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(18) Fellow of the Alfred P. Sloan Foundation, 1977–1979.

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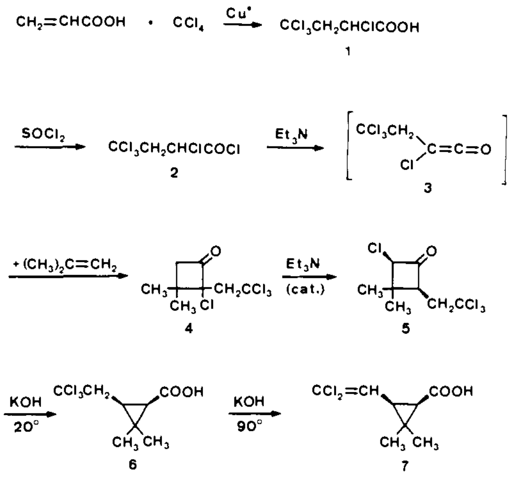
A Simple, Stereoselective, Highly Versatile Synthesis of Dichlorovinylcyclopropanecarboxylic Acids via 2-Chlorocyclobutanones[1]

Sir:

Recent years have seen a rapid growth in the synthetic work on pyrethroids, a class of compounds structurally related to the naturally occurring chrysanthemates.[2] Pyrethroids in general possess high insecticidal activity[3] while showing low mammalian toxicity.[4] Among modern pyrethroids, the ester of halovinylcyclopropanecarboxylic acids were found to be the most promising insecticides owing to their extraordinarily high potency and considerably increased photostability compared with those of the esters of chrysanthemic acid.[3] Consequently, there have been numerous synthetic approaches to the most important precursor, 2,2-dimethyl-3-(2′,2′-dichlorovinyl)-cyclopropane-1-carboxylic acid (**7**).[5,6]

Scheme I



All synthetic strategies to **7** published to date suffer from some serious disadvantages, e.g., a large number of synthetic steps, dangerous reagents or uneconomic processes. We now report a short, conceptually unprecedented synthesis of **7**. We believe that the underlying reactions may also have synthetic implications outside the pyrethroid field.

The copper(I)-catalyzed addition of CCl_4 to acrylic acid (0.05 molar equiv of Cu_2Cl_2, CH_3CN, 140 °C, 4.5 h) followed by treatment of the tetrachlorobutanoic acid (**1**) thus formed with thionyl chloride gave the acid chloride **2** in 76% yield (bp 79 °C (11 mm))[7] (Scheme I). The key 2-chlorocyclobutanone **4**[8] was formed by the [2 + 2] cycloaddition of isobutylene with chlorotrichloroethylketene (**3**), produced in situ from **2** (NEt_3, cyclohexane, 65 °C, 7 h, 67%). The efficient novel isomerization **4** → **5** was achieved using a catalytic amount of triethylamine (0.05 molar equiv, toluene, 120 °C, 15 h). The 4-chlorocyclobutanone **5**, isolated in 90% yield, was the thermodynamically preferred[9] 2,4-cis isomer,[10] **5** readily underwent the Favorskii rearrangement affording either **6**[11] as an 80:20 cis-trans mixture (2 molar equiv of NaOH, H_2O, 25 °C, 4 h, 89%)[12] or under subsequent HCl elimination (NaOH, H_2O, 100 °C, 6 h)—with or without the isolation of **6**—the desired acid **7**[14] in 82% yield with the same stereochemical preference (80;20) for the biologically more interesting cis isomer. Once formed, **6** and **7** proved to be entirely stable to stereoisomerization under alkaline reaction conditions.

From the synthetic point of view several noteworthy features follow: (a) the new *chlorotrichloroethylketene* **3** gives even higher yields of [2 + 2] cycloadducts than one of the most reactive ketene known so far, dichloroketene,[15] and it is the synthetic equivalent of the considerably less reactive chloro-2,2-dichlorovinylketene;[19] (b) a large variety of cyclobutanones of type **4** can readily be prepared using 1,1-dialkyl-substituted ethylenes $R_1R_2C{=}CH_2$ in place of isobutylene; and (c) the "*cine rearrangement*"[20] (e.g., **4** → **5**) proved to be a very useful synthetic reaction providing an excellent new entry into cyclopropanecarboxylic acids of type **7** (2-R_1,2-R_2 = alkyl instead of 2,2-dimethyl) via their precursors of type **5**, which would not be readily accessible by alternative methods.[21]

Acknowledgment. We thank Dr. E. Steiner for valuable assistance and Dr. T. Winkler for his help with NMR problems.

References and Notes

(1) This work was reported at the International Symposium on Chemistry of the Pyrethroids, Oxford, July 16–19, 1979, and at the 1st European Symposium on Organic Chemistry, Cologne, August 20–23, 1979. Synthesis and Reactivity of Compounds with Cyclobutane Ring(s). 13. For 12 see Greuter, H.; Winkler, T.; Belluš, D. *Helv. Chim. Acta* **1979,** *62*, 1275.

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(4) E.g., the ratio of average toxicities of organochlorine compounds to insects vs. mammals is 91, whereas that of pyrethroids is 4500.[3]

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(6) **7** is the acid moiety of the pyrethroids NRDC-143 or Permethrin (ester with 3-phenoxybenzyl alcohol) and NRDC-149 or Cypermethrin (ester with (±)-α-cyano-3-phenoxybenzyl alcohol).[3]

(7) **2**: IR ($CHCl_3$) ν 1790 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 3.28 (dd, J = 4 and 16 Hz, H_a C_3), 3.82 (dd, J = 7.5 and 16 Hz, H_b C_3), 5.09 (dd, J = 4 and 7.5 Hz, H C_2).

(8) **4**: mp 75–76 °C; IR ($CHCl_3$) ν 1805 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 1.42 (s, CH_3), 1.45 (s, CH_3), 3.00 and 3.14 (AB, J = 16 Hz, H_2 C), 3.45 and 3.60 (AB, J = 16 Hz, CH_2 CCl_3); ^{13}C NMR ($CDCl_3$) δ 196.6 (s, C_1), 95.3 (s, CCl_3), 80.8 (s, C_2), 57.0 and 56.4 (2t, $2CH_2$), 37.9 (s, C_3), 25.1 and 23.8 (2q, $2CH_3$).

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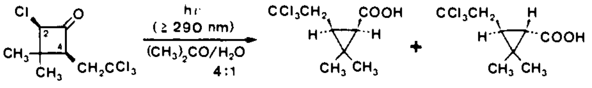
(10) **5**: mp 56–57 °C; IR ($CHCl_3$) ν 1795 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 1.14 and 1.63 (2s, $2CH_3$), 2.87 (dd, J = 6 and 15 Hz, H_aC CCl_3), 3.15 (dd, J = 4 and 15 Hz, H_bC CCl_3), 3.47 (m, J = 2, 4, and 6 Hz, H C_4), 4.76 (d, J = 2 Hz, H C_2); ^{13}C NMR ($CDCl_3$) δ 197.0 (s, C_1), 97.8 (s, CCl_3), 69.4 (d, C_2), 60.6 (d, C_4), 49.5 (t, CH_2CCl_3), 36.8 (s, C_3), 27.4 (q, CH_3 trans), 18.6 (q, CH_3 cis).

(11) After separation on silica gel (hexane–ether). *cis*-**6**: mp 92–93 °C; IR ($CHCl_3$) ν 1695 cm^{-1} (CO); ^1H NMR (360 MHz, $CDCl_3$) δ 1.23 and 1.26 (2s, $2CH_3$), 1.60 (ddd, J = 5, 7, and 9 Hz, H C_2), 1.69 (d, J = 9 Hz,[12] H C_1), 3.00 (dd, J = 7 and 15 Hz, CH_a CCl_3), 3.15 (dd, J = 5 and 15 Hz, CH_b CCl_3); ^{13}C NMR ($CDCl_3$) δ 178.5 (COO), 99.8 (CCl_3), 49.2 (CH_2 CCl_3), 30.6 and 28.7 (C_2 and C_1), 28.6 (*r*-1-CH_3 trans), 26.5 (C_3), 14.7 (*r*-1-CH_3 cis). *trans*-**6**: mp 132–133 °C; IR ($CHCl_3$), ν 1695 cm^{-1} (CO); ^1H NMR (360 MHz, $CDCl_3$) δ 1.23 and 1.32 (2s, $2CH_3$), 1.48 (d, J = 5.5 Hz,[12] H C_1), 1.85 (br q with J = 6.5 Hz, H C_2), 2.70 (dd, J = 6.5 and 14.5 Hz, CH_a CCl_3), 2.86 (dd, J = 6.5 and 14.5 Hz, CH_b CCl_3); ^{13}C NMR ($CDCl_3$) δ 178.5 (COO), 99.0 (CCl_3), 53.4 (CH_2 CCl_3), 32.5 and 30.7 (C_1 and C_2), 28.0 (C_3), 22.0 (*r*-1-CH_3 trans), 20.4 (*r*-1-CH_3 cis).

(12) Since no photo-Favorskii rearrangement of an α-halocycloalkanone[13] leading to a carboxylic acid has yet been described, it is worth mentioning that the photo-Favorskii rearrangement **5** → **6** exhibits a lower degree of retention of configuration than the base-induced rearrangement. Thus the irradiation of an 80% acetone–water (v:v) solution of 2,4-*cis*-**5** (125-W high-pressure Hg lamp, Pyrex, 20 °C, 44 h) afforded a 1:2 mixture of cis and trans isomers of **6** in 97% yield. Since **6** does not absorb above 290 nm, no isomerization was observed when an acetone–water solution of either *cis*- or *trans*-**6** was irradiated through Pyrex glass.



5 cis-6 trans-6

(13) Examples of photo-Favorskii rearrangement of α-chloro ketones in methanol have been reported: (a) Kaplan, B. E.; Hartwig, A. L. *Tetrahedron Lett.* **1970,** 4855. (b) Givens, R. S.; Strekowski, L. *J. Am. Chem. Soc.* **1975,** *97*, 5867. (c) Jones, G., II; McDonnell, L. P. *Ibid.* **1976,** *98*, 16203.

(14) For melting point and ^1H NMR of both stereoisomers of **7**, see: M. Elliott, *Pestic. Sci.* **1974,** *5*, 791.

(15) For comparison, the following yields of [2 + 2] cycloadducts were found using **3** or dichloroketene (both generated in situ by dehydrohalogenation of the corresponding acid chlorides by NEt_3): with methylenecyclobutane, 49 and 33%,[16] respectively; with cyclopentadiene, 89 and 77%,[17] respectively; with indene, 58 and 48%,[18] respectively.

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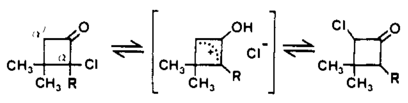
(19) Chloro(2,2-dichlorovinyl)ketene, prepared in situ from 2,4,4-trichlorobut-3-enoic acid chloride, gives the [2 + 2] cycloadduct with isobutylene in only 17% yield.

(20) The name "*cine rearrangement*" is used here with reference to "*cine substitution*", a commonly used term for α' substitution of α-halocyclobutanones by external nucleophiles (Nu ≠ halogen). Cf. Conia, J. M.; Robson, M. J. *Angew. Chem.* **1975,** *87*, 505, and references cited therein. The distribution of products of the "cine rearrangement" was found to depend on the nature of the second α substituent. These product distributions, which are found starting from either i or iii, indicate a transition state with a high degree of ionic character, e.g., ion pair ii (cf. Bordwell, F. G.; Carlson, M. W. *J. Am. Chem. Soc.* **1970,** *92*, 3377), since the α substitution by electron-withdrawing groups such as CH_2CCl_3 or Cl clearly destabilizes the positive charge in the α position of the allyl cation, thus directing the chlorine anion into the α' position and vice versa. We should note here, that the "cine rearrangement" is not restricted to α-chlorocyclobutanones. 2-Bromo-2-(2′,2′,2′-tribromoethyl)-3,3-dimethylcyclobutanone readily underwent (HBr, EtOH, 70 °C) catalyzed rearrangement to give 4-bromo-2-(2′,2′,2′-tribromoethyl)-3,3-dimethylcyclobutanone. The latter compound is a convenient precursor for the biologically very active *cis*-2,2-dimethyl-3-(2′,2′-dibromovinyl)cyclopropane-1-carboxylic acid esters.[3]



i ii iii

	i	iii
R = CH_2CCl_3	0%	100%
R = Cl	0%	100%
R = CH_3	57%	43%
R = $(CH_2)_2CH(CH_3)_2$	15%	85%

(21) From the economic point of view, it is noteworthy that in the present synthesis of **7** only cheapest and readily available substances are used; e.g., triethylamine represents the most expensive substance used in a molar equivalent amount!

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Selection of Nonprotonated Carbon Resonances in Solid-State Nuclear Magnetic Resonance

Sir:

Procedures that simplify NMR spectra are important when studying complex molecules, especially when resonance assignments result from the physical basis of a selection process. Among the most useful spectroscopic techniques of high resolution ^{13}C NMR of liquids is the application of weak modulated proton decoupling to selectively broaden those resonances from carbons with directly bonded protons;[1] additional manipulations[2,3] result in a carbon spectrum with narrow lines from only the nonprotonated carbons. This communication describes a method for obtaining the analogous nonprotonated carbon spectrum for solid samples where the signals from carbons with attached protons are suppressed.

In both solids and liquids the much stronger ^{13}C–^1H interaction for carbons with bonded protons is utilized for selection of the nonprotonated carbons. However, the heteronuclear spin interactions that are effective are different in the two cases: with scalar spin-spin coupling operative in liquids and static dipole-dipole coupling in both amorphous and polycrystalline solids.

Proton-enhanced NMR[4] is combined with magic angle sample rotation[5] to give natural abundance ^{13}C spectra of complex molecules in the solid state. The strongest spin in-

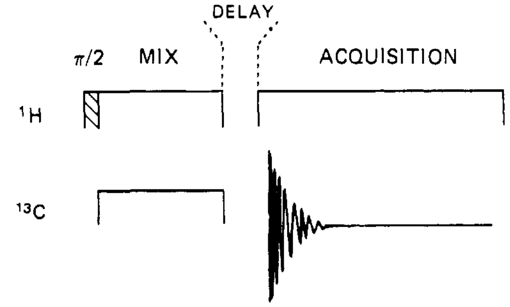

Figure 1. Pulse sequence used to suppress signals from protonated carbons in solid samples. $\pi/2$ represents the initial 90° ^1H pulse. The mix period consists of a long ^1H irradiation that is phase shifted 90° from the initial pulse to spin lock the protons and ^{13}C irradiation that is adjusted in strength to allow magnetization transfer (see ref 4). The delay interval is without any applied radio frequency fields to allow ^{13}C spins to precess in their local ^1H dipolar fields. Proton irradiation is reapplied during the acquisition period to give decoupled carbon signals. Proton magnetization recovers in the static magnetic field during the recycle delay.

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