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DECARBOXYLATION REACTION VII.[1] REACTION OF α-ALKYLIDENEMALONONITRILES WITH TRICHLOROACETIC ACID. A NEW 1,1-DICHLOROCYCLOPROPANE FORMATION THROUGH β-TRICHLOROMETHYLATION

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It has been found that highly electron-deficient carbon-carbon double bond conjugated, in the main, with two cyano groups undergoes 1,1-dichlorocyclopropane formation by reacting with trichloroacetic acid. This reaction is presumed not to involve dichlorocarbene, but trichloromethylated intermediate.

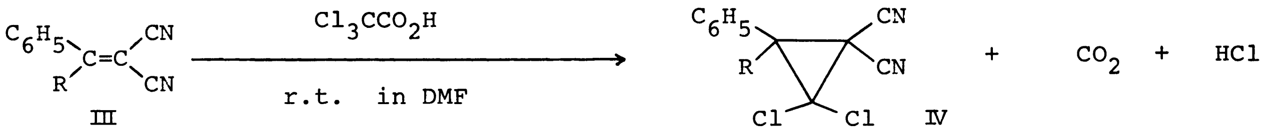
In an earlier paper,[2] it was reported that cyanoacetic acid, malonic acid and acetoacetic acid induce the Michael type addition to conjugated carbon-carbon double bonds adjacent to carbonyl or cyano group with simultaneous decarboxylation. In conjunction with this work, the present paper describes a new decarboxylation reaction of trichloroacetic acid with highly electron-deficient carbon-carbon double bonds conjugated, in the main, with two cyano groups, leading to dichlorocyclopropane formation.

It was observed that, by allowing trichloroacetic acid to react with benzylidenemalononitrile in N,N-dimethylformamide at room temperature, (α-trichloromethylbenzyl)malononitrile was obtained in a good yield. This product is a liquid material, Found: C, 48.58; H, 2.61; N, 10.24%; mol wt (V.P.O. method), 275. Calcd for $C_{11}H_7Cl_3N_2$: C, 48.30; H, 2.58; N, 10.24%; mol wt, 273.6. 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).

$$\underset{\text{I}}{C_6H_5CH{=}C\begin{matrix}CN\\CN\end{matrix}} \xrightarrow[\text{r.t. in DMF}]{Cl_3CCO_2H} \underset{\text{II}}{\begin{matrix}C_6H_5\\Cl_3C\end{matrix}CHCH\begin{matrix}CN\\CN\end{matrix}} + CO_2$$

yield: 71 %

In contrast to this fact, the reactions of α-alkyl-substituted benzylidenemalononitriles under similar conditions gave dichlorocyclopropane derivatives.



Yield: R=CH_3, 20 %; R=C_2H_5, 36 %; R=$C_6H_5CH_2$, 40 %

Better reaction conditions for the dichlorocyclopropane formation by the reaction of 1-phenylpropylidenemalononitrile (III, R=C_2H_5) have been investigated. Thus, much better yield (62-64 %) of 1,1-dichloro-2,2-dicyano-3-phenyl-3-ethylcyclopropane (IV, R=C_2H_5) was obtained by allowing to react in THF or ether solvent in the presence of triethylamine. The procedure is as follows. After a solution of 4.9 g (0.03 mol) of trichloroacetic acid in 10 ml of THF was added to a solution of 1.8 g (0.01 mol) of III (R=C_2H_5) and 3.0 g (0.03 mol) of triethylamine in 20 ml of THF at ice bath temperature, the stirred mixture was warmed to 25-30°C. The progress of the reaction was followed by passing dry air free from CO_2 through the reaction flask into $Ba(OH)_2$ solution. After the evolution of carbon dioxide almost ceased, the solvent was evaporated under reduced pressure and the residue was extracted with benzene. The benzene extract was washed with 3N-HCl, then with water and dried over anhydrous $MgSO_4$. After removal of benzene the residual oil was submitted to vacuum distillation to give a distillate, bp 114-116°C/0.15 mmHg, which was composed of dichlorocyclopropane and the starting nitrile. This distillate was chromatographed on silica gel using hexane-benzene (10/3) as an eluent. Crystals (1.65 g, 62 %) of IV (R=C_2H_5) was obtained in addition to recovery of III (R=C_2H_5). Recrystallization from n-hexane gave colorless prisms, mp 85-87°C. Found: C, 58.72; H, 3.77; N, 10.41%; mol wt (V.P.O. method), 259. Calcd for $C_{13}H_{10}N_2Cl_2$: C, 58.87; H, 3.77; N, 10.57%; mol wt, 264.9. IR ν_{max}^{KBr} cm^{-1}: 2240 (CN), 1027 (cyclopropane ring). NMR ($CDCl_3$) δ: 1.00 (t, 3H, $-CH_2\underline{CH_3}$, J=8.0 Hz), 2.18 (q, 2H, $-\underline{CH_2}CH_3$, J=8.0 Hz), 7.40 (s, 5H, C_6H_5).

The process by trichloroacetic acid-triethylamine has been successfully extended to the syntheses of 1,1-dichloro-2,2-dicyanocyclopropanes from a variety of α-alkylidenemalononitrile, as shown in Table 1. The same treatment of I with trichloroacetic acid in the triethylamine-THF medium, however, resulted in the formation of a resinous material, which was the same result as was observed in the case of the treatment of the trichloromethylated product, II, in the triethylamine-THF medium.

Control experiments by the use of the compounds $C_6H_5C(C_2H_5)=C(CN)X$, in which X=CN, CO_2Et, SO_2Ph, exhibited the following order of reactivities (values in parentheses are yields of dichlorocyclopropanes): $C_6H_5C(C_2H_5)=C(CN)_2$ (62 %) > $C_6H_5C(C_2H_5)=C(CN)CO_2Et$ (4 %) > $C_6H_5C(C_2H_5)=C(CN)SO_2Ph$ (0 %). Consequently, reactive substrate should have highly electron-deficient unsaturated β-carbon conjugated with two electron-withdrawing groups such as cyano group. There was no evidence to support 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. The present dichlorocyclopropane formation is therefore essentially diffrent from the previously reported ones involving dichlorocarbene intermediate.[3)] β-Trichloromethylated intermediate seems to be very likely in view of the isolation of II, although this compound is converted easily into a resinous product under basic conditions. A plausible mechanism may be written as in the following scheme.

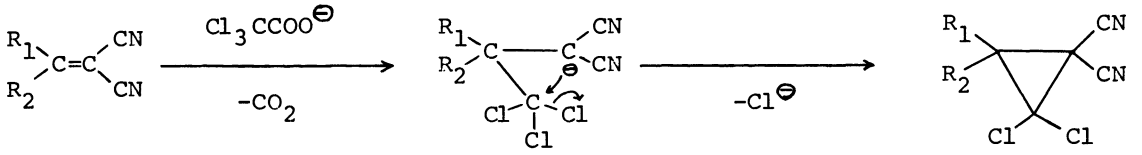
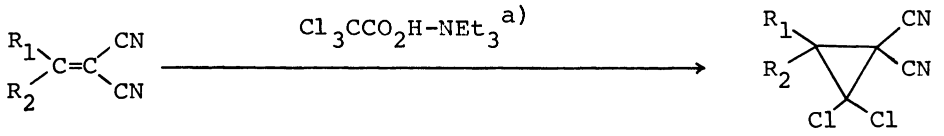


Table 1 A Novel Synthesis of 1,1-Dichloro-2,2-dicyanocyclopropanes



R_1	R_2	Solvent	Reaction Temp. (°C)	Reaction Time (hr)	Yield (%)
C_6H_5	$C_6H_5CH_2$	ether	34-36	3.0	46
$CH_2(CH_2)_3CH_2$		ether	34-36	4.5	74
CH_3CH_2	CH_3CH_2	ether	33-35	5.0	53
$CH_2(CH_2)_2CH_2$		THF	30-35	3.5	60
H	$(CH_3)_2CH$	THF	24-29	7.5	44
CH_3CH_2	$CH_3(CH_2)_2CH_2$	THF	24-28	5.5	78

a) molar ratio; Substrate:Cl_3CCO_2H:NEt_3=1:3:3

References

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3) W. E. Parham and E. E. Schweizer, "Organic Reactions", vol. 13, edited by A. C. Cope, John Wiley & Sons, Inc., New York, 1963, p55-90.

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