Addition of Dichlorocarbene to Diethyl Methylsodiomalonate

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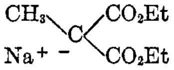
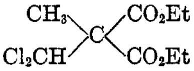
The formation of diethyl dichloromethylmethylmalonate (II) from diethyl methylsodiomalonate (I) in the reaction with chloroform or from the thermal decomposition of sodium trichloroacetate in the presence of this carbanion suggests this product arises from a carbene precursor. The mechanistic implications are discussed.

Following the kinetic demonstration by Hine[1] showing that the basic hydrolysis of chloroform proceeds through dichlorocarbene, many reactions have been reported in which this intermediate has been postulated.[2] The electrophilic nature of bivalent carbon species is substantiated in their reactions with olefins,[3] amines[4] and alkoxide ions.[5] The reaction of bivalent carbon species with carbanions has been postulated in several reactions.[6] Pentene-1 was formed when methylene chloride was added to an ethereal solution of *n*-butyllithium.[6a] It has been suggested that this product arises from addition of chlorocarbene to *n*-butyllithium to yield 1-chloro-*n*-amyllithium, which undergoes α-elimination to form the olefin by way of a hydride transfer. The synthesis of cyclopropenes from the reaction of propenyllithium derivatives with methylene chloride has been suggested as arising from the reaction of the lithio compound with chlorocarbene followed by α-elimination of the chloride ion to yield a vinylcarbene, which then undergoes cyclization to a cyclopropene.[6b] Other nucleophilic organo-lithium compounds such as *t*-butyllithium have been reported[6c] to yield olefins and cyclopropanes on reaction with chlorocarbene, the latter being formed by intramolecular insertion. The reaction of phenylsodium with methyl chloride yields ethylbenzene, *n*-propylbenzene, and isopropylbenzene, which are postulated as arising from the addition of the carbanion to carbene, CH_2.[6d] Kirmse[6e] reports the reaction of alkyllithio compounds with chloroform.

In order to obtain some preliminary information on the reaction of bivalent carbon species with "active" methylene and methinyl groups on conversion to their respective carbanions, the reaction of diethyl methylsodiomalonate (I) with dichlorocarbene was investigated.

The reaction of chloroform with carbanions derived from several monosubstituted malonate esters has been investigated by Kötz and Zörnig.[7] In the case of diethyl methylmalonate, on conversion to I the reaction with chloroform is reported to yield as one of the products a compound formulated as diethyl dichloromethylmethylmalonate, II. In order to elucidate the mechanism of formation of II, a study of this reaction was performed.


I


II

Results

To obtain evidence for the possible intermediacy of dichlorocarbene, the sodium salt of diethyl methylmalonate (I) was prepared in dry 1,2-dimethoxyethane, and to this solution there was added an equivalent amount of sodium trichloroacetate (known to undergo thermal decomposition to dichlorocarbene).[8] The resulting solution was refluxed for two hours and on filtration followed by fractional distillation there was obtained in 34% yield a fraction which was subsequently shown to be of structure II. The infrared spectrum of this fraction was identical in all respects to the fraction of the same boiling range obtained in 30% yield from the reaction of the sodium salt I with chloroform following the procedure of Kötz and Zörnig.[7] In the reaction with chloroform a 40% yield of diethyl methylmalonate was also obtained. Since the original structural assignment of II rested solely on elemental analysis, a more rigorous structural proof was considered desirable.

The interesting behavior of the diester, on saponification, shows that the structure originally proposed is indeed correct. On saponification of the diester II with aqueous ethanolic potassium hydroxide followed by acidification, there was obtained a compound identified as *trans*-β-chloro-

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(1) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

(2) For a recent carbene review, see: W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

(3) (a) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 5430 (1956); (b) W. v. E. Doering and Wm. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958); (c) W. v. E. Doering and P. Laflamme, *ibid.*, **78**, 5447 (1956).

(4) (a) M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960) and references cited therein; (b) A. P. Krapcho, *J. Org. Chem.*, **27**, 1089 (1962).

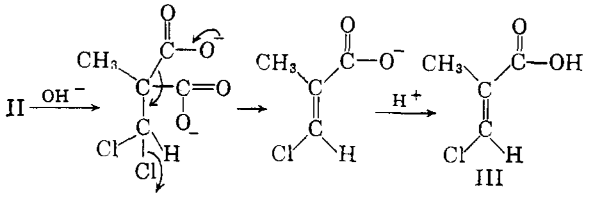
(5) (a) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960); (b) P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959); (c) J. Hine, E. L. Pollitzer and H. Wagner, *ibid.*, **75**, 5607 (1953).

(6) (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4 996 (1959); (b) G. L. Closs and L. E. Closs, *ibid.*, **83**, 1003 (1961); (c) G. L. Closs, presented before the Organic Section of the American Chemical Society, Sept. 1960, page 9; (d) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **82**, 5758 (1960); (e) W. Kirmse, *Angew. Chem.*, **73**, 540 (1961).

(7) A. Kötz and W. Zörnig, *J. prakt. chem.*, **182**, 425 (1906).

(8) (a) W. M. Wagner, *J. Chem. Soc.*, 229 (1959); (b) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

methacrylic acid, III.[9] An authentic sample of this acid was prepared according to the procedure described by Bieber,[10] which consisted of the addition of chlorine to methyl methacrylate and the dehydrohalogenation of this dichloro adduct with alcoholic potassium hydroxide. The infrared spectra of the acids obtained from either route were identical. The formation of the *trans*-chloro acid from II can be rationalized by the following sequence:



The facile loss of carbon dioxide and chloride ion is supported by the fact that the decomposition of salts of β-haloacids is known to proceed quite readily in many cases.[11] The stereospecific nature of this process can readily be rationalized by steric considerations for elimination at the transition state.[12] The general applicability of this reaction to synthetic pursuits of substituted *trans*-β-halo α-substituted acrylic acids is of some interest.

By utilizing bromoform in the reaction with carbanion I the dibromo compound corresponding to II was isolated in 20% yield and on treatment with alcoholic potassium hydroxide was converted into *trans*-β-bromomethacrylic acid, the structure of which was confirmed by infrared comparison with an authentic sample of this acid prepared according to procedure described by Bieber.[10]

Discussion

The formation of II during the thermal decomposition of sodium trichloroacetate in the presence of I is highly suggestive of dichlorocarbene addition to I. The nucleophilic carbanion should readily attack the electrophilic dichlorocarbene and the anion thus formed is immediately protonated. The result can be rationalized in the following mechanistic route:

(1) $CCl_3CO_2Na \xrightarrow{\text{heat}} CCl_3^-Na^+ + CO_2$

(2) $CCl_3^-Na^+ \longrightarrow CCl_2 + NaCl$

(3) $R^-Na^+(I) + CCl_2 \longrightarrow RCCl_2^-Na^+$

(4) $RCCl_2^-Na^+ + \text{Moisture or unchanged RH} \longrightarrow II$

Step 3 is similar to the previously suggested nucleophilic additions to bivalent carbon species.[6]

The formation of II from chloroform (or the corresponding dibromo derivative from bromoform) is also consistent with a carbene mechanism. Closs reports the intermediacy of dichlorocarbene in the reaction of *n*-butyllithium with chloroform (trapped by cyclohexene).[13] The formation of dichlorocarbene from chloroform on reaction with alkoxide ions is well substantiated.[3-5] The carbanion I in the reaction with chloroform can function both as a base (proton abstraction) and a nucleophilic addendum leading to the formation of II. This bears resemblance to the reaction of *n*-butyllithium with methylene chloride to yield 1-pentene.[6a] The formation of II in the reaction of I with chloroform can be rationalized in the following steps:

(1) $R^-Na^+(I) + CHCl_3 \longrightarrow RH + CCl_3^-Na^+$

(2) $CCl_3^-Na^+ \longrightarrow CCl_2 + NaCl$

(3) $R^-Na^+(I) + CCl_2 \longrightarrow RCCl_2^-Na^+$

(4) $RCCl_2^-Na^+ + \text{RH or } CHCl_3 \text{ or } H^+ \text{ in work-up} \longrightarrow II$

Experimental

All melting points (capillary tubes) and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 recording spectrometer.

Reaction of Diethyl Methylsodiomalonate with Sodium Trichloroacetate.—Sodium metal (3.0 g., 0.13 g.-atom) was added to 80 ml. of dry 1,2-dimethoxyethane (distilled from lithium aluminum hydride). Diethyl methylmalonate (20.0 g., 0.12 mole) was added all at once. A vigorous evolution of hydrogen resulted and on stirring for 4 hr. a yellow-brown solution was obtained. Sodium trichloroacetate (22.0 g., 0.12 mole) was added and complete solution resulted. The mixture was refluxed with stirring for 2 hr. during which time a tan solid precipitated. The mixture was cooled and filtered and the residual solid (weight 15 g.) was washed with ether. The brown-black filtrate was concentrated on a Rinco evaporator. The residue was distilled through a Nester-Faust spinning band column and gave a small forerun (2.0 g.) followed by 11.0 g. (34%) of diethyl dichloromethylmethylmalonate (II), b.p. 86–88° (1.5 mm.). A redistilled sample had b.p. 76–77° (0.7 mm.). The vapor phase chromatographic analysis utilizing a 20% Dow 11 Silcone-firebrick column showed only trace amounts of impurities.

Anal. Calcd. for $C_9H_{14}O_4Cl_2$: C, 42.03; H, 5.49; Cl, 27.58. Found: C, 42.30; H, 5.70; Cl, 27.89.

Reaction of Diethyl Methylsodiomalonate with Chloroform.[7]—Sodium (3.0 g., 0.13 g.-atom) was added to anhydrous diethyl ether (50 ml.). Diethyl methylmalonate (23.0 g., 0.13 mole) was added all at once. A vigorous evolution of hydrogen occurred and the reaction was allowed to proceed overnight with stirring and refluxing. A few specks of unchanged sodium were removed and the ether was removed by distillation under reduced pressure. A solid remained which was evacuated with an oil pump to remove the last traces of ether. Chloroform (20.0 g., 0.16 mole) was added and on gentle warming the mixture became yellow and an exothermic reaction occurred. After the exothermic reaction subsided the mixture was refluxed for 1 hr. during which a brown solid precipitated. Water was added and the mixture was acidified with dilute sulfuric acid. The mixture was extracted with ether, the ethereal extracts dried over anhydrous sodium sulfate, and the ethereal solution concentrated on the Rinco evaporator. The residue was distilled

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(9) A. F. Ferris and I. G. Marks, *J. Org. Chem.*, **19**, 1971 (1954).

(10) P. Bieber, *Bull. soc. chim., France*, 199 (1954).

(11) S. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 632 (1953), and references cited therein.

(12) D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, ed., J. Wiley and Sons, Inc., New York, 1956, p. 273.

(13) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

through a Nester-Faust spinning band column to yield 9.0 g. of diethyl methylmalonate (40%), b.p. 43–54° (0.8 mm), and 11.0 g. of diethyl dichloromethylmethylmalonate (33%), b.p. 73–75° (0.5 mm.). A dark pot residue remained (4.0 g.). The infrared spectrum of the dichloro fraction was identical in all respects to that of the fraction formed in the sodium trichloroacetate run listed above.

Reaction of Diethyl Methylsodiomalonate with Bromoform.—The reaction was performed as in the chloroform run listed above. Sodium (2.0 g., 0.09 g.-atom), 100 ml. of anhydrous diethyl ether, and 17.0 g. (0.10 mole) of diethyl methylmalonate were utilized. On removal of the ether, bromoform (33.0 g., 0.13 mole) was added and on gentle warming a vigorous exothermic reaction occurred. The mixture was refluxed for 1 hr. and then filtered from the solid which separated. The mixture was concentrated under reduced pressure and distilled through the spinning band column to yield 8.0 g. of bromoform (26% recovery), b.p. 25–36° (3.5 mm.); 5.0 g. diethyl methylmalonate (30%), b.p. 57–65° (2.5 mm.); and 6.0 g. (20%) of diethyl dibromomethylmethylmalonate, b.p. 105–107° (2 mm.). A redistilled fraction had b.p. 105–107° (2 mm.). A dark pot residue remained.

Anal. Calcd. for $C_9H_{14}O_4Br_2$: C, 31.06; H, 4.05. Found: C, 31.40; H, 4.37.

Saponification of Diethyl Dichloromethylmethylmalonate.—Diethyl dichloromethylmethylmalonate (II) (9.0 g., 0.035 mole) was added to a potassium hydroxide (7.0 g., 0.125 mole) solution in 60 ml. of 95% ethanol and 20 ml. of water. The solution was allowed to reflux overnight. The ethanol and water were removed by distillation under reduced pressure and the pasty solid which resulted was extracted once with ether. The residue was dissolved in ice water and acidified with dilute sulfuric acid. A solid precipitated which was filtered and dried. The solid was dissolved in hot acetonitrile and was filtered to remove insoluble salts. On cooling in the freezer (−20°), 3.0 g. (71%) of *trans*-β-chloromethacrylic acid was obtained of m.p. 57–58°, lit. m.p. 57–58°.[9]

Anal. Calcd. for $C_4H_5O_2Cl$: C, 39.85; H, 4.18; Cl, 29.42. Found: C, 39.99; H, 3.85; Cl, 29.47.

The infrared spectrum and mixed melting point were identical to those of an authentic sample of *trans*-β-chloromethacrylic acid prepared according to the procedure described by Bieber.[10]

Saponification of Diethyl Dibromomethylmethylmalonate.—The reaction was run as in the saponification above. A 63% yield of *trans*-β-bromomethacrylic acid was obtained of m.p. 63.0–64.0°, lit. m.p. 64.5–65.0°.[10] The infrared spectrum and the mixed melting point were identical to those of an authentic sample of this acid prepared according to Bieber's procedure.[10] The analytical sample was crystallized from acetonitrile.

Anal. Calcd. for $C_4H_5O_2Br$: C, 29.12; H, 3.05; Br, 48.44. Found: C, 29.44; H, 3.28; Br, 48.27.

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Dehydration of Alcohols in Dimethyl Sulfoxide[1,2]

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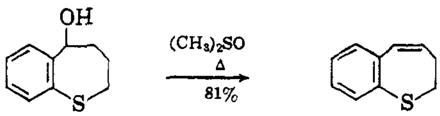
When *sec*- and *tert*-benzylic alcohols or *tert*-aliphatic alcohols were heated in dimethyl sulfoxide at 160–185° for nine to sixteen hours, dehydration produced olefins in 70–85% yield. The direction and stereochemistry of this elimination are reported, and based on these data a mechanism is offered. In general the suggested path involves carbonium ions.

In recent years several interesting reports have appeared in the literature describing new reactions and applications of dimethyl sulfoxide.[4] Among these was a paper by Searles and Hays[5] in which they describe the formation of simple sulfoxides by heating the corresponding sulfide in dimethyl sulfoxide. When 5-hydroxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin (I) was treated under these conditions, instead of a sulfoxide 2,3-dihydrobenzo[*b*]thiepin (II) was formed. In this report we wish to describe a number of examples of this dehydration and comment on the course of this reaction.



I II

The general experimental conditions involved heating one mole of the alcohol in four to eight moles of dimethyl sulfoxide at 160–185° for nine to sixteen hours. When low boiling olefins were products, these distilled during the reaction and were collected in an appropriate trap, while the high boiling olefins were conveniently isolated by dilution of the reaction mixture with water, extraction with petroleum ether followed by distillation. In addition to compound I, the other alcohols dehydrated by this procedure are listed in Table I. The resulting olefins were identified by physical constants, infrared spectra, and in some cases by conversion to solid dibromides.

The dehydration of α-phenethyl alcohol in dimethyl sulfoxide gave styrene which under the

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(2) Presented in part at the 138th Meeting of the American Chemical Society at New York City, New York, in September, 1960.

(3) Smith, Kline and French Foundation Fellow, 1959–1960.

(4) For a review of the literature see "Technical Information on Dimethyl Sulfoxide" issued by Crown Zellerback Corp.

(5) S. Searles, Jr., and H. R. Hays, *J. Org. Chem.*, **23**, 2028 (1958).