The Thermal Decarboxylation of Sodium Trichloroacetate in the Presence of Active Hydrogen and Halogen Compounds

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The thermal decomposition of sodium trichloroacetate in aprotic media yields the CCl_3^- ion.

$$CCl_3CO_2^- \longrightarrow CO_2 + CCl_3^-$$

Evidence for the carbanion can be found by performing decomposition in the presence of carbonyl compounds, from which the products formed by the addition of the CCl_3^- to the carbonyl group can be isolated.[2] The decomposition product of CCl_3^-, $:CCl_2$, has been trapped in the presence of olefins.[2] More recently it has been shown that the thermal decomposition leads to α,β-elimination of halogen ions from perchloro compounds with formation of carbon tetrachloride.[3] This recent publication prompts us to report the results of our investigation, underway for some time, of the decomposition of sodium trichloroacetate in the presence of active hydrogen and halogen compounds.

In an initial experiment it was found that good yields of the sodium salt of tetraethyl propene-1,1,3,3-tetracarboxylate (I) could be obtained when sodium trichloroacetate was thermally decomposed in the presence of diethyl malonate with 1,2-dimethoxyethane as solvent. In this case the role of the CCl_3^- was to abstract a proton from diethyl malonate to yield chloroform and the sodium salt of diethyl malonate. The presence of chloroform was ascertained by vapor phase chromatographic analysis of the reaction mixture. The formation of the sodium salt I can then be readily rationalized by the mechanistic route previously proposed.[4]

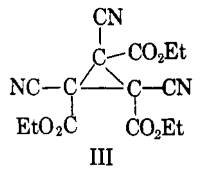
This result led us to investigate the synthetic utility of the CCl_3^- ion formed under these conditions with regard to its ability to abstract a proton or a halogen atom from a substrate to generate a new carbanion, which might then undergo a subsequent reaction. The thermal decomposition was studied in the presence of several monohalo and dihalo derivatives of diethyl malonate and ethyl cyanoacetate. The results of this study are recorded in Table I.

$(CO_2Et)_2C{=}CH{-}\bar{C}(CO_2Et)_2Na^+$

I

$(CO_2Et)_2C{=}C(CO_2Et)_2$

II



III

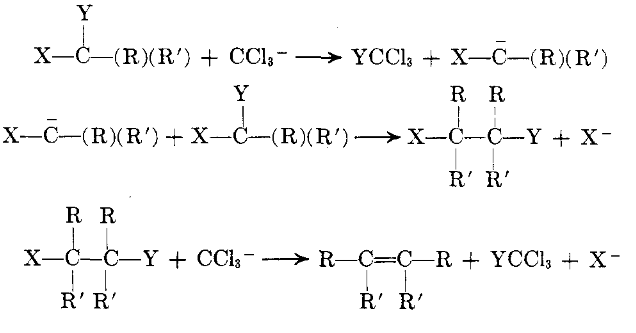
TABLE I

PRODUCTS OBTAINED FROM THE SODIUM TRICHLOROACETATE DECOMPOSITIONS

Compound[a]	Product	Yield, %	Reaction period, hr.	Haloform[c]
$H_2C(CO_2Et)_2$[b]	I	55	0.5	$CHCl_3$
$HCBr(CO_2Et)_2$	II	42	0.5	$CHCl_3$[d]
$HCCl(CO_2Et)_2$	II	30	12	$CHCl_3$
$Br_2C(CO_2Et)_2$	II	66	1	$CBrCl_3$[d]
$Br_2C(CN)(CO_2Et)$	III	53	12	. . .
$BrCH(CN)(CO_2Et)$	III	50	1	. . .

[a] All runs were performed in refluxing 1,2-dimethoxyethane using equimolar quantities of reactants except where noted. No attempt was made to optimize reaction conditions. [b] A 2:1 molar ratio of sodium trichloroacetate to diethyl malonate. [c] The crude reaction mixture was analyzed by v.p.c. [d] Small amounts of carbon tetrachloride were present in the reaction mixture and arise from the reaction reported by Wagner.[5]

The data presented in Table I indicate that the CCl_3^- functions as a proton or "positive" halogen abstractor. Other basic reagents yield II in the reaction with diethyl monochloro-, monobromo-, and dibromomalonate.[6] The products can be rationalized by the subsequent reactions of the carbanion which is formed. These observations are consistent with the mechanistic sequence that is depicted in the following scheme



$$X{-}\overset{Y}{\overset{|}{C}}{-}(R)(R') + CCl_3^- \longrightarrow YCCl_3 + X{-}\bar{C}{-}(R)(R')$$

$$X{-}\bar{C}{-}(R)(R') + X{-}\overset{Y}{\overset{|}{C}}{-}(R)(R') \longrightarrow X{-}\underset{R'}{\overset{R}{C}}{-}\underset{R'}{\overset{R}{C}}{-}Y + X^-$$

$$X{-}\underset{R'}{\overset{R}{C}}{-}\underset{R'}{\overset{R}{C}}{-}Y + CCl_3^- \longrightarrow R{-}\underset{R'}{C}{=}\underset{R'}{C}{-}R + YCCl_3 + X^-$$

where X = Br or Cl, Y = H, R = CO_2Et, R′ = CO_2Et or CN: X = Y = Br, R = CO_2Et, R′ = CO_2Et or CN.

The formation of III can be explained by the further reaction of the initially formed ethylene system (R = CO_2Et, R′ = CN) with the anion formed in the first step to yield an anion which then undergoes intramolecular displacement of the bromide ion. Felton[7] reports the formation of III from the reaction of ethyl dibromocyanoacetate with the sodium salt of ethyl cyanoacetate.

The application of this method of forming CCl_3^- in neutral, aprotic media is of potential value for performing other reactions of the type reported here.

Experimental

A. Sodium Salt of Tetraethyl Propene-1,1,3,3-tetracarboxylate (I).—To a solution of diethyl malonate (4.0 g., 0.025 mole) in 50 ml. of 1,2-dimethoxyethane, sodium trichloroacetate (9.4 g., 0.050 mole) was added and the solution was refluxed for 30 min. On cooling, yellow crystals commenced to separate. The supernatant liquid was analyzed by v.p.c. using a 12-ft. column of 20% Ucon Polar on firebrick in an Aerograph Model A-90-P instrument. The chromatogram indicated about 8% of chloroform in the solvent (calculated from the chromatogram peak areas and uncorrected). The mixture was heated and the hot mixture was filtered. The filtrate was partially concentrated, and the solution

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[1] Fellow, National Defense Education Act.

[2] W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. trav. chim.* **80**, 740 (1961).

[3] W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *ibid.*, **81**, 925, 933 (1962).

[4] A. P. Krapcho, P. S. Huyffer, and I. Starer, *J. Org. Chem.*, **27**, 3096 (1962).

[5] W. M. Wagner, H. Kloosterziel, S. van der Ven, and A. F. Bickel, *Rec. trav. chim.*, **81**, 947 (1962).

[6] For a summary see "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 275.

[7] D. G. I. Felton, *J. Chem. Soc.*, 515 (1955).

was placed in the freezer (−20°). The crystalline material which separated was collected (3.0 g.) and recrystallized from acetonitrile to yield 2.3 g. (55% yield) of the pure salt. The infrared spectrum was identical to that of an authentic sample of this salt.[4]

B. Tetraethyl Ethylenetetracarboxylate (II).—The following reaction illustrates a typical procedure, and the pertinent data for the other reactions can be found in Table I.

A solution of diethyl dibromomalonate (8.0 g., 0.025 mole) and sodium trichloroacetate (4.7 g., 0.025 mole) in 25 ml. of 1,2-dimethoxyethane was refluxed under a nitrogen atmosphere for 1 hr. The v.p.c. analysis of the mixture using a 12-ft. column of 20% tritolyl phosphate on chromosorb W indicated the presence of 2% carbon tetrachloride and 10% bromotrichloromethane in the solvent (raw data). The precipitated salt was filtered from the hot solution and washed with ether. The solvent was removed *in vacuo* and an ethanol–hexane mixture (20 ml.) was added to the resultant red oil. After standing in the freezer overnight, pale yellow crystals separated. Recrystallization from ethanol–hexane yielded 2.6 g. (66% yield) of the pure product of m.p. 52–53° (lit.[6] m.p. 52–53°).

C. Triethyl 1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate (III).—Ethyl bromocyanoacetate (10 g., 0.05 mole) and sodium trichloroacetate (9.7 g., 0.05 mole) were refluxed in 50 ml. of 1,2-dimethoxyethane under a nitrogen atmosphere for 1 hr. The solid (3.0 g.) was filtered from the hot solution and washed with hot solvent. The filtrate was concentrated to a red oil. Ethanol (15 ml.) was added and the mixture was allowed to stand in the freezer overnight. The crystalline solid was collected (3.5 g., 50% yield) and had m.p. 122–123° (lit. m.p. 122–123°). The infrared spectrum was identical to that of an independently prepared sample.[7]

The ethyl dibromocyanoacetate run was performed in the same manner using a longer reflux period.

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Reaction of Octaphenylcyclotetrasilane with Mercuric Acetate

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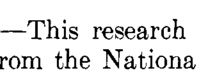
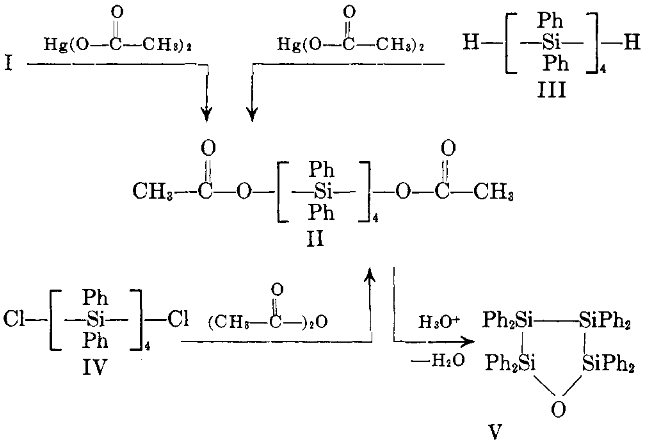
Among the compounds isolated by Kipping from the reaction of dichlorodiphenylsilane with sodium, was a material which he designated as compound "A".[1] In order to explain the high reactivity of this compound in free radical-type reactions, he assigned to Compound "A" a biradical structure (...$SiPh_2SiPh_2SiPh_2SiPh_2$...).[1,2] However, this compound has recently been shown to be octaphenylcyclotetrasilane (I).[3] The high reactivity



I

of I has been attributed to the strained four-membered ring system. For example, I is readily cleaved by certain metal[4] and nonmetal[5] halides, halogens,[3b,6] organometallic compounds,[7] and by numerous polyhalo-organic compounds.[6] In addition, I was found to reduce an ethanolic silver nitrate solution at room temperature.[5] A similar reduction previously has been reported for the strained ring compounds, 1,1,3,3-tetramethyl-1,3-disilacyclobutane.[8] Under the same conditions, we obtained no observable reduction with decaphenylcyclopentasilane.[9]

We now wish to report the cleavage of I by mercuric acetate to give 1,4-diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane (II). An alternate synthesis of II was achieved by heating 1,1,2,2,3,3,4,4-octaphenyltetrasilane (III)[10] and mercuric acetate in glacial acetic acid.[11] In addition, II was obtained by refluxing the previously described 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane (IV)[2b,3] in acetic anhydride.[12] Further proof of structure was obtained by hydrolysis of II to the monoxide V.[13]



The infrared and n.m.r. spectra of II also were examined and found to be in agreement with the proposed structure.

When either hexaphenyldisilane or decaphenylcyclopentasilane[9] was treated with mercuric acetate under even more forcing conditions, the starting materials were recovered in good yields. Under such conditions where silicon–silicon bond cleavage is not observed, it may be possible to employ mercuric acetate to effect nuclear substitution.[14]

Experimental[15]

1,4-Diacetoxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane (II). From Octaphenylcyclotetrasilane (I) and Mercuric Acetate.—Fifteen grams (0.02 mole) of octaphenylcyclotetrasilane and 13.1 g. (0.041 mole) of mercuric acetate in *ca.* 150 ml. of sodium-dried benzene were heated at reflux for 24 hr. A small amount of mercury was observed on the bottom of the flask. The tan mixture was cooled and filtered. Evaporation of the solvent gave 16.62 g. (95.8%) of a light yellow solid, m.p. 212–234°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) gave 13.1 g. (79%) of a white solid, m.p. 233–235°.

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(1) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830, 848 (1921).

(2) (a) F. S. Kipping, *ibid.*, **123**, 2590 (1923); (b) **125**, 2291 (1924).

(3) (a) H. Gilman, D. J. Peterson, A. W. P. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *ibid.*, **83**, 1921 (1961).

(4) H. Gilman and A. W. P. Jarvie, *Chem. Ind.* (London), 965 (1960).

(5) W. H. Atwell, unpublished studies.

(6) J. M. Kraemer, unpublished studies.

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(10) H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **27**, 254 (1962).

(11) For similar reactions of this type see B. N. Polgov, N. P. Kharitanov, and M. G. Voronkov, *Zh. Obshch. Khim.*, **24**, 861 (1954); *Chem. Abstr.*, **49**, 8094 (1955).

(12) For a general method see N. S. Nametkin, A. V. Topchiev, and F. F. Machus, *Dokl. Akad. Nauk, SSSR*, **87**, 233 (1952); *Chem. Abstr.*, **47**, 12,281 (1953).

(13) A. W. P. Jarvie, H. J. S. Winkler, and H. Gilman, *J. Org. Chem.*, **27**, 614 (1962).

(14) K. A. Kobe and P. F. Lueth, Jr., *Ind. Eng. Chem.*, **34**, 309 (1942).

(15) All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen and all melting points are uncorrected.