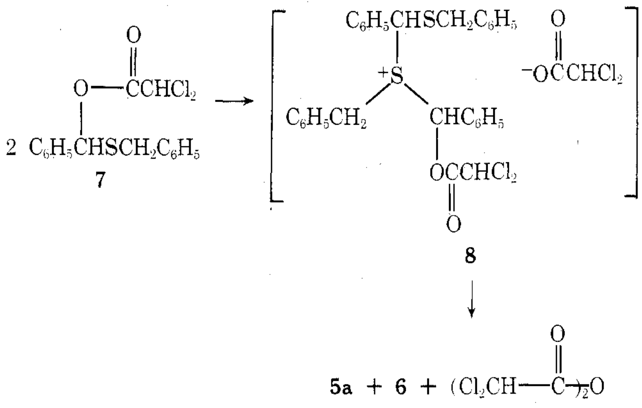
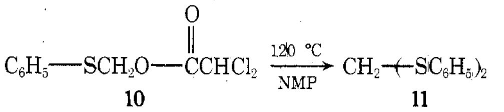
benzyl sulfide (**9**) with sodium dichloracetate in anhydrous acetonitrile, which would be expected to give **7** directly, was found instead to produce the dibenzylmercaptal of benzaldehyde (**5a**) in 70% yield. This result provides good evidence for the intermediacy of α-acyloxy sulfide **7** in the formation of **5a** and is supportive of the mechanism proposed in Scheme I.

Scheme I



If an α-acyloxy sulfide is first formed during the reaction of a sulfoxide with an acid anhydride or an acid chloride, the question of whether the α-acyloxy sulfide survives intact or is converted to the corresponding thioacetal would be expected to be governed by the usual factors affecting rates of SN1–SN2 reactions. Thus, the nature of the substituents in the sulfoxide as well as the stability of the departing acyloxy anion should play a role. We have carried out several experiments to gain insight regarding these factors and the results are summarized in Table I.

Thus, the reaction of benzyl phenyl sulfoxide (**4b**) with dichloroacetyl chloride under the same conditions as before gave mainly the diphenylmercaptal of benzaldehyde (**5b**) as would be expected. Although methyl phenyl sulfoxide, which lacks benzylic activation, was converted by dichloroacetyl chloride to the corresponding diphenylmercaptal of formaldehyde, the yield was quite poor. Furthermore, the reaction of methyl phenyl sulfoxide with either acetic anhydride or dichloroactic anhydride gave the corresponding α-acyloxy sulfides in good yield. In these instances the reaction conditions were not sufficiently severe for the further conversion of the α-acyloxy sulfides to the acetals. However, when the product, dichloroacetoxymethyl phenyl sulfide (**10**), was heated in N-methylpyrrolidone (NMP) at 120 °C for 48 h, it was converted to the diphenylmercaptal of formaldehyde (**11**) in 45% yield.



$$C_6H_5\text{—}SCH_2O\text{—}\overset{\overset{\displaystyle O}{\|}}{C}CHCl_2 \xrightarrow[\text{NMP}]{120\ ^\circ C} CH_2(SC_6H_5)_2$$

10 **11**

From these studies it can be concluded that the reaction of sulfoxides with acid halides or acid anhydrides may yield either α-acyloxy sulfides or thioacetals, depending upon the substituents present and the nature of the acid halide or acid anhydride.

Experimental Section

General. Infrared spectra were recorded on a Beckman IR7 spectrophotometer. Solids were recorded as KBr pellets whereas liquids were recorded as thin films on NaCl plates. NMR spectra were recorded on a Varian XL-100 spectrometer using $CDCl_3$ as solvent. Elemental analyses were obtained with a Perkin-Elmer Model 240 C, H, N analyzer. Mass spectra were recorded on a CEC 21-110B mass spectrometer. Melting points were taken with a Dreschel melting point apparatus and are uncorrected. Boiling points were obtained using a micro boiling point tube and are uncorrected. All preparative layer chromatography was done on Analtech silica gel plates.

General Procedure for Reaction of Sulfoxides with Acid Chlorides. A solution of 2 mmol of sulfoxide in 25 ml of anhydrous THF at 25 °C was treated with an equimolar amount of acid chloride. After 15 min 1 equiv of triethylamine was added. The reaction mixture was stirred overnight at 25 °C and the triethylamine hydrochloride was removed by filtration. Concentration of the filtrate under reduced pressure gave an oil which was purified by chromatography.

General Procedure for Reaction of Sulfoxides with Acid Anhydrides. A solution of 2 mmol of sulfoxide in 10 ml of solvent was allowed to react with the appropriate acid anhydride. After completion of the reaction the solution was concentrated under reduced pressure and the resulting oil was purified by chromatography. For specific experimental details see the footnotes of Table I.

Reaction of α-Chlorobenzyl Benzyl Sulfide (9) with Sodium Dichloroacetate. A solution of 0.46 g (2 mmol) of dibenzyl sulfoxide (**4a**) in 10 ml of anhydrous CH_2Cl_2 was added dropwise over a 30-min period to a refluxing solution of 0.17 ml (15% excess) of thionyl chloride in 20 ml of anhydrous CH_2Cl_2. The solution was refluxed for 3 h and concentrated under reduced pressure to give **9** as a slightly yellow oil. A solution of **9** in anhydrous acetonitrile was treated with 0.30 g (2 mmol) of sodium dichloroacetate. A milky precipitate formed immediately. The mixture was stirred for 3 days at 25 °C, the precipitate was removed by filtration, and the filtrate was concentrated under reduced pressure to give a viscous oil. Preparative layer chromatography gave 235 mg (70%) of the dibenzylmercaptal of benzaldehyde (**5a**), mp 59–61 °C (lit.[9] mp 61 °C).

Pyrolysis of Dichloroacetylmethyl Phenyl Sulfide (10). A solution of 120 mg (0.48 mmol) of **10** in 1 ml of anhydrous oxygen-free N-methylpyrrolidinone was heated at 120 °C for 48 h. The solution was diluted with 25 ml of $CHCl_3$ and washed with three 15-ml portions of H_2O. The solution was dried ($MgSO_4$) and concentrated under reduced pressure to give a dark oil. Preparative layer chromatography gave 25 mg (45%) of the diphenylmercaptal of formaldehyde (**11**).

Acknowledgment. This investigation was supported in part by PHS Research Grant 1 ROI CA15004 from the National Cancer Institute and we thank the National Institutes of Health for a postdoctoral award, 1 F32 GM 05326, to one of us (Thomas D. Harris), from the National Institute of General Medical Sciences.

Registry No.—**9,** 51317-73-8; thionyl chloride, 7719-09-7; sodium dichloroacetate, 2156-56-1.

References and Notes

(1) C. King, *J. Org. Chem.*, **25**, 352 (1960).
(2) G. Schulz and G. Kresze, *Angew. Chem.*, **75**, 1022 (1963).
(3) C. R. Johnson and W. G. Phillips, *J. Am. Chem. Soc.*, **91**, 682 (1969).
(4) L. Horner, *Justus Liebigs Ann. Chem.*, **631**, 198 (1960).
(5) L. Horner and P. Kaiser, *Justus Liebigs Ann. Chem.*, **626**, 19 (1959).
(6) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).
(7) W. E. Parham et al., *J. Org. Chem.*, **29**, 2211 (1964).
(8) E. Vedejs and M. Mullins, *Tetrahedron Lett.*, 2017 (1975).
(9) R. J. Kern, *J. Am. Chem. Soc.*, **75**, 1865 (1953).
(10) H. S. Struck and W. J. Jorison, *J. Am. Chem. Soc.*, **52**, 2060 (1930).
(11) T. Numata and S. Oae, *Chem. Ind. (London)*, 277 (1973).

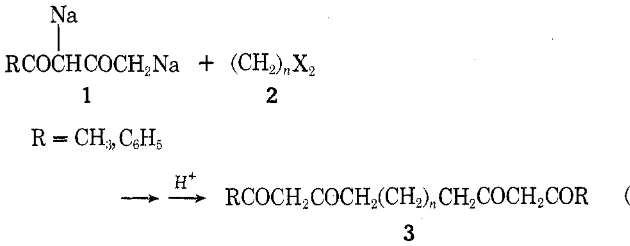
Cuprous Chloride Catalyzed Alkylations of β Diketones with Methylene Halides

K. Gerald Hampton* and J. Joseph Christie

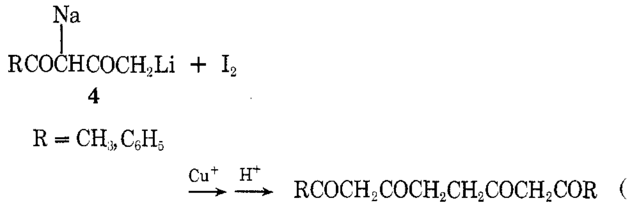
Department of Chemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39401

Received January 29, 1976

It has been observed previously that α,ω dihaloalkanes will alkylate dianions of β diketones to form bis-β diketones (eq 1) where $n = 3$ or higher. However, it was also observed that the alkylation reaction did not work for $n = 1$ or 2 under the same conditions.[1] We have recently found that cuprous ions can catalyze coupling reaction of dianions of β diketones that do not readily occur under the conditions or with reagents usually used for coupling in the absence of cuprous ions (eq 2).[2]



$$\overset{\text{Na}}{\text{RCOCHCOCH}_2\text{Na}} + (\text{CH}_2)_n\text{X}_2 \qquad \mathbf{1} \quad \mathbf{2} \qquad \text{R} = \text{CH}_3, \text{C}_6\text{H}_5 \longrightarrow \xrightarrow{\text{H}^+} \text{RCOCH}_2\text{COCH}_2(\text{CH}_2)_n\text{CH}_2\text{COCH}_2\text{COR} \; \mathbf{3} \qquad (1)$$



$$\overset{\text{Na}}{\text{RCOCHCOCH}_2\text{Li}} + \text{I}_2 \qquad \mathbf{4} \qquad \text{R} = \text{CH}_3, \text{C}_6\text{H}_5 \xrightarrow{\text{Cu}^+} \xrightarrow{\text{H}^+} \text{RCOCH}_2\text{COCH}_2\text{CH}_2\text{COCH}_2\text{COR} \qquad (2)$$

We now report that sodiolithio-2,4-pentanedione (**4**, R = CH_3) reacts with methylene and ethylene bromide (**2**, $n = 1$ and 2, respectively) to form the alkylation products **3**. These products were not obtained when the reaction was run under the same conditions in the absence of the copper catalyst. When dibromomethane was used (−63 to 0 °C, 3 h) as the substrate, 2,4,8,10-undecanetetrone was isolated in 8–10% yields. The low yield could be attributed to unreacted starting material (observed by gas chromatography) and intramolecular condensation of the alkylation product.[3] When diiodomethane was used as the substrate, a tar was formed from which the bis-β diketone **3** could not be isolated nor could starting material be detected by gas chromatography.

When 1,2-dibromoethane (**2**, $n = 2$) was used as substrate with **1** in the presence of cuprous ions 2,4,9,11-dodecanetetrone was isolated as a solid in 25–33% yield. The somewhat low yield of the bis-β diketone may be caused by incomplete crystallization of the low-melting product or intramolecular condensation side reactions[3] since ethylene bromide was shown to be absent from the crude reaction product. When 1,2-dichlorethane was used as the substrate, 2,4-pentanedione and 1,2-dichlorethane were recovered in 52 and 33% yields, respectively. This suggests that E_2 elimination may be the main reaction as in the reaction between disodio-2,4-pentanedione and ethylene chloride in liquid ammonia.[1] This difference in alkylation reactivity of bromo compounds vs. chloro compounds is consistent with previous observations of reactions of some haloacetals[4] and halocarboxylates[5] with dianions of β diketones.

That the alkylation products from these reactions are **3**, $n = 1$ and 2, respectively, is supported by analogy with homologues, ir and ^1H NMR spectra, and elemental analysis (see Experimental Section).

Experimental Section

Melting points were determined using capillary tubes in a Thomas-Hoover melting point apparatus. Infrared spectra were obtained with a Perkin-Elmer 257 grating infrared spectrophotometer using KBr pellets. The ^1H NMR spectra were obtained using a Varian Model A-60D spectrometer and samples dissolved in CCl_4 with Me_4Si as internal standard.

Condensation of Dibromomethane with 4. The sodiolithio-2,4-pentanedione (0.05 mol)–cuprous chloride (0.0076 mol) reagent was prepared in the THF as described previously.[2] To this mixture at −63 °C under an argon atmosphere was added a solution of 4.4 g (0.025 mol) of dibromomethane in 15 ml of THF over 15 min. After the mixture had stirred for 3 h, the reaction mixture was allowed to warm to 0 °C. It was quenched with ice and acidified with cold concentrated hydrochloric acid. The aqueous phase was extracted three times with 25 ml of ether. The ethereal solution was washed once with 30 ml of saturated sodium chloride solution and dried over anhydrous sodium sulfate.

Removal of solvent afforded about 8.0 g of a green, viscous liquid containing 2,4-pentanedione and dibromomethane as major components (VPC analysis). It was triturated in absolute ethanol and petroleum ether (bp 35–60 °C) and cooled in liquid nitrogen to afford 8–10% of 2,4,8,10-undecanetetrone as a light yellow solid, mp 59–60 °C. The solid was enolic to ferric chloride solution (red-brown color): ir (CCl_4) 2980, 2950, 1730, 1710 (m), 1680 cm^{-1}; ^1H NMR (CCl_4) τ 8.0 (s, 6 H) $O{=}CCH_3$, 7.4–7.85 (m, 6 H) $O{=}CCH_2CH_2CH_2C{=}O$, 4.55 (s, 2 H) $-CH{=}C$, and −4.50 (broad hump, 2 H) $-C{=}COH$. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.27; H, 7.55. Found: C, 62.18; H, 7.46.

The reaction was repeated using diiodomethane. A yellow, viscous liquid (4.8 g) was obtained. VPC analysis showed the absence of 2,4-pentanedione and diiodomethane. No **3**, $n = 1$, could be isolated from the liquid.

Condensation of 1,2-Dibromoethane with 4. To the sodiolithio-2,4-pentanedione–cuprous chloride reagent at −5 °C under a nitrogen atmosphere was added a solution of 4.7 g (0.025 mol) of 1,2-dibromomethane in 20 ml of dry THF over 15–20 min. The resulting yellowish-brown mixture was stirred for 8 h while the temperature slowly rose to 25 °C. The workup procedure described above afforded 4.0 g of a yellowish-green syrup. The liquid was dissolved in absolute ethanol and cooled in a freezer to obtain 1.4–1.8 g (25–33%) of 2,4,9,11-dodecanetetrone as a pale yellow solid, mp 48–52 °C. The compound gave a red-brown coloration with ferric chloride solutions. Recrystallization from absolute ethanol and vacuum drying gave an analytical sample: mp 52–53 °C; ir (CCl_4) 2960, 2930, 2860, 1715, 1680–1550 (broad), 1460, 1430, 1360, 1235, 1130, 1000 cm^{-1}; ^1H NMR (CCl_4) τ 8.3 (m, 4 H), 8.0 (s, 6 H), 7.7 (m, 4 H), 7.4 (s, ~1.5 H), 4.64 (s, ~2 H), −5.0 (hump, ~2 H).[6] Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 64.17; H, 8.17.

The reaction was repeated using 1,2-dichloroethane. This afforded 8.0 g of a liquid which showed starting materials by VPC. Fractional distillation gave 2.6 g (52%) of 2,4-pentanedione and 0.8 g (33%) of ethylene chloride and about 2.4 g of intractable pot residue.

Registry No.—**3** (R = CH_3; $n = 1$), 58816-10-7; **3** (R = CH_3; $n = 2$), 58816-11-8; **4** (R = CH_3), 56580-16-6; cuprous chloride, 7758-89-6; dibromomethane, 74-95-3; 2,4-pentanedione, 123-54-6; 1,2-dibromoethane, 106-93-4; 1,2-dichloroethane, 107-06-2; diiodomethane, 75-11-6.

References and Notes

(1) K. G. Hampton, R. J. Light, and C. R. Hauser, *J. Org. Chem.*, **30**, 1413 (1965).
(2) K. G. Hampton and J. J. Christie, *J. Org. Chem.*, **40**, 3887 (1975).
(3) L. Weiler and S. H. Huskin, *J. Am. Chem. Soc.*, **96**, 1082 (1974).
(4) K. G. Hampton and R. E. Flannery, *J. Chem. Soc., Perkin Trans. 1*, 2308 (1973).
(5) R. O. Pendarvis and K. G. Hampton, *J. Org. Chem.*, **39**, 2289 (1974).
(6) NMR spectra of β diketones are complicated by extensive keto-enol tautomerism. It is observed that the absorptions may not be of integral intensity in this series of compounds because of this phenomenon.

A Facile Synthesis of (+)-Pinol from (−)-Carvone

Lee Garver and Paul van Eikeren*

Department of Chemistry, Harvey Mudd College, Claremont, California 91711

James E. Byrd

Department of Chemistry, California State College, Stanislaus, Turlock, California 95880

Received January 19, 1976

The use of chiral solvents in the determination of optical purity, particularly in the presence of lanthanide shift reagents, has received a great deal of recent attention.[1] In our studies of synthetic schemes leading to chiral solvents, we have developed a new and convenient route to the chiral bicyclic ether, (+)-pinol[2,3] (**4**), by the use of the oxymercuration–demercuration reaction. The route involves the stereospecific reduction of (−)-carvone with lithium aluminum hydride to