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Decarboxylation Reaction. VIII.[1] Reaction of Electron-deficient Carbon-Carbon Double Bonds with Trichloroacetic Acid. A Unique 1,1-Dichlorocyclopropane Formation through β-Trichloromethylation

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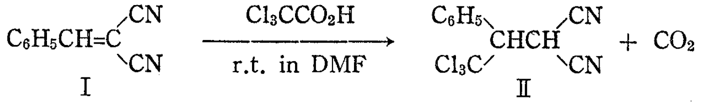
The present paper describes the 1,1-dichlorocyclopropane formation from highly electron-deficient carbon-carbon double bonds conjugated, in the main, with two cyano groups by allowing to react with trichloroacetic acid. β-Trichloromethylation was indicated in some cases. Path of the 1,1-dichlorocyclopropane formation is presumed not to involve dichlorocarbene, but β-trichloromethylated intermediate.

Keywords——decarboxylation reaction; trichloromethylation; trichloroacetic acid; alkylidenemalononitrile; 1,1-dichlorocyclopropane

The preceding communication[1] describes a finding of a new decarboxylation reaction of trichloroacetic acid with electron-deficient carbon-carbon double bonds conjugated, in the main, with two cyano groups leading to the 1,1-dichlorocyclopropane formation. We now wish to disclose the details of this work with some extensive studies.

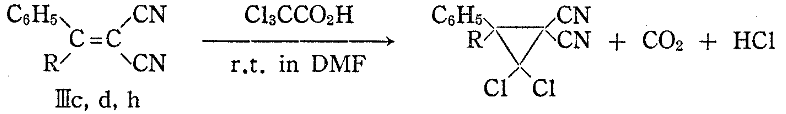
Preliminary examination involves experiments of the reaction of benzylidenemalononitrile (I) and its derivatives, $C_6H_5C(R)=C(CN)_2$ (IIIc: $R=CH_3$, IIId: $R=CH_3CH_2$, IIIh: $R=C_6H_5CH_2$), with trichloroacetic acid in DMF at room temperature. The reaction of I was shown to result in the formation of (α-trichloromethyl)benzylmalononitrile (II) in 71% yield. The reactions of IIIc, d, h were markedly distinguished from the above reaction resulting in the formation of 1,1-dichlorocyclopropane derivatives, IVc, d, h.



$$C_6H_5CH{=}C(CN)_2 \xrightarrow[\text{r.t. in DMF}]{Cl_3CCO_2H} C_6H_5CH(CCl_3)CH(CN)_2 + CO_2$$

I II

yield: 71%



$$C_6H_5C(R){=}C(CN)_2 \xrightarrow[\text{r.t. in DMF}]{Cl_3CCO_2H} \text{IVc, d, h} + CO_2 + HCl$$

IIIc, d, h IVc, d, h

yield: IVc ($R=CH_3$), 20%; IVd ($R=CH_3CH_2$), 36%; IVh ($R=C_6H_5CH_2$), 40%

In search for better reaction conditions for the 1,1-dichlorocyclopropane formation from IIId we found that the reaction was promoted in the presence of triethylamine. Effect of a number of solvents on the yield of the IVd was examined and results are summarized in Table I. Thus, much better yield (62—64%) of IVd was obtained by allowing to react in tetrahydrofuran (THF) or ether solvent in the presence of triethylamine. The same treatment of I with trichloroacetic acid in the triethylamine–THF medium, however, resulted in the formation of a resinous material, and a similar result was obtained in treatment of II in the triethylamine–THF medium.

The 1,1-dichlorocyclopropane formation by the reaction with trichloroacetic acid in the

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[1] Part VII: K. Nanjo, K. Suzuki, and M. Sekiya, *Chem. Lett.*, **1977**, 553.

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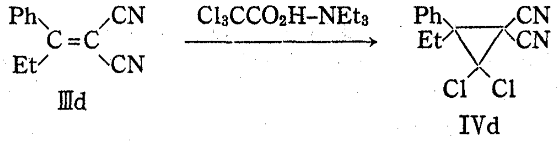
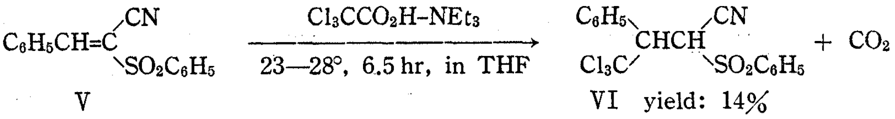
Table I. Reaction of 1-Phenylpropylidenemalononitrile with Trichloroacetic Acid in Various Solvent



Solvent	Reaction temperature (°C)	Reaction time (hr)	Yield (%)
CCl_4	26—27	4.0	37.7
Dioxane	25	5.0	45.3
THF	25—26	5.0	62.3
Ether	36	2.5	64.1
Anisole	26—27	6.5	32.0
DMF	11—16	2.5	45.3
Ethyl Acetate	25—28	5.5	24.5
t-BuOH	45—46	3.5	30.2

Substrate: 0.1 mol; trichloroacetic acid: 0.03 mol; triethylamine: 0.03 mol; solvent: 20 ml.

triethylamine–THF (or ether) system was extended by the uses of a variety of the substrates possessing electron-deficient carbon-carbon double bonds conjugated with two cyano groups and with both cyano and other electron-withdrawing group, COC_6H_5, CO_2Et or $SO_2C_6H_5$. Results are summarized in Table II. The following experiments do not result in the 1,1-dichlorocyclopropane formation resulting in the β-trichloromethylation.



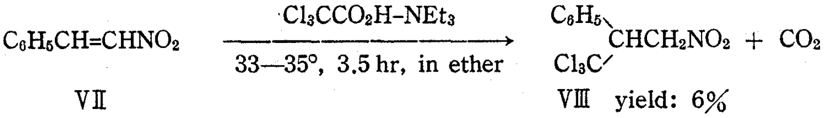
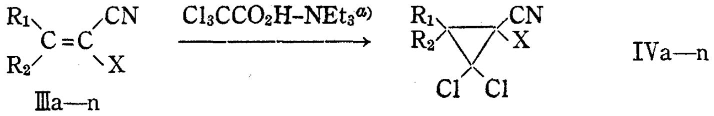


Table II. Reaction of Carbon-Carbon Double Bonds conjugated with Cyano, Carbonyl and Sulfonyl Groups with Trichloroacetic Acid

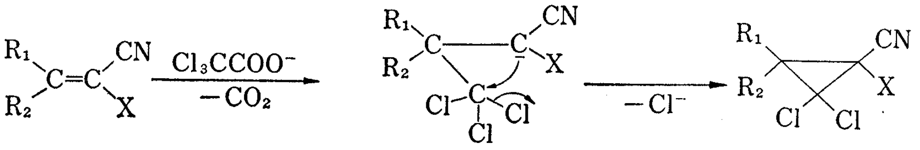


Compd. No.	R_1	R_2	X	Solvent	React. temp. (°C)	React. time (hr)	Yield (%)
IIIa	Ph	H	CO_2Et	Ether	23—28	3.5	21
IIIb	Ph	H	COPh	THF	25—28	6.5	13
IIIc	Ph	CH_3	CN	THF	12—13	9.0	32
IIId	Ph	C_2H_5	CN	THF	25—26	5.0	62
IIIe	Ph	C_2H_5	CO_2Et	THF	25—26	5.0	4
IIIf	Ph	C_2H_5	SO_2Ph	THF	25—26	10.0	0[b)]
IIIg	Ph	Ph	CN	THF	10—15	10.0	39
IIIh	Ph	$PhCH_2$	CN	Ether	34—36	3.0	46
IIIi	$CH_2(CH_2)_3CH_2$		CN	Ether	34—36	4.5	74
IIIj	$CH_2(CH_2)_3CH_2$		CO_2Et	Ether	35—36	5.5	0[b)]
IIIk	$CH_2(CH_2)_2CH_2$		CN	THF	30—35	3.5	60
IIIl	C_2H_5	$CH_3(CH_2)_2CH_2$	CN	THF	24—28	5.5	78
IIIm	C_2H_5	C_2H_5	CN	Ether	33—35	5.0	53
IIIn	$(CH_3)_2CH$	H	CN	THF	24—29	7.5	44

a) Molar Ratio; Substrate: Cl_3CCO_2H: NEt_3=1: 3: 3.
b) Starting material was recovered.

The obtained data shown in Table II indicate scope and limitation of the 1,1-dichlorocyclopropane formation. The reaction exceedingly proceeded in the uses of the highly electron-deficient carbon-carbon double bonds conjugated with two cyano groups, and when other groups are introduced in place of one of cyano groups, their reactivities are in the order, $CN > CO_2Et > SO_2C_6H_5$, as realized in the runs with IIId, IIIe, and IIIf in Table II.

Although the 1,1-dichlorocyclopropane formation from olefin involving the dichlorocarbene intermediate have been dealt in many papers,[3] the present reaction is characterized by the occurrence only in the case of highly electron-deficient carbon-carbon double bonds. There is no evidence to support the dichlorocarbene intermediate, since under similar reaction conditions, cyclohexene and 1-cyanocyclohexene did not give the corresponding 7,7-dichloronorcaranes, and no reaction occurred on replacement of trichloroacetic acid by chloroform. In view of the formation of the β-trichloromethylated products in certain cases, the β-trichloromethylation seems very likely as an intermediate course in the 1,1-dichlorocyclopropane formation. The 1,1-dichlorocyclopropane formation *via* β-trichloromethylation may depend upon the structure of the conjugated olefins. Although the structural factor responsible for the β-trichloromethylation are not clear, the following path may be plausible for the 1,1-dichlorocyclopropane formation. Trichloroacetate ion may attack at β-carbon to form β-trichloromethylated anion with a concomitant decarboxylation and an internal nucleophilic substitution of the anion leads to the 1,1-dichlorocyclopropane formation with the leave of a chlorine anion.



Identities of the 1,1-dichlorocyclopropanes and the β-trichloromethylated compounds obtained in the present work were made by noting well correspondences of their micro analytical data, infrared (IR) and nuclear magnetic resonance (NMR) data, and in certain cases, molecular weight data measured by the vapor-phase osmometric (V. P. O.) method.

Experimental[4]

Materials——All the compounds, I, IIIa—IIIn and V were prepared by condensation of the corresponding aldehydes or ketones and active methylene compounds using both ammonium acetate and acetic acid as catalysts, in a manner similar to the method reported by Cope *et al.*[5] I: colorless needles (MeOH), mp 82—84° (lit.[6] mp 83.5—84°), IIIa: prisms (EtOH), mp 46—47° (lit.[7] mp 51°), IIIb: colorless pillars (EtOH), mp 83—84° (lit.[8] mp 85°), IIIc: colorless prisms (MeOH), mp 93—95° (lit.[9] mp 93—94°), IIId: colorless prisms (EtOH), mp 68—69° (lit[9] mp 69—70°), IIIe: colorless oil, bp 122—130°/1 mmHg (lit.[10] bp 138—140°/2 mmHg), IIIf: colorless oil. *Anal.* Calcd. for $C_{17}H_{15}NO_2S$: C, 68.67; H, 5.08; N, 4.71. Found:

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4) All melting points and boiling points are uncorrected. IR spectra were recorded on a Hitachi EPI-G2 spectrophotometer. NMR spectra were taken with a Hitachi R-24 spectrophotometer (at 60 MHz). Chemical shift values are given in δ (ppm) relative to tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet.

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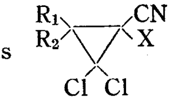
TABLE III. Physical and Analytical Data of the 1,1-Dichlorocyclopropanes



R_1	R_2	X	Appearance (Recryst. solv.)	mp(°C) or bp(°C/mmHg)	Formula	Analysis (%) Calcd. (Found)			IR ν_{max} cm^{-1}				NMR (δ)
						C	H	N	CN	CO	Cyclopropane ring		
Ph	H	CO_2Et	Colorless oil		$C_{13}H_{11}$-Cl_2NO_2	52.96 (53.25)	4.07 (3.97)	5.13 (4.93)	2240	1750	1030	855	1.40 (3H, t, $C\underline{H}_3CH_2-$, $J=8.0$ Hz), 3.95 (1H, s, $-CH\langle$), 4.40 (2H, q, $CH_3C\underline{H}_2-$, $J=8.0$ Hz), 7.35 (5H, s, C_6H_5)
Ph	H	COPh	Colorless prisms (*n*-hexane)	123—125	$C_{17}H_{11}$-Cl_2NO	64.58 (64.50)	3.51 (3.55)	4.43 (4.46)	2220	1695	1030	855	4.80 (1H, s, $-CH\langle$), 7.37 (5H, s, C_6H_5), 7.48—8.15 (5H, m, C_6H_5CO)
Ph	CH_3	CN	Colorless prisms (*n*-hexane)	118—119	$C_{12}H_8$-Cl_2N_2	57.39 (57.26)	3.21 (3.20)	11.16 (11.24)	2230		1020	830	1.90 (3H, s, CH_3-), 7.46 (5H, s, C_6H_5)
Ph	CH_3CH_2	CN	Colorless prisms (*n*-hexane)	85—87	$C_{13}H_{10}$-Cl_2N_2[a]	58.87 (58.72)	3.77 (3.77)	10.57 (10.45)	2240		1027	855	1.00 (3H, t, $C\underline{H}_3CH_2-$, $J=8.0$ Hz), 2.18 (2H, q, $CH_3C\underline{H}_2-$, $J=8.0$ Hz)
Ph	Ph	CN	Colorless prisms (EtOH)	167—168	$C_{17}H_{10}$-Cl_2N_2	65.20 (65.08)	3.22 (3.20)	8.94 (8.90)	2240		1030	865	7.13—7.60 (10H, m, two C_6H_5)
Ph	$PhCH_2$	CN	Colorless prisms (*n*-hexane)	120—120.5	$C_{18}H_{12}$-Cl_2N_2	66.07 (66.09)	3.70 (3.70)	8.50 (8.62)	2240		1025	850	3.44 (2H, s, $C_6H_5C\underline{H}_2-$), 6.72—7.35 (10H, m, two C_6H_5)
$CH_2(CH_2)_3CH_2$		CN	Colorless needles (*n*-hexane)	77—79	$C_{10}H_{10}$-Cl_2N_2	52.42 (52.51)	4.40 (4.45)	12.23 (12.36)	2240		1010	860	1.44—2.10 (10H, m, cyclohexyl)
$CH_2(CH_2)_2CH_2$		CN	Colorless plates (*n*-hexane)	88—89	C_9H_8-Cl_2N_2	50.20 (50.16)	3.75 (3.72)	13.02 (12.96)	2230		1030		1.78—2.23 (8H, m, cyclopentyl)
CH_3CH_2	$CH_3(CH_2)_2CH_2$	CN	Colorless oil	131/0.2	$C_{11}H_{14}$-Cl_2N_2	53.89 (54.23)	5.76 (5.79)	11.43 (11.40)	2240		1015	860	0.77—2.15 (14H, m, alkyl protons)
CH_3CH_2	CH_3CH_2	CN	Colorless prisms	35—36	C_9H_{10}-Cl_2N_2	49.79 (49.82)	4.64 (4.58)	12.90 (12.93)	2240		1020	860	1.14 (6H, t, $C\underline{H}_3CH_2-$, $J=8.0$ Hz), 1.96 (4H, q, $CH_3C\underline{H}_2-$, $J=8.0$ Hz)
$(CH_3)_2CH$	H	CN	Colorless prisms (*n*-hexane)	53.5—54.5	C_8H_8-Cl_2N_2	47.32 (47.02)	3.97 (3.93)	13.80 (13.70)	2240		1005	850	1.20 (6H, d, $(C\underline{H}_3)_2CH-$, $J=8.0$ Hz), 1.41—2.10 (1H, m, $(CH_3)_2C\underline{H}-$), 2.26 (1H, d, $-CH\langle$, $J=10.0$ Hz)
Ph	CH_3CH_2	CO_2Et	Colorless prisms (*n*-hexane)	77—78	$C_{15}H_{15}$-Cl_2NO_2	57.71 (57.84)	4.84 (4.85)	4.49 (4.52)	2240	1745	1010	855	0.86 (3H, t, $C\underline{H}_3CH_2-$, $J=8.0$ Hz), 1.42 (3H, t, $C\underline{H}_3CH_2CO-$, $J=7.0$ Hz), 1.90—2.30 (2H, m, $CH_3C\underline{H}_2-$), 4.39 (2H, q, $CH_3C\underline{H}_2CO-$, $J=7.0$ Hz)

a) Mol. Wt., Calcd.: 264.9; Found: 259 (V.P.O. method).

C, 69.06; H, 5.23; N, 4.55. IIIg: colorless needles (EtOH), mp 137—138° (lit.[9] mp 140—141°), IIIh: colorless needles (EtOH), mp 80—81° (lit.[11] mp 80—81°), IIIi: colorless liquid, bp 113°/4 mmHg (lit.[12] bp 137—138°/10 mmHg), IIIj: colorless oil, bp 105—106°/0.08 mmHg (lit.[13] bp 150—151°/13 mmHg), IIIk: colorless liquid, bp 111°/5 mmHg (lit.[14] bp 137°/10 mmHg), IIIl: colorless liquid, bp 129—130°/15 mmHg (lit.[14] bp 109—110°/4 mmHg), IIIm: colorless liquid, bp 78—79°/3 mmHg (lit.[15] bp 150°/19 mmHg), IIIn: colorless liquid, bp 58°/3 mmHg (lit.[16] bp 38—41°/0.4 mmHg), V: colorless prisms (AcOH), mp 133—134° (lit.[17] mp 140°). 1-Cyanocyclohexene and VII were prepared according to the methods described in the literature cited. 1-Cyanocyclohexene: colorless liquid, bp 56—61°/3 mmHg (lit[18] bp 77—87°/12 mmHg), VII: pale yellow needles (EtOH), mp 56—57° (lit.[19] mp 57—58°).

Reaction of I and IIIc, d, h with Trichloroacetic Acid in DMF——To a solution of 0.01 mol of the substrate in 20 ml of DMF, 4.9 g (0.03 mol) of trichloroacetic acid was added in small portions with stirring at room temperature. Dry air free from CO_2 was introduced in order to check evolution of CO_2 by a $Ba(OH)_2$ solution. The stirring was continued at room temperature until evolution of CO_2 almost ceased. Then, the reaction solution was poured into 80 ml of ice-water and a liberated oily material was extracted twice with benzene. The benzene extracts combined were washed with water and dried over anhydrous $MgSO_4$. After removal of benzene, the residual oily material was chromatographed on silica gel. Using *n*-hexane–chloroform as an eluent the β-trichloromethylated II was obtained from I in 71% yield. II: colorless oil. *Anal.* Calcd. for $C_{11}H_7Cl_3N_2$: C, 48.30; H, 2.58; N, 10.24; mol. wt., 273.6. Found: C, 48.58; H, 2.61; N, 10.24; mol. wt. wt. (V. P. O. method), 275. IR $\nu_{\max}^{\text{liq}}$ cm^{-1}: 2260 (CN). NMR ($CDCl_3$) δ: 4.22 (d, 1H, $-CH<$, $J=4.5$ Hz), 4.82 (d, 1H, $-CH<$, $J=4.5$ Hz), 7.30—7.70 (m, 5H, C_6H_5). By the chromatography using *n*-hexane–benzene as an eluent IVc, d, h was obtained from IIIc, d, h in 20%, 36% and 40% yield, respectively. Spectral and analytical data of IVc, d, h are listed in Table III.

Reaction of IIId with Trichloroacetic Acid in the Presenece of Triethylamine (Solvent Effect in Table I)——To a stirring solution of 1.8 g (0.01 mol) of IIId and 3.0 g (0.03 mol) of triethylamine in 20 ml each of the solvents (see Table I), a solution of 4.9 g (0.03 mol) of trichloroacetic acid in 10 ml of the same solvent was added at ice bath temperature and the reaction solution was then warmed to the temperature effecting considerable evolution of CO_2. After the evolution of CO_2 almost ceased, the solvent was evaporated under reduced pressure except in the use of DMF. The resulting residue was extracted with benzene. In the use of DMF, the reaction solution was poured into ice-water and a liberated oily material was extracted with benzene. The benzene solution was washed with water and dried over anhydrous $MgSO_4$. After removal of benzene, chromatography of the residual oil gave IVd in the yields shown in Table I.

Reaction of IIIa—IIIn, V and VII with Trichloroacetic Acid in the Presence of Triethylamine——To a stirring solution of 0.01 mol each of IIIa—IIIn, V or VII and 3.0 g (0.03 mol) of triethylamine in 20 ml of THF or ether, a solution of 4.9 g (0.03 mol) of trichloroacetic acid in 10 ml of the same solvent was added at ice bath temperature, and the reaction solution was then warmed to the appropriate temperature (see Table II). Dry air free from CO_2 was introduced in order to check evolution of CO_2 by a $Ba(OH)_2$ solution. After the evolution of CO_2 almost ceased, the solvent was evaporated under reduced pressure. The resulting residue was extracted with benzene. The benzene solution was washed with water and dried over anhydrous $MgSO_4$. After removal of benzene, the resulting residue was submitted to chromatography on silica gel using *n*-hexane–benzene as an eluent. IIIa—IIIn gave the corresponding 1,1-dichlorocyclopropane derivatives, IVa—IVn and, V and VII gave β-trichloromethylated products, VI and VIII, respectively. Physical and analytical data of IVa—IVn were shown in Table III and those of VI and VIII were as follows. VI: colorless oil, yield, 14%. *Anal.* Calcd. for $C_{16}H_{20}Cl_3NO_2S$: C, 49.42; H, 3.09; N, 3.06. Found: C, 49.86; H, 3.20; N, 3.54. IR $\nu_{\max}^{\text{liq}}$ cm^{-1}: 2240 (CN), 1345, 1155 ($SO_2<$). NMR ($CDCl_3$) δ: 4.65 (d, 1H, $-CH<$, $J=2.0$ Hz), 5.00 (d, 1H, $-CH<$, $J=2.0$ Hz), 7.18—7.75 (m, 10H, two C_6H_5). VIII: colorless crystals, mp 64—66°, yield, 6%. *Anal.* Calcd. for $C_9H_8Cl_3NO_2$: C, 40.26; H, 3.00; N, 5.22. Found: C, 40.49; H, 2.98; N, 5.31. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1560 (NO_2). NMR ($CDCl_3$) δ: 4.52—4.88 (m, 1H, $-CH<$), 5.09—5.51 (m, 2H, $-CH_2-$), 7.43 (s, 5H, C_6H_5).

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