diselenide and 1-adamantyl methyl ketone.

14-(Phenylseleno)-*N*-(trifluoroacetyl)daunorubicin. Reaction of 1 (X = Br; 250 mg, 0.36 mmol) in ethanol (50 mL) with benzeneselenol (65.5 mg 0.41 mmol) and K_2CO_3 (100 mg) for 15 min, followed by normal workup and chromatography ($CHCl_3$ elution), afforded pure product (175 mg, 63% yield), mp 137–139 °C. Anal. Calcd for $C_{35}H_{32}F_3NO_{11}Se$: C, 53.99; H, 4.15; F, 7.32; N, 1.80; Se, 10.14. Found: C, 53.87; H, 4.17; F, 7.28; N, 1.89; Se, 9.90.

When the 14-iodo compound 1 was substituted for the bromo compound reaction gave diphenyl diselenide and 3 in quantitative yields.

Registry No. 1 (X = I), 26295-55-6; 1 (X = Br), 77270-18-9; 1 (X = SeC_6H_5), 77270-19-0; 2 (R = C_6H_5), 77270-20-3; 3, 26388-52-3; 4 (X = I), 4636-16-2; 4 (X = SC_6H_5), 16222-10-9; 4 (X = $SC_{12}H_{25}$-*n*), 77270-21-4; 4 (X = SeC_6H_5), 35050-01-2; 4 (X = Cl), 532-27-4; 4 (X = Br), 70-11-1; 4 (X = H), 98-86-2; 5 (X = I), 77270-22-5; 5 (X = Br), 5122-82-7; 5 (X = SC_6H_5), 77270-23-6; 5 (X = SeC_6H_5), 77270-24-7; 5 (X = H), 1660-04-4; benzenethiol, 108-98-5; *n*-dodecanethiol, 112-55-0; benzeneselenol, 645-96-5; diphenyl disulfide, 882-33-7; di-*n*-dodecyl disulfide, 2757-37-1; diphenyl diselenide, 1666-13-3.

Diethyl Oxomalonate. An Improved Synthesis

Simon N. Pardo and Robert G. Salomon*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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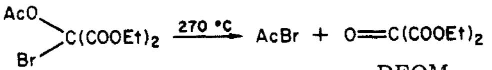
Diethyl oxomalonate (DEOM), a versatile reagent for organic synthesis, is reactive in a wide selection of C–C bond forming processes including Diels–Alder,[1] ene,[2] aldol (especially enamine modification),[3] and Friedel–Crafts[4] reactions. We recently described a synthetic application in which DEOM serves as an eneophilic equivalent of carbon dioxide for elaboration of allylcarboxylic acids from olefins.[5] We now report an improved procedure for preparation of DEOM.[6]

Decomposition of diethyl α-acetoxy-α-bromomalonate (1) at 270 °C is reported to produce DEOM and acetyl bromide.[7] Besides the inconvenience of the metal bath required for this pyrolysis, the published procedure calls for treatment of the crude product with water and $NaHCO_3$. The crude DEOM hydrate, obtained after rotary evaporation, must then be dehydrated. We discovered that *impure* 1 eliminates acetyl bromide under considerably milder conditions. Thus, impure 1 is obtained by bromination of diethyl malonate followed by reaction of the crude dibromide with potassium acetate in ethanol, filtration to remove precipitated potassium bromide, and rotary evaporation of the solvent.[7] The impure diethyl α-acetoxy-α-bromomalonate is transformed to DEOM during slow distillation under reduced pressure. Acetyl bromide collects in a suitable trap cooled to −78 °C, and the distillate collected at 98–110 °C (11 mm) consists of nearly pure DEOM.

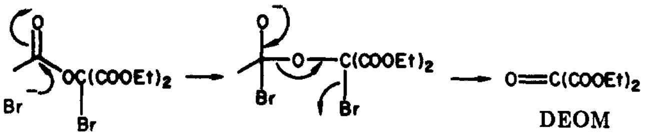


$$\mathrm{(AcO)(Br)C(COOEt)_2} \xrightarrow{270\ ^\circ\mathrm{C}} \mathrm{AcBr} + \mathrm{O{=}C(COOEt)_2}$$

1

DEOM

We suspect that the elimination of acetyl bromide is catalyzed by traces of KBr which converts 1 to 2 since 1 can be distilled without decomposition if the crude product is partitioned between ether and water, the ether layer is dried, and solvent removed prior to distillation to remove the last traces of KBr. Powdered anhydrous reagent KBr does *not* catalyze decomposition of 1, probably owing to insolubility. However, the presumed bromide ion catalyst is soluble in impure 1. Therefore, we examined distillation of 1 in the presence of tetrabutylammonium bromide. As expected, this soluble bromide salt catalyzes complete conversion of 1 to DEOM and acetyl bromide.



1

2

DEOM

Experimental Section

Diethyl Oxomalonate. Since HBr gas is evolved, the bromination of diethyl malonate is conducted in an efficient fume hood. A dry 5-L three-necked round-bottom flask is fitted with a mechanical stirrer, a condenser topped with a nitrogen inlet connected to a nitrogen source and a pressure-releasing oil bubbler, and a 500-mL pressure-equalizing addition funnel. Diethyl malonate (400 g, 2.5 mol) is placed in the flask. Diethyl malonate purchased from Fisher Scientific Co. is used as received. The addition funnel is charged with bromine (850 g, 5.5 mol) of which 10 mL are added to the flask, and the resulting mixture is stirred until HBr gas evolution is observed and the red color of bromine fades. The remainder of the bromine is added dropwise at a rate which maintains a steady evolution of HBr gas. After the addition is complete, the mixture is heated with an oil bath at 60 °C for 1 h and then at 90 °C for an additional 1 h. The reaction mixture is cooled to 50 °C and after removal of the addition funnel a stream of nitrogen is bubbled through the mixture until only a slight turbidity is observed when the effluent gas stream is bubbled through 0.05 N $AgNO_3$. It is crucial that HBr is thoroughly removed in this manner prior to addition of KOAc to the reaction mixture. The reaction mixture is diluted with 500 mL of absolute ethanol and warmed to 50 °C. Anhydrous KOAc (52 g) in a minimum volume of boiling hot ethanol (about 150 mL) is added to the reaction mixture. Over a period of 4 h four additional portions (50 g each) of KOAc, each *partially* dissolved in 100 mL of boiling hot ethanol, are added (2.5 mol total of KOAc). After addition of the last portion the reaction mixture is stirred for 2 h at 50 °C and then boiled under reflux overnight. The precipitated KBr is removed by filtration with suction and washed with 100 mL of absolute ethanol. Solvent is removed from the combined filtrate and washings by rotary evaporation. The crude residual oily product is slowly distilled under reduced pressure. In order to collect the liberated acetyl bromide, a 250-mL trap is inserted between the distillation gas outlet and the vacuum pump and maintained at −78 °C. The fraction with bp 89–110 °C (11 mm) is nearly pure DEOM. Redistillation of this fraction through a 50-cm adiabatic column packed with glass helicies gives

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DEOM, bp 92–96 °C (11 mm) [lit.[7] bp 106–108 °C (17 mm)]. The yield, based on diethyl malonate, is 180–205 g (41–47%).

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Registry No. 1, 60308-73-8; diethyl malonate, 105-53-3; diethyl oxomalonate, 609-09-6.

Thermal Decomposition of Benzyl α-Disulfone: The Question of Rate-Determining Homolysis of More Than One Bond in the Thermal Decomposition of an α-Disulfone

Lieh-pao O. Farng and John L. Kice*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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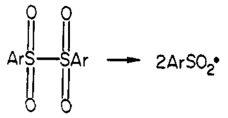
Aryl α-disulfones, $ArSO_2SO_2Ar$ (1), have been shown[1] to undergo thermal decomposition at elevated temperatures (145–165 °C) by a mechanism that involves rate-determining homolysis of the S–S bond (eq 1). The



$$ArS(O_2)\text{—}S(O_2)Ar \longrightarrow 2ArSO_2\cdot \qquad (1)$$

$ArSO_2\cdot$ radicals formed in eq 1 then react further in a variety of ways to yield the final decomposition products. Only a few lose sulfur dioxide, however, since only ~0.2 mol of SO_2 is produced per mole of 1 decomposing.

During a study of nucleophilic substitution of alkyl α-disulfones reported elsewhere[2] we had occasion to synthesize benzyl α-disulfone, $PhCH_2SO_2SO_2CH_2Ph$ (2). The present note describes a study of the thermal decomposition of 2 and presents evidence suggestive that the rate-determining step of this reaction may involve the homolysis of *two* bonds, rather than cleavage of only the S–S bond.

Thermal decomposition of 2 was achieved by heating a deaerated solution of the α-disulfone (0.04 M) in bromobenzene at 138 °C for 6 h. A slow stream of nitrogen was passed through the solution throughout the decomposition in order to sweep out sulfur dioxide as it was formed, and the large amount of sulfur dioxide liberated (1.6 mmol/mmol of 2) was determined by passing the exit gas stream through a trap containing standard iodine solution and measuring the amount of I_2 remaining at the end of the decomposition. Chromatography of the nonvolatile residue remaining after in vacuo removal of the bromobenzene solvent gave bibenzyl (0.41 mmol/mmol of 2) and dibenzyl sulfone (0.12 mmol/mmol of 2) as identifiable products.

The kinetics of the thermal decomposition of 2 in bromobenzene was followed by monitoring the rate of evolution of sulfur dioxide by using a technique (see Experimental Section) that has proved reliable in the past[3] for following the kinetics of decompositions where significant quantities of SO_2 are liberated. Plots of log $(1 - SO_2/SO_{2\infty})$ vs. time were nicely linear, showing that the thermal decomposition of 2 exhibits first-order kinetics. Their slope, the experimental first-order rate constant (k_1), was independent of initial concentration of 2. The results of the various kinetic runs are summarized in Table I. The dependence of k_1 on temperature indicates that $\Delta H^{\ddagger} = 37.8$ kcal/mol and $\Delta S^{\ddagger} = +17.3$ eu.

The clean first-order kinetics for the thermal decomposition of 2 is consistent with the rate-determining step of that decomposition being a unimolecular reaction of the α-disulfone. The large positive $\Delta S^{\ddagger}$ suggests this unimolecular reaction is a homolytic dissociation of 2. A heterolytic dissociation ($2 \rightarrow PhCH_2^+\ {}^-O_2SSO_2CH_2Ph$) would certainly not be expected to have a large positive $\Delta S^{\ddagger}$ in a nonpolar solvent like bromobenzene,[4] and neither would a concerted rearrangement. The formation of sizeable amounts of bibenzyl indicates that benzyl radicals are produced during the decomposition of 2, either directly or by loss of sulfur dioxide from $PhCH_2SO_2\cdot$. It thus appears that the thermal decomposition of 2, like that[1] of aryl α-disulfones (1), is a free-radical reaction involving rate-determining homolytic dissociation of the α-disulfone.

Comparison of the kinetic data for 2 in Table I with similar data[1] for the decomposition of 1 indicates that 2 decomposes about 50 times faster than 1 and that $\Delta H^{\ddagger}$ for 2 (37.8 kcal/mol) is 3 kcal/mol less than that for 1 (41 kcal/mol). The much faster rate, and lower $\Delta H^{\ddagger}$, for the thermal decomposition of 2 as compared to 1 brings to mind the rate behavior of the decompositions of *tert*-butyl peresters, RC(O)OOBu-*t*.[6] In the homolysis of such peresters those, like $PhCH_2C(O)OOBu$-*t*, where R, as R·, is a resonance-stabilized radical decompose by a mechanism (eq 2) where there is concerted cleavage of *both* the R–C(O) and O–O bonds in the rate-determining step, while those, like $CH_3C(O)OOBu$-*t* or $PhC(O)OOBu$-*t*, where R· would not be resonance-stabilized decompose considerably more slowly by a mechanism (eq 3) in which *only* the O–O bond is cleaved in the rate-determining step.[6]

$$PhCH_2CO_2OBu\text{-}t \xrightarrow[\text{determining}]{\text{rate}} [PhCH_2\cdots CO_2\cdots OBu\text{-}t] \rightarrow PhCH_2\cdot + CO_2 + t\text{-}BuO\cdot \qquad (2)$$

$$PhCO_2OBu\text{-}t \xrightarrow[\text{determining}]{\text{rate}} [PhCO_2\cdots OBu\text{-}t] \rightarrow PhCO_2\cdot + \cdot OBu\text{-}t \qquad (3)$$

The concerted mechanism has a significantly lower $\Delta H^{\ddagger}$ than the mechanism where only the O–O bond is cleaved in the rate-determining step. However, $\Delta S^{\ddagger}$ for the concerted mechanism is less positive than $\Delta S^{\ddagger}$ for eq 3, and this partially offsets the rate acceleration provided by the lower $\Delta H^{\ddagger}$. Bartlett and Hiatt[6] suggested that the reason $\Delta S^{\ddagger}$ is less positive is because the concerted mechanism requires restrictions to rotation about certain bonds in the transition state that are not required when only the O–O bond is being cleaved in the rate-determining step. Pryor and Smith[7] have subsequently pointed out that, while the insights of Bartlett and Hiatt[6] are useful when treated as qualitative trends, one should not attempt to use relationships between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for perester and other peroxide homolyses to assign the *exact* number of bonds undergoing cleavage, or the number about which rotation is restricted, in the rate-determining transition state.

To gain further insight into whether concerted homolysis of more than one bond in the rate-determining step could

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[4] In 90% dioxane reactions of the type $RX \rightarrow R^+X^-$ generally have entropies of activation of the order of −20 eu;[5] $\Delta S^{\ddagger}$ for a process of this type should be *at least* this negative in bromobenzene.

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