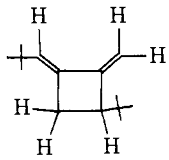
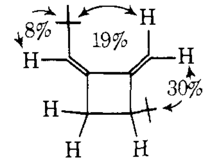
oxidation to the sulfone with *m*-chloroperbenzoic acid ($ArCO_3H$) followed by pyrolysis[9] affords exclusively **7** (overall 83%). Hydrolysis–decarboxylation using the excellent method of Kopecky and Evani[10] gave a hydrazine derivative (not isolated) that was dehydrogenated to **8** using dimethyl azodicarboxylate as hydrogen acceptor.[11] The overall yield was 100% determined by nmr. Even trace amounts of water catalyze rapid tautomerization to **9**. Solutions of **8** must be prepared under rigorously dry and oxygen-free conditions. In the pmr spectrum (C_6D_6) **8** displays δ 1.00 (s, 9, *t*-Bu), 1.03 (s, 9, *t*-Bu), 4.52 (br s, 2, CH_2), 4.99 (br s, 2, CH_2), 5.10 (br s, 1, vinyl H), and 5.33 (br s, 1, vinyl H).

As a 0.1 *M* solution in hydrocarbon solvent **8** is completely decomposed within 240 sec at 190°. A mixture of two isomeric ($C_{14}H_{24}$, **8** less N_2) compounds, **10** and **11**, is formed in 85 ± 5% yield (glpc analysis).[12]



10

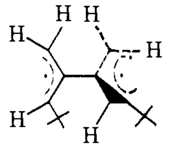


11

After 240 sec the ratio of **10** to **11** is about 1:4 but **11** is thermally unstable and rearranges to **10** on further pyrolysis; **10** eventually becomes virtually the only product.[13] Pure **10** has 100-MHz nmr (C_6D_6): δ 0.93 (s, 9, *t*-Bu), 1.06 (s, 9, *t*-Bu), 2.57–2.68 (complex absorption, 3, ring H), 4.77 (d, J = 1.5 Hz, 1, vinyl H), 5.24 (d, J = 2.2 Hz, 1, vinyl H), and 5.68 (d of d, J = 2.0, 2.5 Hz, 1, vinyl H); uv (C_2H_5OH) λ_{max} 256 nm (ϵ 17,000). These data uniquely describe **10** as being 3-*tert*-butyl-2-methylene-*anti*-neopentylidenecyclobutane.[14] The anti configurational assignment rests on the normal value for the ultraviolet absorption indicating the absence of unusual steric distortion.

To demonstrate that **11** is the primary thermolysis product, a sample of *neat* **8** was pyrolyzed at 190°. The volatile product distilled immediately from the reaction mixture was at least 95% pure **11** (considerable polymer forms also). No **10** was detectable in the distillate. Compound **11** has 100-MHz nmr (C_6D_6): δ 0.91 (s, 9, *t*-Bu), 1.18 (s, 9, *t*-Bu), 2.08–2.70 (complex absorption, 3, ring H), 5.02 (complex t, 1, vinyl H), 5.26 (complex m, 1, vinyl H), and 5.33 (complex d, 1, vinyl H); there is no uv absorption above 220 nm.[15] In independent experiments **11** was shown to rearrange to **10** either thermally or at room temperature with iodine. These data indicate **11** to be the badly twisted syn isomer of **10**. This conclusion is also supported by nuclear Overhauser effects measured between the *tert*-butyl groups and the vinylic protons; the observed per cent enhancements in integration are shown in the structural formula (effects with ring protons were not measured).[16]

The original thesis of this work, that a tetramethyleneethane derivative should be formed from **8**, is substantiated. An effectively orthogonal structural arrangement **12** is virtually mandatory at some point on the reaction profile to explain the "turning over" of the two allylic units from their initial orientation in **8** to their ultimate arrangement in **11**. It is surprising that ring closure leads nearly exclusively to sterically hindered **11** rather than **10** or another isomer. The thermal rearrangement of **11** probably also goes through a tetramethyleneethane.[17] The possibility that **11** is formed from a thermally labile isomer cannot be excluded rigorously.



12

Related to these observations are the reports of Jacobs and coworkers[18] and also Gajewski and Shih[14] who find that substituents prefer syn positions on the vinylic carbons in 1,2-dimethylenecyclobutanes formed from dimerizations of allenes. The present results suggest that at least in part the preference for syn orientation lies in a remarkable facet, probably stereochemical, of the ring closure of tetramethyleneethane.[19] Further work is in progress.

Acknowledgment. We thank Dr. J. de Wit of this department for carrying out the XL-100 experiments and Mr. F. A. Pinkse (University of Amsterdam) for some mass spectral measurements.

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[9] (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

[10] K. T. Kopecky and S. Evani, *Can. J. Chem.*, **47**, 4041 (1969).

[11] F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966).

[12] Spectral and analytical data are in order for all new compounds. Unstable **8** was characterized only by nmr and mass spectra.

[13] Up to 5% of unidentified isomers are present. Tautomer **9** gave no hydrocarbon products on thermolysis.

[14] This compares well with the spectra for 3-methyl-2-methylene-ethylidenecyclobutanes; J. J. Gajewski and C. N. Shih, *J. Org. Chem.*, **37**, 64 (1972).

[15] Ozonolysis produces pivaldehyde and an unstable compound thought to be 3-*tert*-butyl-1,2-cyclobutadione with ir (CCl_4) absorptions at 1735 and 1775 cm^{-1} and λ_{max} 510 nm. Closely analogous 3,4-di-*tert*-butyl-1,2-cyclobutadione has ir absorptions at 1758 and 1785 cm^{-1} and λ_{max} 536 nm [Ae. de Groot, D. Oudman, and H. Wynberg, *Tetrahedron Lett.*, 1529 (1969)].

[16] Complete details of nmr experiments with **10** and **11** will be published in a full article.

[17] Similar observations have been made with the corresponding methyl-substituted compound.[2b]

[18] (a) T. L. Jacobs, J. R. McClennon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969); (b) O. J. Muscio and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969); (c) S. R. Byrn, E. Maverick, O. J. Muscio, Jr., K. N. Trueblood, and T. L. Jacobs, *J. Amer. Chem. Soc.*, **93**, 6680 (1971).

[19] NOTE ADDED IN PROOF. On irradiation through Pyrex at −65° in carbon disulfide, **8** is converted cleanly and exclusively to **11**.

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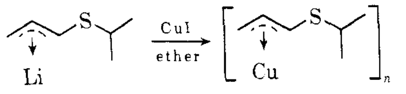
Received August 27, 1973

Carbon–Carbon Bond Formation by Selective Coupling of Alkylthioallylcopper Reagent with Allylic Halides

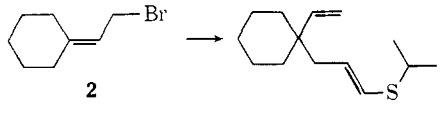
Sir:

The role of the allylic anion bearing a terminal arylthio group in synthetic chemistry has become increasingly apparent. Efficient and useful methods for the extension of carbon chain by means of such reactive species have recently been described.[1] Similar types of anions have proved to be highly effective for the construction of 1,5-diene systems.[2] The further extension of this investigation toward even more selective methods for assembling a carbon skeleton and to organotransition metal compounds has yielded results which are of considerable synthetic interest. This communication deals with the reaction between alkylthioallylcopper anion (**1**) and allylic halides as a promising new general synthetic method.

Addition of cuprous iodide to an ethereal solution of isopropylthioallyllithium at −78° under nitrogen led to formation of a white insoluble product which by analogy with previous work[3] is probably due to the polymeric species **1**. A similar complex has also been prepared from *tert*-butylthioallyllithium but not from phenylthioallyllithium.[4] Our studies indicated that this kind of complex, referred to herein as alkylthioallylcopper, is an excellent reagent for the selective coupling with allylic halides. Thus, the reaction of isopropylthioallylcopper (**1**, 2 molar equiv) with 2-cyclohexylideneethyl bromide (**2**)[5] at −78° for 4 hr furnished the sulfide **3**[6,7] as a sole product (92% yield).[8]

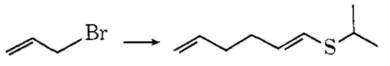


1

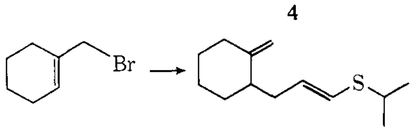


2 **3**

The reaction appears to be a pure SN2′ type displacement of bromine by the isopropylthioallyl group.[9] In addition this ambident anion undergoes alkylation in high yield, *exclusively γ to sulfur.*[10] In a similar experiment, allyl bromide and 1-cyclohexenylmethyl bromide gave the sulfides **4**[11] (88% yield by glpc assay) and **5**[12] (87% yield after chromatography), respectively, the structures of which are in good accord with the above prediction. Further study is required before the stereochemical and mechanistic details of these reactions can be understood. However, the broad scope and utility of the method are apparent. It should be noted that alkylthioallyllithium itself is a totally unsatisfactory reagent for such transformations. The following experimental procedure illustrates the method.

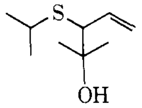


4



5

sec-Butyllithium[1] in pentane (1.02 *M*, 20 ml, 20 mmol) was added to a solution of allyl isopropyl sulfide (2.35 g, 20 mmol)[13] in dry ether (70 ml)[14] with stirring under nitrogen at −78°.[8] After 30 min at −25°, the solution was recooled to −78° and treated with cuprous iodide (4.95 g, 26 mmol), which formed a white suspension. After the mixture was stirred for 15 min at −78°, 2-cyclohexylideneethyl bromide (**2**, 1.90 g, 10 mmol) was added. The suspension became dark after 10 min. After 4 hr at −78°, the mixture was partitioned between dilute hydrochloric acid and ether. The organic phase was washed with water, dried, and freed of solvent. The remaining pale yellow liquid was subjected to column chromatography (silica gel, 100 g) using hexane as eluent to give the desired sulfide **3** as a colorless liquid (2.07 g, 92%),[7] bp 145° (bath temp, 3 mm).[15]



6

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(1) K. Oshima, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 2693 (1973); K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 4446 (1973); H. Takahashi, K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 5803 (1973).

(2) (a) Juvenile hormone synthesis: K. Kondo, A. Negishi, K. Matsui, D. Tunemoto, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 1311 (1972); E. E. van Tamelen, P. MuCurry, and N. Huber, *Proc. Nat. Acad. Sci. U. S.*, **68**, 1294 (1971); P. L. Stotter and R. E. Hornish, *J. Amer. Chem. Soc.*, **95**, 4444 (1973). (b) *dl*-Tetrahymanol: E. E. van Tamelen, R. A. Holton, R. E. Hopla, and W. E. Knoz, *ibid.*, **94**, 8228 (1972); (c) see also, J. F. Biellmann and J. B. Ducep, *Tetrahedron Lett.*, 5629 (1968); *Tetrahedron*, **27**, 5861 (1971).

(3) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952); H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55**, 821 (1936); for a review see J. F. Normant, *Synthesis*, **2**, 63 (1972).

(4) Phenylthioallylcopper reagent was found to be very unstable even at −78°.

(5) M. C. Chaco and B. H. Iyer, *J. Org. Chem.*, **25**, 186 (1960).

(6) All new compounds encountered in this work were characterized spectrometrically and analytically.

(7) Mass *m/e* 224 (M^+); ir (neat) 1640 (m, vinyl sulfide), 1612, 1000, 945, 913 cm^{-1} (terminal vinyl); nmr (CCl_4, TMS) δ 1.25 (d, *J* = 7 Hz, CH_3), 1.40 (br s), 2.03 (d, *J* = 7 Hz, $CH_2CH{=}$), 3.00 (d of q, *J* = 7 and 7 Hz, $CH(CH_3)_2$), 4.96 (d of d, *J* = 2 and 17 Hz, $CH{=}CH_2$ (trans)), 5.09 (d of d, *J* = 2 and 12 Hz, $CH{=}CH_2$ (cis)), 5.70 (d of d, *J* = 12 and 17 Hz, $CH{=}CH_2$), 5.60 (d of t, *J* = 7 and 15 Hz, $CH{=}CHS$), 6.02 ppm (d, *J* = 15 Hz, $CH{=}CHS$); homogeneous by tlc (R_f 0.50; SiO_2–hexane) and >96% pure by glpc (t_r = 7.4 min, 160°, 1.5-m column of 10% Carbowax 20M) analysis.

(8) All reactions involving the copper reagent **1** must be conducted with rigorous exclusion of air and moisture. In addition, because of the thermal lability of **1**, the safe upper limit of the reaction is −50°. The initial temperature for the reaction described herein was −78°, and reactions requiring a few hours at −78° (as judged by the appearance of black precipitate) were conducted at this temperature; with relatively unreactive halides a reaction temperature of −50 to −60° is recommended.

(9) Dimethylcopper and its homologs undergo the similar substitution reaction with allylic or propargylic acetate, although *n*-C_4H_9Cu-LiI does not react. Allylic acetate: P. Rona, L. Tökes, J. Tremble, and P. Crabbe, *Chem. Commun.*, 43 (1969); R. J. Anderson, C. A. Henrick, and J. B. Siddal, *J. Amer. Chem. Soc.*, **92**, 735 (1970); E. E. van Tamelen and J. P. McCormick, *ibid.*, **92**, 737 (1970). Propargyl acetate: P. Rona and P. Crabbe, *ibid.*, **90**, 4733 (1968); **91**, 3289 (1969).

(10) The simple arylthioallyllithium reagent reacts with halides to give an α-alkylation product as the major product. See ref 1 and 2.

(11) Bp 110° (bath temp, 45 mm); mass *m/e* 156 (M^+); ir (neat) 1640, 993, 942, 912 cm^{-1}; nmr (CCl_4, TMS) δ 1.30 (d, *J* = 7 Hz, CH_3), 2.02–2.38 (m, CH_2CH_2), 2.98 (d of q, *J* = 7 and 7 Hz, $CH(CH_3)$), 4.75–5.16 (m, $={CH_2}$), 5.40–6.05 ppm (m, $CH{=}CHS$ and $CH{=}CH_2$); homogeneous by tlc (R_f 0.40, SiO_2–hexane) and >98% pure by glpc assay.

(12) Bp 130° (bath temp, 3 mm); mass *m/e* 210 (M^+); ir (neat) 1645, 945, 885 cm^{-1} ($R_2C{=}CH_2$); nmr (CCl_4, TMS) δ 1.25 (d, *J* = 7 Hz, CH_3), 2.95 (d of q, *J* = 7 and 7 Hz, $CH(CH_3)_2$), 4.58 (br d, *J* = 7 Hz, $={CH_2}$), 5.63 (d of t, *J* = 15 and 7 Hz, $CH{=}CHS$), 5.90 ppm (d, *J* = 15 Hz, $CH{=}CHS$); homogeneous by tlc (R_f 0.45, SiO_2–hexane) and >95% pure by glpc assay.

(13) Prepared from sodium isopropylmercaptide and allyl bromide in ethanol (79% after distillation; bp 127–128°).

(14) Tetrahydrofuran was found to be an unsatisfactory solvent for the formation of the copper reagent **1**.

(15) The major by-product, the dimer of allyl isopropyl sulfide, was eluted with benzene as a pale yellow liquid (480 mg): *m/e* 230 (M^+).

Alkylthioallylcopper also reacts with substances other than allylic halides. The isopropylthio complex **1** reacts with acetone in ether at −78° to yield **6** as a major product. Thus, the behavior of carbonyl compounds toward the copper derivative **1** contrasts sharply with that of allylic halides as those appearing above.

Investigations are continuing on the extension, refinement, and application of the cross-coupling method reported here.

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Received September 18, 1973

Additions and Corrections

Carbonium Ions with Multiple Neighboring Groups. II. Physical Studies [*J. Amer. Chem. Soc.*, **90,** 4056 (1968)]. By Ronald Breslow,* Leonard Kaplan, and Douglas LaFollette, Department of Chemistry, Columbia University, New York, New York 10027.

On page 4062, for structure IIv′′, the right hand figure is incorrectly drawn. The heavy lines for the two benzene rings should be on the other side of the ring, as they are in the figure just above.

Reactions of Monomeric Cobalt–Oxygen Complexes. I. Thermodynamics of Reaction of Molecular Oxygen with Five- and Six-Coordinate Amine Complexes of a Cobalt Porphyrin [*J. Amer. Chem. Soc.*, **95,** 1154 (1973)]. By F. Ann Walker, Department of Chemistry, California State University at San Francisco, San Francisco, California 94132.

Due to an oversight, a 21° correction to the esr temperature controller reading was not applied to the data for the reaction of Co(*p*-OCH_3)TPP·5-chloro-*N*-methylimidazole with molecular oxygen. Thus the data of Table I are for the reaction at −59°, and the ordinate of Figure 2 is incorrect. When replotted, the data give a linear slope and revised values in Table II of $\Delta H_3 = -9.7$ kcal/mol, $\log K_3 = 3.04$ (1 *M* standard state), $\Delta G_3 = -2.89$ kcal/mol (1 *M* standard state), $\Delta S_3 = -33$ cal/(mol deg) (1 *M* standard state), $\Delta G_3 = 2.15$ kcal/mol (1 Torr standard state), $\Delta S_3 = -56$ cal/(mol deg) (1 Torr standard state) for B = 5-chloro-*N*-methylimidazole. The appropriate correction had been applied to the other data of Table II before publication. This correction has no effect upon the conclusions.

Preparation of Cyclopropyldiphenylsulfonium and 2-Methylcyclopropyldiphenylsulfonium Fluoroborate and Their Ylides. Stereochemistry of Sulfur Ylides [*J. Amer. Chem. Soc.*, **95,** 5298 (1973)]. By Barry M. Trost* and Mitchell J. Bogdanowicz, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

The yields listed under structures **22** and **23** should read as follows: For 80:20 **14**:**15**, 78% **22** and 22% **23**; for 70:30 **14**:**15**, 70% **22** and 30% **23**.

Reactions of Diaryl Carbonates and Methylphosphonates with Cycloamyloses [*J. Amer. Chem. Soc.*, **95,** 5391 (1973)]. By Herbert J. Brass and Myron L. Bender,* Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

On page 5392, line 2 after eq 3 should read "$-K_D$ as the slope...," not K_D. In Tables I and VII, K_D has the units *M* instead of M^{-1}. In Table II, for IV at pH 7.63 in cycloheptaamylose, the values of $2k_1$ and k_2 should read 0.12 and 0.13, respectively, instead of 1.2 and 1.3.

Methylation of Anisole by Methyl-d_3 Chloroformate. Intermolecular Reaction of an n Complex in Electrophilic Aromatic Substitution [*J. Amer. Chem. Soc.*, **95,** 6027 (1973)]. By Peter Beak,* Jerome T. Adams, Peter D. Klein, Patricia A. Szczepanik, David A. Simpson, and Stanley G. Smith, Department of Chemistry, University of Illinois, Urbana, Illinois 61801, and the Division of Biological and Medical Research, Argonne National Laboratory, Argonne, Illinois 60439.

The seventh word in the second sentence of the abstract should read intramolecular and not intermolecular.

Structures of Two Dithiazolidines Containing Four Colinear Sulfur Atoms: $C_7H_{13}N_5S_4$ and $C_{12}H_{17}N_5S_4$ [*J. Amer. Chem. Soc.*, **95,** 6073 (1973)]. By Judith L. Flippen, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375.

The title of this paper should read "Structures of Two Dithiazolidines Containing Four Colinear Sulfur Atoms: $C_9H_{15}N_5S_4$ and $C_{14}H_{17}N_5S_4$."

Pteridines. XXVIII. A New, General, and Unequivocal Pterin Synthesis [*J. Amer. Chem. Soc.*, **95,** 6407 (1973)]. By Edward C. Taylor,* Katherine L. Perlman, Ian P. Sword, Margareta Séquin-Frey, and Peter A. Jacobi, Department of Chemistry, Princeton University, Princeton, New Jersey 08540.

In Scheme III the correct designation for compound **14** should read: **14** (**2**, R = CH_3).