olate (156.2 and 105.4 ppm) differed slightly from the spectrum of the enolate **3** described above, reflecting the facts that the concentrations of the two solutions were different and that one solution contained an equimolar amount of *t*-BuOLi while the other solution contained equimolar amounts of LiBr and Me_2S. However, in all other respects, the two enolate ^{13}C NMR spectra were the same.

The remaining 18.2-ml aliquot of the supernatant liquid was partitioned between aqueous $NaHCO_3$ and pentane. After the organic layer had been dried and concentrated, distillation of the residual liquid separated 1.51 g (corresponding to a 66% yield of ketone **2** in the supernatant solution) of the pure (GLC) ketone **2** as a colorless liquid, bp 47–49 °C (5 mm), $n^{25}D$ 1.4454 [lit.[13] bp 74–74.5 °C (16 mm), $n^{25}D$ 1.4458], that was identified with an authentic sample[13] by comparison of ir and NMR spectra.

Registry No.—**1**, 1193-18-6; **2**, 2978-19-3; **3**, 57074-02-9; **4**, 54200-64-5; Me_2CuLi, 15681-48-8.

References and Notes

(1) This research has been supported by Public Health Service Grant 9-RO1-GM-20197 from the National Institute of General Medical Sciences. The execution of this research was also assisted by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

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Organocopper Intermediates. Synthesis of 2-Isoxazoline *N*-Oxides and Cyclopropanes

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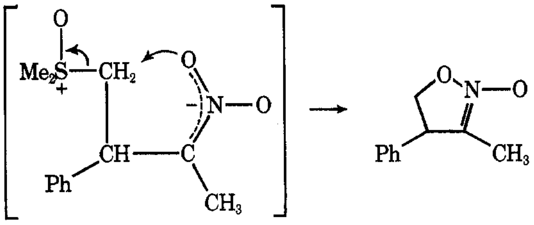
We had as a synthetic objective the preparation of the cyclopropane derived from β-methyl-β-nitrostyrene. Since palladium-catalyzed cyclopropanation has been effective for olefins bearing electron-withdrawing groups, this route was evaluated.[2] Upon treatment of the styrene with diazomethane and palladium nitrate, 60% of the starting material was recovered and there was no evidence of cyclopropane formation. An alternative route, employing a Me_2SO-derived ylide, was then investigated. Treatment of β-methyl-β-nitrostyrene with dimethylsulfoxonium methylide led to the immediate precipitation of an amorphous solid.[3,4] Noting that a transient red color appeared during this reaction and that electron transfer processes often display this behavior,[5] it was considered that the electron-donating characteristics of the ylide might be altered by complexation with copper.[6] Thus, the ylide was prepared in the usual fashion and a copper halide was then added. In dimethylformamide (DMF), with copper(I) iodide, the reagent was red-brown; in methyl sulfoxide (Me_2SO) the same halide resulted in an intense orange-pink color.[7] Because of greater solubility, Me_2SO was typically employed as the solvent. Upon addition of the styrene to the ylide–copper complex no precipitate was formed and after 2 h the products were isolated and purified. Instead of finding the cyclopropane, we identified the product as a 2-isoxazoline *N*-oxide. A likely intermediate in its formation is the ylide adduct, which O-alkylates instead of closing to form the cyclopropane.[8] To determine the generality of this reaction, other unsaturated compounds were treated with copper–ylide complexes (Table I).



The reaction has greater significance as a synthetic approach to 2-isoxazoline *N*-oxides than to cyclopropanes. The cyclopropanation yield from benzalacetophenone is comparable to that reported from the ylide without the use of copper.[3] By contrast, there is no cyclopropanation of ethyl cinnamate in the presence of the copper reagent.[3b,c] The yields from the α,β-unsaturated ester and ketones are lower than those obtained using (dimethylamino)methyloxosulfonium methylide.[3d]

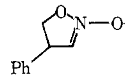
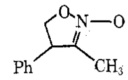
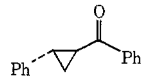
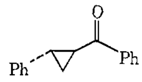
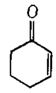
The experimental results are consistent with the relationship between product formation and polarographic reduction potential reported initially by House.[9] In this study, compounds having reduction potentials less negative than −1.8 V vs. SCE react with the ylide–copper complex whereas compounds with reduction potentials more negative than −1.8 V vs. SCE are recovered unchanged. Thus, the utility of this reaction lies in those applications in which derivatives are desired of compounds having low reduction potentials.

Experimental Section

Melting points were taken with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 710 infrared spectrometer. Proton magnetic resonance spectra were recorded on a Varian A-60A spectrometer using Me_4Si as the internal standard. The carbon-13 magnetic spectra were obtained with a Varian CFT-20. The mass spectrum was recorded on a Perkin-Elmer RMU7, ionizing voltage 70 and 10 eV.

3-Methyl-4-phenyl-2-isoxazoline *N*-Oxide. To 250 ml of dry deoxygenated (N_2) DMF were added 12.8 g (58.2 mmol) of trimethylsulfoxonium iodide and 2.6 g (50% in oil, 55 mmol) of sodium hydride. After stirring for 2 h, 3.00 g (15.8 mmol) of copper(I) iodide was added. Upon stirring for 0.5 h, during which the color changed from gray to red-brown, the solution was cooled in an ice bath and 8.00 g (49.2 mmol) of β-methyl-β-nitrostyrene dissolved in 60 ml of DMF was added dropwise over the course of 20 min. After addition was complete, the ice bath was removed. After stirring for 2 h, ice water was added, the organic products were extracted with methylene chloride, and 6.4 g (74%) of crude 3-methyl-4-phenyl-2-isoxazoline *N*-oxide was isolated, mp 45–54 °C. Recrystallization from anhydrous ethanol resulted in 5.6 g (64%) of the purified product: mp 63–64 °C; NMR (CCl_4) δ 1.82 (d, 3 H, CH_3), 4.12–4.93 (m, 3 H, CH and CH_2),

Table I. Reactions of the Dimethylsulfoxonium Methylide–Copper(I) Complex with Olefins[a]

Registry no.	Entry	Compd	$E_{1/2}$, V vs. SCE	Product (%)	Registry no.
102-96-5	1	PhCH=CHNO$_2$	−0.58[b]	 (71)	60239-08-9
705-60-2	2	PhCH=C(CH$_3$)NO$_2$	−0.64[b]	 (64)	60239-09-0
5292-53-5	3	PhCH=C(CO$_2$Et)$_2$	−0.78[c]	Polymer	
1885-38-7	4	PhCH=CHCN	−1.36[d]	Polymer	
94-41-7	5	PhCH=CHCOPh	−1.41[e]	 (76)	1145-92-2
	6	PhCH=CHCOPh	−1.41[e]	 (25)	
103-36-6	7	PhCH=CHCO$_2$Et	−1.81[e]	(80% recovered)	
930-68-7	8		−2.07[f]	(65% recovered)	

[a] All but experiment 6, which employed the copper(I) complex of triphenylphosphonium methylide. [b] R. F. Silver and H. L. Holmes, *Can. J. Chem.*, 44, 1031 (1966). [c] M. Bargain, *C. R. Acad. Sci.*, 255, 1948 (1962). [d] I. G. Sevast'yanova and A. P. Tomilov, *Zh. Obshch. Khim.*, 33, 2815 (1963). [e] H. O. House and J. Umen, *J. Am. Chem. Soc.*, 94, 5495 (1972). [f] For 5-methyl-2-cyclohexen-1-one, ref *e*.

7.40 (s, 5 H, aryl); ^{13}C NMR (CDCl$_3$, 5000 transients, norm decoupling) 137.54, 128.97, 128.04, 127.19, 114.81, (quaternary), 70.45 (methylene), 52.09 (methine), and 10.29 ppm (methyl); ir (CCl$_4$) 1640 cm^{-1} (C=N); MS (70 eV) *m/e* (rel intensity) 160 (13), 159 (100), 158 (15), 131 (56), 130 (60), 116 (33), 105 (8), 104 (15), 103 (39), 102 (6), 90 (18), 89 (17), 77 (15), 63 (34), 51 (18); (10eV) 159.

Anal. Calcd for C$_{10}$H$_{11}$NO$_2$: C, 67.79; H, 6.21; N, 7.91. Found: C, 67.98; H, 6.34; N, 7.81.

4-Phenyl-2-isoxazoline *N*-Oxide. The procedure was the same as that reported above except that 7.00 g (47.0 mmol) of β-nitrostyrene was added. Isolation eventuated in 6.4 g (83%) of crude oil. Elution from a silica gel column with absolute ethanol gave 5.5 g (71%) of pure 4-phenyl-2-isoxazoline *N*-oxide: NMR (CDCl$_3$) δ 2.92 (d, 3 H, CH and CH$_2$), 7.12–7.61 (m, 5 H, aryl), 8.08 (bs, 1 H, vinyl); ir (CHCl$_3$), 1660 cm^{-1} (C=N).

Cinnamonitrile. To 25 ml of dry deoxygenated DMF were added 1.30 g (5.82 mmol) of trimethylsulfoxonium iodide and 0.26 g (50% in oil, 5.5 mmol) of sodium hydride. Upon stirring for 0.5 h, 0.30 g (1.6 mmol) of copper(I) iodide was added. After stirring for 0.5 h, 0.71 g (5.5 mmol) of cinnamonitrile was added. A precipitate appeared within 5 min. After stirring for 2 h, water was added and an amorphous solid, 0.75 g, separated, having an ir band at 2340 cm^{-1} (CN). The aqueous portion was extracted several times with ether, and the combined ether portions were washed with water, dried, and evaporated to leave a smear of product.

Benzylidenediethyl Malonate. The reaction was performed analogous to the description of the cinnamonitrile experiment. An amorphous solid was isolated.

***trans*-1-Benzoyl-2-phenylcyclopropane (from Dimethylsulfoxonium Methylide).** To 90 ml of dry, deoxgenated (N$_2$) methyl sulfoxide were added 6.4 g (29.1 mmol) of trimethylsulfoxonium iodide and 1.4 g (50% in oil, 29.1 mmol) of sodium hydride. After stirring for 2 h, 1.50 g (7.9 mmol) of copper iodide was added. After 1 h, 5.1 g (24.5 mmol) of benzalacetophenone was added; 13 h later workup resulted in 4.9 g (91%) of crude *trans*-1-benzoyl-2-phenylcyclopropane. Purification by column chromatography from silica gel, eluting with chloroform-petroleum ether, resulted in the isolation of 4.1 g (76%) of the product whose data were identical with literature data:[3d] ir (film) 1670 cm^{-1} (C=O); NMR (CDCl$_3$) δ 7.1–8.3 (m, 10, aryl), 2.45–3.50 (m, 2, COH and CH), 1.20–2.00 (m, 2, CH$_2$).

***trans*-1-Benzoyl-2-phenylcyclopropane (from Triphenylphosphonium Methylide).** To 90 ml of dry, deoxgenated methyl sulfoxide were added 85.4 g (21.0 mmol) of methyltriphenylphosphonium iodide and 9.2 ml (2.4 M, 22 mmol) of *n*-butyllithium. After stirring for 5 min, 3.80 g (20.0 mmol) of copper(I) iodide was added. After 1 h, 4.16 g (20.0 mmol) of benzalacetophenone was added. Upon stirring for 1.5 h, workup gave 3.8 g of product containing 25% of the cyclopropane.

Ethyl Cinnamate. To 150 ml of dry, deoxygenated methyl sulfoxide was added 6.4 g (29.1 mmol) of trimethylsulfoxonium iodide and 1.4 g (50%, 20.1 mmol) of sodium hydride. After stirring for 2 h, 1.50 g (7.9 mmol) of copper iodide was added. After 1 h, 4.65 g (26.4 mmol) of ethyl cinnamate was added. After 21 h, there was no indication of reaction by TLC. Workup eventuated in the recovery of 3.8 g (80%) of ethyl cinnamate.

Acknowledgments. We wish to thank Drs. Stan Smith and John Layton for the carbon-13 spectrum of 3-methyl-4-phenyl-2-isoxazoline *N*-oxide and Ms. Penny Purdue for its mass spectrum.

Registry No.—Dimethylsulfoxonium methylide–copper(I) complex, 60260-29-9; triphenylphosphonium methylide–copper(I) complex, 60260-30-2; trimethylsulfoxonium iodide, 2181-42-2; copper(I) iodide, 7681-65-4; methyltriphenylphosphonium iodide, 2065-66-9.

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Tin–Copper Couple. A New Reagent for Selective Debromination of Activated Dibromides

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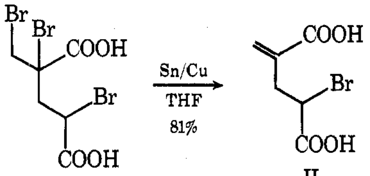
We wished to prepare the α-methylene-γ-bromoglutaric acid II. Attempts to accomplish this from the known[1] γ-methyleneglutamic acid by diazotization in the presence of sodium bromide[2] were frustrated by persistent lactone formation. As an alternative, the selective debromination of the tribromide I was explored. The latter is readily prepared by Hell–Volhard–Zelinsky bromination of α-methyleneglutaryl chloride.



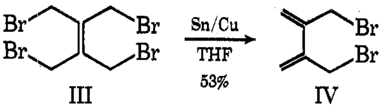
I II

Of the many possible reagents appropriate for the reductive removal of vicinal dibromides,[3] zinc–copper couple[4] was chosen for this purpose. Tetrahydrofuran was used as solvent in order to avoid lactone formation to whatever extent possible.

Attempts to carry out the desired reduction with zinc–copper couple led in every case to substantial overreduction, with production of starting α-methyleneglutaric acid (60%). A lesser amount (40%) of the desired monobromide II was also observed. It seemed reasonable to suppose, since tin has a lower reduction potential than zinc, that improved selectivity might be realized if the reduction could be induced to proceed with tin[5] instead of with zinc.

We have found that the bromoglutarate II can be prepared in 81% yield (recrystallized) from the tribromide I using tin–copper couple in tetrahydrofuran. In the total crude product approximately 3% of the fully reduced α-methyleneglutaric acid can be detected by NMR.[9] This impurity is readily removed by one crystallization from chloroform–ethyl acetate. An interesting feature of this reduction is the requirement of only 0.5 mol of tin–copper couple for complete reaction. This facet has not been explored further. However, it appears that Sn(II) is also sufficiently reactive to promote elimination of such active dibromides and that a further refinement in selectivity might be realized using the latter as a reagent.

Tin–copper couple reacts very slowly, if at all, with 1,2-dibromoethane. On this limited basis, it appears that unactivated dibromides will be relatively unreactive toward this reagent. By contrast, the tin–copper reagent quite effectively reduced tetrakis(bromomethyl)ethylene (III) to the labile dibromide IV.[6]



III IV

Because of its simplicity and ready availability, the tin–copper couple reagent may serve, in favorable instances, as an alternative to electrochemical reduction as it is used to select among several readily reduced functional groups.

Experimental Section

α-Methyleneglutaryl Chloride.[7] α-Methyleneglutaric acid (5.76 g, 0.04 mol) was carefully mixed with phosphorus pentachloride (18.35 g, 0.09 mol) in a round-bottom flask. A vigorous reaction began immediately, and the reaction mixture became liquid. When the initial exothermic part of the reaction had subsided, the mixture was heated at 110–115 °C for 15 min. Phosphorus oxychloride was removed by distillation under aspirator vacuum. The liquid remaining was distilled through a 14-cm Vigreux column yielding 6.15 g (85%), bp 84–86 °C (2 mm), of a colorless liquid: infrared (neat) 5.59 and 5.78 μ; NMR (CCl_4) one-proton vinyl singlet at δ 6.6, one-proton vinyl singlet at δ 6.2, and two two-proton aliphatic multiplets at δ 3.2 and 2.8.

α-Bromomethyl-α,γ-dibromoglutaric Acid (I). Dry bromine (5.65 ml, 0.11 mol) was added dropwise to α-methyleneglutaryl chloride (9.05 g, 0.05 mol) with stirring at room temperature. When the addition was complete (ca. 30 min), the reaction mixture was heated in an oil bath at 80–85 °C for 14 h. The reaction mixture was allowed to cool to room temperature, then transferred to a large watchglass for slow hydrolysis in the air. After 36 h a solid mass was formed. It was collected and washed with 15 ml of chloroform yielding 5.85 g (71%) of the desired tribromo diacid I, mp 148–152 °C. One crystallization from a mixture of chloroform–ethyl acetate (2:1) yielded 5.52 g (67%) of white solid, mp 153–155 °C. The melting point was not improved by further crystallization. Infrared (KBr) 5.81 μ; NMR (acetone-d_6) two-proton broad singlet at δ 9.7, one-proton quartet (H_γ, $J_{\beta\gamma} = 4.4$, $J_{\beta'\gamma} = 7$ Hz) at δ 4.67, two-proton bromomethyl singlet at δ 4.25, one-proton quartet (H_β, $J_{\beta\gamma} = 7$, $J_{\beta\beta'} = 17$ Hz) at δ 3.57, and a one-proton quartet ($H_{\beta'}$, $J_{\beta'\gamma} = 4.4$, $J_{\beta\beta'} = 17$ Hz) at δ 2.78. At 250 MHz the singlet at δ 4.25 is split further into an AB quartet ($J = 12$ Hz).

Anal. Calcd for $C_6H_7O_4Br_3$: C, 18.81; H, 1.82; Br, 62.63. Found: C, 19.04; H, 1.90; Br, 62.58.

Tin–Copper Couple. The procedure of Le Goff,[4] developed for the preparation of zinc–copper couple, was followed. Thirty mesh granular tin (3.5 g, 0.0295 mol, Mallinckrodt) was added to a hot solution of cupric acetate monohydrate (0.050 g, 0.0025 mol) in acetic acid (25 ml). The mixture was stirred and shaken until the blue color of the cupric acetate was no longer evident (ca. 3 min). The acetic acid was decanted and the reddish tin–copper couple washed with two 15-ml portions of acetic acid followed by three 20-ml portions of ether. The tin–copper couple was used freshly prepared and was kept covered with ether.

α-Methylene-γ-bromoglutaric Acid (II). A solution of α-bromomethyl-α,γ-dibromoglutaric acid (I, 3.83 g, 0.01 mol) in dry tetrahydrofuran (6 ml), freshly distilled from $LiAlH_4$, was stirred magnetically with freshly prepared tin–copper couple (0.590 g, 0.005 mol) for 1 h. The precipitated tin bromide was removed by filtration and washed with carbon tetrachloride. Removal of the solvent from the filtrate and addition of chloroform to the concentrate afforded 1.92 g (86%) of white, crystalline α-methylene-γ-bromoglutaric acid (II), mp 133–136 °C. Crystallization from a 2:1 mixture of chloroform–ethyl acetate yielded 1.80 g (81%) of the pure bromo acid II: mp 136–137 °C; infrared (KBr) 5.81, 5.92, and 6.13 μ; NMR (acetone-d_6) two-proton, broad carboxylic acid singlet at δ 8.83, one-proton vinyl singlet at δ 6.33, one-proton vinyl doublet ($J = 1$ Hz) at δ 5.83, one-proton bromomethylene triplet (H_γ, $J_{\beta\gamma} = J_{\beta'\gamma} = 7$ Hz) at δ 4.60, allylic one-proton quartet (H_β, $J_{\beta\beta'} = 14$, $J_{\beta\gamma} = 7$ Hz) at δ 3.25, and allylic one-proton quartet ($H_{\beta'}$, $J_{\beta\beta'} = 14$, $J_{\beta'\gamma} = 7$ Hz) at γ 2.83. The NMR spectrum of the total crude product shows approximately 3% of the fully reduced α-methyleneglutaric acid, which is easily removed in the crystallization step.

Anal. Calcd for $C_6H_7O_4Br$: C, 32.30; H, 3.14; Br, 35.84. Found: C, 32.41; H, 3.28; Br, 35.67.

2,3-Bis(bromomethyl)-1,3-butadiene (IV). Tetrakis(bromomethyl)ethylene (III) was prepared according to Cope and Kagan,[8] NMR ($CDCl_3$) singlet at δ 4.18. A solution of the tetrabromide III (50 g, 0.125 mol) in 300 ml of tetrahydrofuran was stirred for 48 h in the refrigerator (4 °C) with 250 g (2.106 mol) of freshly prepared tin–copper couple. The progress of the reaction was conveniently followed in the same solvent using NMR. The bromomethyl protons of IV are