 6.17 (m, 2, vinyl), and 7.2 (m, 5, phenyl); ir (film) 1370, 1385 [*sym* doublet, -CH(CH₃)₂], 968 (*trans*-CH=CH-), and 745, 694 cm⁻¹ (-C₆H₅); mass spectrum (75 eV) *m/e* (relative intensity) 146 (34) (C₁₁H₁₄⁺), 131 (100) (M⁺ - 15), and 91 (49) (C₇H₇⁺).

Reaction of Lithium Di-*t*-butylcopper with β -Bromostyrene.—To a suspension of 9.5 g (0.05 mol) of cuprous iodide in 20 ml of anhydrous ether at -15° was added 50 ml (0.10 mol) of commercial 2.0 *M* *t*-butyllithium in pentane.⁵ The solution was cooled to -78° , 2.0 g (0.011 mol) of β -bromostyrene⁶ in 15 ml of ether was added, and the solution was stirred at -78° for 1 hr. It was allowed to warm slowly to 0° with a stream of nitrogen passing through the flask and into a test tube (protected from light) containing bromine in carbon tetrachloride. The bromine solution warmed and decolorized; the solvent was removed; and the residue was distilled to give 1,2-dibromo-2-methylpropane: bp 50° (10 mm); nmr (CDCl₃) δ 1.88 (s, 6, CH₃) and 3.88 (s, 2, CH₂Br), comparable with literature values.⁷ The main reaction mixture was worked up in the usual way and distilled to give 1.2 g, bp 75-78° (6 mm), of a mixture of 1-phenyl-3,3-dimethylbutane (50%) and *trans*-1-phenyl-3,3-dimethylbutene (50%). The two

(4) All melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian A-60A instrument and reported in δ units from tetramethylsilane. Mass spectra were obtained on a Hitachi RMU-6A mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer Infracord. Unless otherwise stated, vapor phase chromatography (vpc) was carried out on a 25% QF-1 column; analytical compositions have not been corrected for thermal conductivity differences. All reaction vessels were flamed out; anhydrous ether was distilled from an ethereal solution of lithium aluminum hydride.

(5) Obtained from Alfa Inorganics, Inc.

(6) Obtained as a mixture of 90% *trans* and 10% *cis* isomers by action of aqueous sodium carbonate on the dibromide of *trans*-cinnamic acid; see C. Dufraisse, *Ann. Chim. (Paris)*, **17**, 133 (1922).

(7) N. S. Bhacca, D. P. Hollis, L. F. Johnson, E. A. Pier, and J. N. Shooley, "Varian NMR Spectra Catalog," Vol. II, National Press, 1963, Spectrum 412.

products were separated by vpc. 1-Phenyl-3,3-dimethylbutane: nmr (CDCl₃) δ 0.94 (s, 9, *t*-Bu), 1.50 (m, 2, RCH₂R), 2.55 (m, 2, ArCH₂R), and 7.20 (s, 5, phenyl); ir (film) 1370, 1390 (*unsym* doublet, *t*-Bu), and 698, 733 cm⁻¹ (C₆H₅); mass spectrum (75 eV) *m/e* (relative intensity) 162 (14) (C₁₂H₁₈⁺), 57 (100) (C₄H₉⁺). 1-Phenyl-3,3-dimethylbutene: nmr (CDCl₃) δ 0.94 (s, 9, *t*-Bu), 6.24 (s, 2, vinyl), and 7.25 (m, 5, phenyl); ir (film) 1375, 1390 (*unsym* doublet, *t*-Bu), 975 (*trans* -CH=CH-), and 747, 694 cm⁻¹ (-C₆H₅); mass spectrum (75 eV) *m/e* (relative intensity) 160 (27) (C₁₂H₁₆⁺), 145 (100) (M⁺ - 15), 91 (50) (C₇H₇⁺), and 57 (7) (C₄H₉⁺).

A repetition, using the products above in place of the β-bromostyrene, gave no change in the composition of the product, indicating that the olefin is not reduced by the organometallic.

Reaction of Lithium Diphenylcopper with *trans*- and *cis*-β-Bromostyrenes.—To a suspension of 5.2 g (0.027 mol) of cuprous iodide in 10 ml of ether at 0° was added 25 ml (0.055 mol) of commercial phenyllithium in 70:30 benzene-ether.⁵ The solution was cooled to -78° and a solution of 1.0 g (0.0055 mol) of vpc-purified *trans*-β-bromostyrene in 10 ml of ether was added. The solution was stirred at -78° for 3 hr and then worked up in the usual way to give 1.0 g of a heavy oil containing large amounts of biphenyl and styrene (80% of the mixture). The stilbene fraction (20%) contained, by vpc analysis and isolation, using a 20% Apiezon L column, 16% *cis*-stilbene, mp 4-7° (lit.⁸ mp 5-6°), and 84% *trans*-stilbene, mp 124-125 (lit.⁹ mp 124°).

When the above reaction was repeated using vpc-purified *cis*-β-bromostyrene, the stilbene fraction contained 70% *cis*- and 30% *trans*-stilbene.

Registry No.—LiCuR₂, R = *i*-C₃H₇, 24012-11-1; LiCuR₂, R = *t*-C₄H₉, 23924-63-2; LiCuR₂, R = Ph, 23402-69-9; *cis*-1, 588-73-8; *trans*-1, 588-72-7.

(8) D. S. Brackman and P. H. Plesch, *J. Chem. Soc.*, 2188 (1952).

(9) J. C. Irvine and J. Weir, *ibid.*, 91, 1384 (1907).

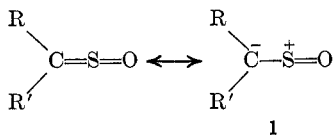
Diphenylcyclopropenethione S-Oxide¹

J. W. LOWN AND T. W. MALONEY

Department of Chemistry, University of Alberta,
Edmonton, Alberta

Received September 8, 1969

The S-oxides of thiocarbonyl compounds have recently attracted considerable attention. Sulfines have been synthesized by Sheppard and Dieckmann,² and by Strating and coworkers³ by dehydrochlorination of sulfinyl chlorides and the oxidation of thio ketones. *syn* and *anti* isomerism in sulfines has been detected by nmr spectroscopy.^{2,4} Cycloaddition of enamines occurs across the C=S double bond of sulfines and the related sulfenes by nucleophilic attack at the sulfur,^{2,3c} and Ulrich has pointed out that the products obtained are consistent with a bond polarization of the following type.⁵



(1) Supported by Grant-A-2305 from the National Research Council of Canada. This support is gratefully acknowledged.

(2) W. A. Sheppard and J. Dieckmann, *J. Amer. Chem. Soc.*, **86**, 1891 (1964).

(3) (a) B. Zwanenberg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 2871 (1968). (b) B. Zwanenberg, L. Thijs, and J. Strating, *ibid.*, 3453 (1967). (c) J. Strating, L. Thijs, and B. Zwanenberg, *ibid.*, 65 (1966); J. Strating, L. Thijs, and B. Zwanenberg, *Rec. Trav. Chim. Pays-Bas*, **83**, 631 (1964).

(4) S. Ghersetti, L. Lunazzi, G. Maccagnani, and A. Mangini, *Chem. Commun.*, 834 (1962).

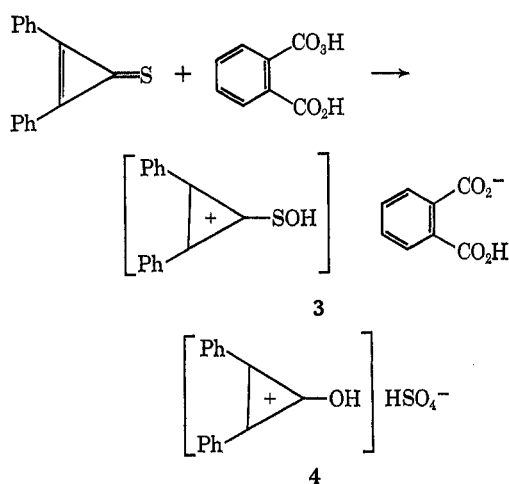
The range of known S-oxides has been extended to include those of thioamides 1 (R' = NR''),⁶ thioacid chlorides 1 (R' = Cl),⁷ dithiocarboxylic esters,^{3b} and sulfinyl and sulfonyl sulfines.^{3a}

Diphenylcyclopropenethione S-oxide was prepared in anticipation of chemical properties quite different from that of S-oxides prepared hitherto.

In the initial experiments direct oxidation of diphenylcyclopropenethione (2) with lead tetraacetate, following a procedure of Owen,⁸ gave diphenylcyclopropenone, elemental sulfur, and lead acetate. Scheme I represents a possible mechanism for this conversion.

The products of the reaction demand attack by the oxidant at the thione carbon rather than at the sulfur. Similar results were obtained with *m*-chloroperbenzoic acid.

A successful route to the S-oxide involved reaction with monopero-phthalic acid at low temperature with very rapid work-up of the product. The initial product of the reaction proved to be the salt of the S-oxide with phthalic acid 3 obtained in nearly quantitative yield, analogous to the hydrosulfate of diphenylcyclopropenone (4).⁹



Compound 3 was completely insoluble in nonpolar solvents, but the orange solution in acetonitrile allowed determination of the absorption spectrum. This showed maxima at 225, 270, 295, and 310 mμ, consistent with the presence of a diphenylcyclopropene moiety,⁹ while the visible absorption maxima at 333 and 438 mμ were tentatively assigned to the S-oxide absorption.^{3c} A potassium bromide disk infrared spectrum showed bands at 1685 and 1695 (carboxylate carbonyl), 1842 (cyclopropene C=C stretch¹⁰), and 3420 cm⁻¹ (hydroxyl) consistent with the structure proposed for 3. The salt 3 was hygroscopic, and, while it was somewhat more stable than the free S-oxide 5, decomposed slowly at room temperature with the evolution of sulfur dioxide. Owing to the antiaro-

(5) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, p 188.

(6) W. Walter and K. D. Bode, *Justus Liebigs Ann. Chem.*, **681**, 64 (1965).

(7) J. F. King and T. Durst, *Tetrahedron Lett.*, 585 (1963).

(8) T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc.*, **C**, 807 (1967).

(9) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

(10) G. L. Closs, *Advan. Alicycl. Chem.*, **1** (1966).