individual k_T values were determined at 366 nm by NMR and compared to the standard reductant in each case, as described in the text. Isooctane was the solvent for the studies with **42**-X, deuteriobenzene for TBTH and TPGH.

In a number of reductions, the solvent was removed and the products were collected by GC. In every case the expected product (C–X → C–H) was found. The yields were >90%.

Ultraviolet spectral data are collected in Table XIV. The data indicate that TBTH is the more likely initiator, rather than **1**, in those reductions not containing AIBN or DTBP.

Acknowledgment. We express our gratitude to the Dow Corning Corp. and the Loyola Research Committee for financial assistance. The several individuals to whom we are indebted for their cooperation and help are cited in appropriate references. We particularly thank Professor John F. Reed of this department for the development of eq 18 and 19.

Registry No. 1, 2344-80-1; **2**, 15267-95-5; **3**, 1833-51-8; **4**, 17067-65-1; **5**, 543-59-9; **6**, 753-89-9; **7**, 507-20-0; **8**, 13401-56-4; **9**, 13401-57-5; **9** 2,4-DNP derivative, 86392-88-3; **10**, 65870-89-5; **11**, 65870-88-4; **12**, 65870-90-8; **13**, 65870-91-9; **14**, 7787-87-3; **15**, 86392-89-4; **16**, 18162-52-2; **17**, 30608-90-3; **18**, 74128-22-6; **19**, 1719-57-9; **20**, 1558-33-4; **21**, 1558-25-4; **22**, 5926-38-5; **23**, 5181-46-4; **24**, 16709-86-7; **25**, 33558-75-7; (+)-**26**, 86392-90-7; (−)-**26**, 86393-01-3; **27**, 17336-78-6; **28**, 2344-83-4; **29**, 18243-41-9; **30**, 18156-67-7; **31**, 10545-34-3; **32**, 86392-91-8; **33**, 86392-92-9; **34**, 3121-77-5; **35**, 3439-38-1; **36**, 17336-79-7; **38**, 13959-92-7; (±)-**39**, 86392-93-0; (+)-**39**, 86393-08-0; (−)-**39**, 86393-02-4; (±)-**39** hydrogen phthalate ester, 86393-03-5; (+)-**39** hydrogen phthalate ester, 86393-06-8; (−)-**39** hydrogen phthalate ester, 86393-04-6; (+)-**39** hydrogen phthalate strychnine salt, 86393-07-9; (−)-**39** hydrogen phthalate strychnine salt, 86393-05-7; **40**, 86392-94-1; **41**-X (X = *p*-CF_3), 77491-01-1; **41**-X (X = *m*-CF_3), 779-69-1; **41**-X (X = *m*-F), 86392-95-2; **41**-X (X = *p*-Cl), 770-89-8; **41**-X (X = *p*-F), 770-90-1; **41**-X (X = *p*-*t*-Bu), 85491-13-0; **41**-X (X = *m*-CH_3), 86392-96-3; **41**-X (X = *p*-CH_3), 1833-32-5; **41**-X (X = *p*-OCH_3), 17903-46-7; **A** (X = H), 1080-43-9; **A** (X = CH_3), 1213-36-1; **A** (X = OCH_3), 61726-36-1; **A** (X = F), 23781-90-0; **A** (X = CF_3), 86393-09-1; **B** (X = H), 27490-87-5; **B** (X = CH_3), 86393-10-4; **B** (X = OCH_3), 86393-11-5; **B** (X = F), 51693-78-8; **B** (X = CF_3), 86393-12-6; **C** (X = H), 78764-88-2; **C** (X = CH_3), 86392-97-4; **C** (X = OCH_3), 86392-98-5; **C** (X = F), 86392-99-6; **C** (X = CF_3), 86393-00-2; (pyr)$H^+CrO_3Cl^-$, 26299-14-9; $ClCH_2SiHMe_2$, 3144-74-9; $PhCH_2OH$, 100-51-6; $ClsiEt_3$, 994-30-9; PhBr, 108-86-1; *p*-$CH_3C_6H_4Br$, 106-38-7; *p*-$CH_3OC_6H_4Br$, 104-92-7; *p*-FC_6H_4Br, 460-00-4; *p*-$F_3CC_6H_4Br$, 402-43-7; Me_2SnCl_2, 753-73-1; *p*-$Me_2NC_6H_4Br$, 586-77-6; TBTH, 688-73-3; AIBN, 78-67-1; DTBP, 110-05-4; dimethylchlorosilane, 1066-35-9; neohexene, 558-37-2; phthalic anhydride, 85-44-9; (−)-strychnine, 57-24-9; methyltriphenylphosphonium bromide, 1779-49-3; benzoyl peroxide, 94-36-0; galvinoxyl, 2370-18-5; hydroquinone, 123-31-9; oxygen, 7782-44-7.

Generation and Chemical Properties of Dicyclopropylcarbene. Ring Expansion, Chlorine Abstraction, C–H Insertion, and Alkene Addition Reactions

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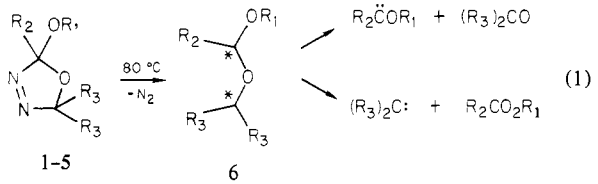
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1. *Received November 5, 1982. Revised Manuscript Received May 9, 1983*

Abstract: Thermolysis of 5,5-dicyclopropyl-2-methoxy-2-methyl-Δ^3-1,3,4-oxadiazoline in solution at 80 °C affords dicyclopropylcarbene and methyl acetate in high yields. Dicyclopropylcarbene undergoes a variety of reactions including ring expansion to 1-cyclopropylcyclobutene, chlorine atom abstraction from carbon tetrachloride, and efficient insertion into the CH bond of chloroform. A rationale for the very different reactions of the carbene with CCl_4 and $CHCl_3$ is suggested. Carbene trapping by addition to tetrachloroethylene, using the oxadiazoline as the carbene source, is illustrated with the preparation of an adduct.

Recently we reported[1,2] the thermal generation of carbenes by thermolysis of 2-substituted 2,5,5-trialkyl-Δ^3-1,3,4-oxadiazolines (**1–3**) (eq 1). The carbenes are formed from a short-lived



1-5 6 (1)

1, $R_1 = R_2 = R_3 = CH_3$
2, $R_1 = COCH_3$; $R_2 = CH_3$; $R_3 = c\text{-}C_3H_5$
3, $R_1 = COCH_3$; $R_2 = CH_2CH_3$; $R_3 = c\text{-}C_3H_5$
4, $R_1 = R_2 = CH_3$; $R_3 = c\text{-}C_3H_5$
5, $R_1 = H$; $R_2 = CH_3$; $R_3 = c\text{-}C_3H_5$

carbonyl ylide precursor (**6**) that can be trapped with methanol[1] or with dipolarophiles.[3] Fragmentation of the ylide **6** is not very selective in the case of **1–3**, which detracts from the synthetic utility of the oxadiazolines as carbene precursors.

As part of a search for oxadiazolines that fragment to only one of two possible carbenes, we synthesized **4**, and we now report that its thermolysis in solution affords dicyclopropylcarbene in about 80% yield. Some intramolecular and intermolecular reactions of that carbene are also reported.

Experimental Section

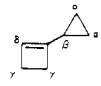
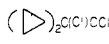
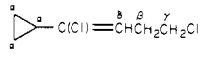
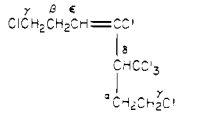
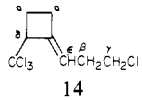
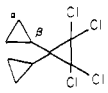
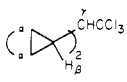
Dicyclopropyl Ketone *N*-Acetylhydrazone. A solution of dicyclopropyl ketone (11.0 g, 0.100 mol) and acetylhydrazine (7.4 g, 0.10 mol) in 95% ethanol (100 mL) containing acetic acid (2 mL) was refluxed for 30 min. Most of the solvent was distilled off, and the residue was heated at 120 °C for 3 h. The residue, which solidified on cooling, was recrystallized from acetone to give material melting at 114–115 °C in 90% yield: ^1H NMR ($CDCl_3$) δ 0.50–1.01 (m, 8 H), 1.13–1.60 (m, 2 H), 2.20 (s, 3 H). Anal. Calcd for $C_9H_{14}NO$: C, 65.03; H, 8.50; N, 16.85. Found: C, 65.00; H, 8.39; N, 16.98.

5,5-Dicyclopropyl-2-methoxy-2-methyl-Δ^3-1,3,4-oxadiazoline (4). To lead tetraacetate (4.44 g, 0.010 mol) in ice-cold absolute methanol was added, with stirring, dicyclopropyl ketone-*N*-acetylhydrazone (1.66 g, 0.010 mol). When the initial yellow color of the solution had faded, KOH (pellets, 2 g) was added to hydrolyze the 5,5-dicyclopropyl-2-acetoxy-2-methyl-Δ^3-1,3,4-oxadiazoline (**2**), which is a coproduct of the oxidation. Stirring and cooling were maintained for 2 h after which most of the methanol was removed with a rotary evaporator. Water and methylene chloride were added to the residue and the organic layer was separated. It was washed with water and dried over calcium chloride before the solvent was evaporated to afford **4** in 71% yield as an oil that

(1) Bĕkhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 2473.
(2) Bĕkhazi, M.; Warkentin, J. *J. Org. Chem.* **1982**, *47*, 4870.
(3) Bĕkhazi, M.; Warkentin, J. *Can. J. Chem.* **1983**, *61*, 619.

0002-7863/83/1505-5675$01.50/0

Table I. Spectra of Products from 4 and 8

compound	^{1}H NMR ($CDCl_3$), δ	MS, m/z (rel abundance) composition of cation
 8	0.27–0.75 (m, 4 H, H_α), 1.10–1.43 (m, 1 H, H_β), 2.20 (s, 4 H, H_γ), 5.51 (s, 1 H, H_δ)	*a*
CH_3COCCl_3 9	*a*	*b*
 11	*c*	246 (3.6), 248 (4.7), 250 (2.2), $C_8H_{10}Cl_4$, 211 (3.6), 213 (4.0) $C_8H_{10}Cl_3$, 183 (30), 185 (28), 187 (9.4) $C_6H_6Cl_3$, 170 (42), 172 (41), 174 (14) $C_5H_5Cl_3$, 129 (45), 131 (14), $C_7H_{10}Cl$, 93 (72), C_7H_9, 77 (100) C_6H_5
 12	0.60–1.20 (m, 5 H, H_α), 2.65 (t, 2 H, J = 7.0 Hz, H_β), 3.55 (t, 2 H, J = 7.0 Hz, H_γ), 5.74 (t, 1 H, J = 7.0 Hz, H_δ)	164 (19), 166 (12), 168 (2) $C_7H_{10}Cl_2$, 129 (10), 131 (3) $C_7H_{10}Cl$, 115 (92) C_6H_8Cl, 79 (100) C_6H_7
 13	2.48 (m, 2 H, H_α), 2.78 (m, 2 H, H_β), 3.51–3.78 (m, 7 H, H_γ, H_δ, and imp.), 6.03 (t, 1 H, H_ϵ, J = 6.8 Hz)	316 (4.3), 318 (9.3), 320 (7.5), 322 (2.9) $C_8H_{10}Cl_6$, 245 (5.7), 247 (7.1), 249 (3.6) $C_8H_9Cl_4$, 199 (100), 201 (96), 203 (29), 205 (13) $C_7H_{10}Cl_3$, 163 (82), 165 (49), 167 (8) $C_7H_9Cl_2$, 127 (71), 129 (22) C_7H_8Cl, 101 (78), 103 (26) C_5H_6Cl, 91 (75) C_7H_7, 75 (66), 77 (41) C_3H_4Cl
 14	2.15–2.70 (m, 6 H, H_α and H_β), 3.47 (t, 2 H, H_γ, J = 6.9 Hz), 3.96 (m, 1 H, H_δ), 5.72 (m, 1 H, H_ϵ)	246 (13), 248 (17), 250 (8.2), 252 (1.8) $C_8H_{10}Cl_4$, 211 (19), 213 (18), 215 (5.7) $C_8H_{10}Cl_3$, 175 (46), 177 (29), 179 (5.0) $C_8H_9Cl_2$, 139 (86), 141 (27) C_8H_8Cl, 129 (31), 131 (8.6) $C_7H_{10}Cl$, 109 (80), 111 (64), 113 (40) unknown, 93 (100) C_7H_9, 77 (76), 67 (86) unknown
 15[d]	0.27–0.54 (m, 8 H, H_α), 0.8–1.0 (m, 2 H, H_β)	258 (7.1), 260 (9.3), 262 (4.6) $C_9H_{10}Cl_4$, 223 (68), 225 (59), 227 (21) $C_9H_{10}Cl_3$, 187 (66), 189 (48) $C_9H_9Cl_2$, 151 (59), 153 (34) C_9H_8Cl, 135 (100), 137 (60), 139 (13) $C_5H_5Cl_2$
 16	0.53–0.68 (m, 8 H, H_α), 0.97–1.15 (m, 2 H, H_β), 1.42 (t, 1 H, H_γ)	149 (6.6), 151 (3.4) $C_6H_7Cl_2$,[e] 147 (2.8) $C_6H_5Cl_2$, 136 (39), 138 (25), 140 (3.6) $C_5H_6Cl_2$, 101 (61), 103 (19) C_5H_6Cl, 95 (94) C_7H_{11}, 77 (29), 75 (15) unknown, 67 (86) C_5H_7, 65 (34) C_5H_5, 41 (100) C_3H_5, 39 (54) C_3H_3

[a] Not determined. [b] Mass spectrum identical with that in the literature.[18] [c] Separated from other materials on analytical scale only. [d] An alternative structure that is not ruled out by the data is 1,1,2,3-tetrachloro-**3**,3-dicyclopropyl-1-propene, from Cl migration in a diradical intermediate derived from addition of triplet dicyclopropylcarbene to tetrachloroethane. [e] Molecular ion not observed at 70 or 12 eV.

was distilled at 10^{-2} torr from a bulb at room temperature to a cold receiver: ^{1}H NMR ($CDCl_3$) δ 0.17–1.47 (m, 10 H), 1.60 (s, 3 H), 3.27 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 1.13, 1.34, 2.37, 16.47, 55.96 (OCH_3), 124.33 (C-5), 132.23 (C-2).

Thermolysis of 4 in C_6D_6. In a typical procedure, a solution of **4** (20 mg, 10 mmol) in 0.5 mL of the solvent was sealed into a medium-walled NMR tube after three freeze–pump–thaw cycles at 10^{-2} torr. The tube was heated for 3 days at 79.5 °C before it was opened and the contents were subjected to bulb-to-bulb distillation in a closed system at 10^{-2} torr. The distillate was examined by GC, GC/MS, IR, and ^{1}H NMR spectroscopy. It contained methyl acetate (**7**), 1-cyclopropylcyclobutene (**8**), and dicyclopropyl ketone. A distillation residue (trace) was not examined.

Thermolysis of 4 in CCl_4. A solution of **4** (40 mg, 20 mmol) in 0.5 mL of CCl_4 was degassed, sealed, and heated as described above. After the ^{1}H NMR spectrum and integral had been recorded the tube was opened, and bulb-to-bulb distillation was performed to separate volatile products and CCl_4 from products of low volatility. The distillate contained methyl acetate and chloroform together with trace amounts of other compounds.

The residue was partially separated by TLC (silica gel, 60F-254, 2 mm thick), and fractions from the plates were examined by GC/MS and by ^{1}H NMR spectroscopy. The entire residue was also examined by GC/MS. Although at least 12 compounds were indicated, only four (compounds **9–12**) are listed in Table I because of incomplete separations and some thermal decomposition or rearrangement on the columns.

Thermolysis of 4 in $CHCl_3$. A sample of **4** in $CHCl_3$, prepared as described above, was heated for 18 h. The ^{1}H NMR spectrum showed that **4** had decomposed and that methyl acetate (84%) and cyclopropyl compounds (δ 0.5–1.2) were the major products. Gas chromatography, GC/MS, and ^{1}H NMR spectroscopy of material collected from the GC column were used to confirm the assignments. Spectra of **16**, formed in ca. 77% yield (estimate from GC trace), are in Table I.

Radical-Initiated Reaction of CCl_4 with 1-Cyclopropylcyclobutene (8). A solution of 1-cyclopropylcyclobutene (0.040 g, 4.3×10^{-4} mol) in CCl_4 (0.5 mL) containing benzoyl peroxide (0.003 g, 1.2×10^{-5} mol) was sealed into an NMR tube after three cycles of freeze–pump–thaw degassing at 10^{-2} torr. After 1.5 h in an oil bath at 80 °C, the sample no longer contained **8**, as shown by the ^{1}H NMR spectrum. The contents of the tube were subjected to bulb-to-bulb distillation in a closed system at 0.1 torr, with the receiver in liquid nitrogen and the pot ultimately at 60 °C. The distillate so obtained was redistilled in the same maner, except that the pot was at room temperature, to separate CCl_4 and methyl acetate from less volatile materials.

Examination of the distillation residue by ^{1}H NMR spectroscopy at 250 MHz and by GC/MS showed that it contained 2-trichloromethyl-1-(3-chloropropylidene)cyclobutane (**14**, spectra in Table I) as a major component.

The analogous experiment, but with 0.015 g of benzoyl peroxide and a reaction time of 3 h, gave a product mixture with a ^{1}H NMR spectrum nearly identical with that from the experiment described above, suggesting that **14** is not converted rapidly to other products by reaction with trichloromethyl radicals.

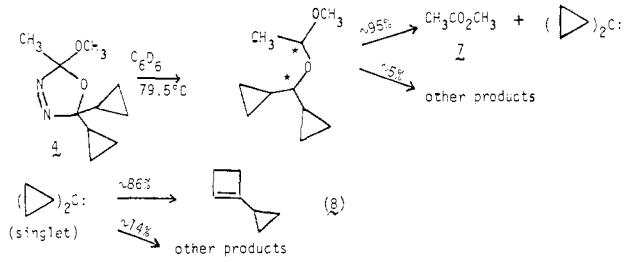
Addition of Dicyclopropylcarbene to Tetrachloroethylene. A solution of **4** (0.040 g) in tetrachloroethylene (0.5 mL) was degassed and sealed into an NMR tube, and the sample was heated for 20 h in an oil bath at 79.5 °C. The ^{1}H NMR spectrum showed that essentially all of the **4** had reacted and that the major products were methyl acetate (78%) and 1-cyclopropylcyclobutene (**8**, 74%), the remaining signal being in the high-field region. Separation of the components by gas chromatography and examination of a high-boiling fraction by MS and by ^{1}H NMR spectroscopy suggested that it was 1,1,2,2-tetrachloro-3,3-dicyclopropylcyclopropane (**15**). The yield was estimated to be about 15%. It spectra are in Table I.

Results and Discussion

The synthesis of **4** involves the well-established route depicted in eq 2.[4] Removal of the acetoxy analogue **2**, which constitutes

$$(c\text{-}C_3H_5)_2CO + H_2NNHCOCH_3 \rightarrow (c\text{-}C_3H_5)_2C{=}NNHCOCH_3 \xrightarrow[CH_3OH]{Pb(OAc)_4} \mathbf{4} + \mathbf{2} \quad (2)$$

Scheme I



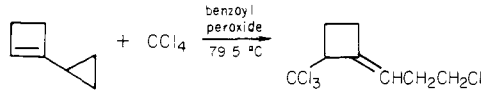
about 20% of the crude product, is accomplished most conveniently by hydrolysis with alkali. Although that procedure (Experimental Section) removes **2**, the final products of the hydrolysis were not identified. 5,5-Dicyclopropyl-2-hydroxy-2-methyl-Δ^3-1,3,4-oxadiazoline (**5**), which is the expected initial product of ester hydrolysis, is probably unstable like other members of that family.[5]

Thermolysis of **4** in C_6D_6 gave methyl acetate (**7**, 95%) and 1-cyclopropylcyclobutene (**8**, 80%). The latter is a well-known compound available by heating the tosylhydrazone of dicyclopropyl ketone with strong base.[6] Ring expansion appears to be a reaction common to all cyclopropylcarbenes[7] and is not restricted to the dicyclopropyl system. That expansion occurs from the singlet state,[8] and formation of **8** is therefore a sign of the intermediacy of singlet dicyclopropylcarbene in the thermolysis of **4** in benzene. The singlet is the state expected initially from thermolysis of **4** and it is assumed, in the following discussion, that it is also the state undergoing the intermolecular reactions that are reported. Scheme I summarizes the results of thermolysis of **4** in benzene.

Thermal decomposition of **4** in CCl_4 gave the interesting and informative set of products (**7**, **9**–**13**) shown in Scheme II, which also suggests their origins.

Methyl acetate (88%) is formed in essentially the same yield as that in benzene, suggesting that the carbonyl ylide does not attack CCl_4 fast enough to compete effectively with fragmentation. There is some evidence, in the form of 1,1,1-trichloroacetone (**9**, ca. 3%) that can be interpreted in terms of very limited attack on CCl_4 by the ylide. A plausible but not unique route to **9** (Scheme II) involves Cl-abstraction by the ylide, collapse of the resulting caged pair to a mixed ketal of trichloroacetone, and hydrolytic decomposition of the latter to the ketone.[9]

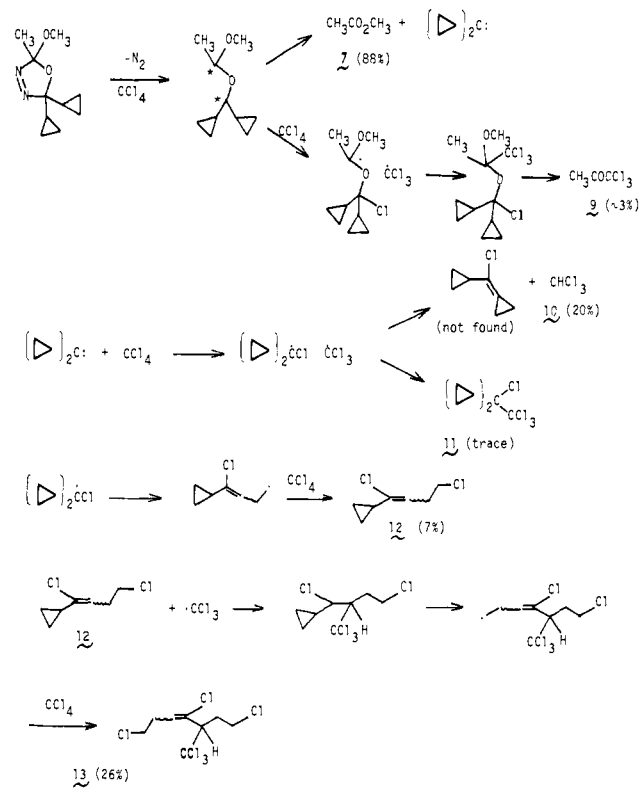
In contrast to the high yield of **8** from thermolysis of **4** in benzene, **8** could not be detected in the complex mixture of products from analogous thermolysis of **4** in carbon tetrachloride. In view of the possibility that **8** had been formed but had not survived the reaction conditions, a sample of pure **8** was heated in CCl_4 containing benzoyl peroxide (Experimental Section) to simulate the radical chain processes that are initiated by thermolysis of **4** in CCl_4. The alkene **8** was destroyed rapidly and quantitatively, giving rise to 2-(trichloromethyl)-1-(3-chloropropylidene)cyclobutane (**14**) as a major product (eq 3) (spectra



8 14 (3)

in Table I). Product **14** appeared to be fairly stable under the reaction conditions (Experimental Section). Although the products obtained from thermolysis of **4** in CCl_4 included at least 12 chlorinated compounds, **14** was not one of them. It follows that

Scheme II



dicyclopropylcarbene does not undergo ring expansion to 1-cyclopropylcyclobutene during its lifetime in neat CCl_4.

The final mixture of products from reaction of dicyclopropylcarbene with CCl_4 was not fully separable on several gas chromatography columns. Moreover, some of the components appeared to rearrange or to decompose under some GC conditions. In spite of the fact that many of those components remain unidentified, it was possible to determine what the major initial step in the reaction of dicyclopropylcarbene with CCl_4 must be. The composite evidence, on the basis of ^1H NMR spectra of the crude and of impure fractions collected from preparative GC columns, mass spectra, and analogy to the known chemistry of cyclopropylcarbinyl radicals, is summarized below.

Integration of the ^1H NMR spectrum (250 MHz) of the entire reaction mixture, except for chloroform and methyl acetate that had been distilled off, showed that 15% of the total remaining signal was in the high-field region characteristic of cyclopropylmethylene protons (δ = 0.5–0.9). Since 80% of the signal should be found there if all cyclopropane rings had remained intact, it follows that no more than 19% of the product could have two cyclopropane rings and no more than 38% could have one cyclopropane ring. Thus, at least 62% of the dicyclopropylcarbene that was generated led to acyclic products or to products with only one cyclopropane ring. Moreover, none of those products arose through unimolecular ring expansion of the carbene to 1-cyclopropylcyclobutene, since neither that compound nor the major product (**14**) from its radical chain reactions in CCl_4 were detectable by GC or ^1H NMR spectroscopy.

The major or exclusive reaction of dicyclopropylcarbene with CCl_4 must therefore be Cl-abstraction to form a radical pair (Scheme II). There is much precedent for halogen abstraction by singlet carbenes,[10] for which an ylide mechanism is often postulated[11-15] (eq 4).

$$(c\text{-}C_3H_5)_2C: + Cl\text{–}CCl_3 \rightarrow (c\text{-}C_3H_5)_2\overset{+}{C}\text{–}\dot{Cl}\text{–}CCl_3 \rightarrow (c\text{-}C_3H_5)_2\dot{C}Cl\ \dot{C}Cl_3 \quad (4)$$

(4) (a) Warkentin, J. *Synthesis* **1970**, 279. (b) Butler, R. N.; Scott, F. L.; O'Mahony, T. A. F. *Chem. Rev.* **1973**, *73*, 93.
(5) (a) Knittel, P.; Warkentin, J. *Can. J. Chem.* **1975**, *53*, 2275; (b) *Ibid.* **1976**, *54*, 1341.
(6) Teraji, T.; Moritani, I.; Tsuda, E.; Nishida, S. *J. Chem. Soc. C* **1971**, 3252.
(7) Kirmse, W. "Carbene Chemsitry", 2nd ed.; Academic Press: New York, 1971; p 467.
(8) Schoeller, W. W. *J. Org. Chem.* **1980**, *45*, 2161.
(9) An alternative route involves insertion of 1-methoxy-ethylidene, from fragmentation of the ylide in the other sense, into CCl_4 and subsequent ion pair formation from the α-halo ether, followed by demethylation.
(10) Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.
(11) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, **1971**; p 442–447.

The chlorodicyclopropylmethyl radical resulting from ylide dissociation should be capable of coupling and disproportionation reactions with trichloromethyl radical and of unimolecular ring opening, as shown in Scheme II. The proposal that ring opening is competitive with coupling and disproportionation, and with Cl-abstraction from CCl_4, is based on the large rate constant ($k^{25°C} = 1.3 \times 10^9\ s^{-1}$) for opening of the cyclopropylmethyl radical to the homoallyl radical.[16]

The 1,1,1,2-tetrachloro-2,2-dicyclopropylethane (**11**), a minor product, could be attributed to concerted insertion into the C–Cl bond. It is simpler, however, and mechanistically sufficient, to attribute all of that material to the coupling reaction (Scheme II). The presence of chloroform (**10**) is suggestive of disproportionation, but there is no evidence that it occurs from the initially formed radical pair.

Ring opening is expected to lead initially to a pair (geometric isomers) of homoallylic, primary radicals that ought to abstract Cl from solvent to form **12** (Scheme II). Although **12** was found, it is probably reactive toward $\dot{C}Cl_3$ and is largely consumed by the addition, further ring-opening, and chlorine-abstraction steps show at the bottom of Scheme II, to form **13**. Compound **13** was a major product, the vinyl triplet of which dominated the low-field signals in the ^1H NMR spectrum of the crude reaction mixture.

Scheme II is a simplified mechanistic proposal, showing only generalized formulas for compounds that are likely to be generated as *E*,*Z* pairs. Some additions of $\dot{C}Cl_3$ have not been considered and all coupling products, save for those from the initial cage, have been omitted. The consequences of abstraction of allylic hydrogen by $\dot{C}Cl_3$ from initially formed products are not shown. Some of the chloroform presumably should be attributed to such processes. Although a more complete characterization of the complex reaction mixture would be of some interest, the radical chemistry that follows initial attack of the carbene on CCl_4 is not relevant to the carbene's chemical properties except insofar as it establishes that an early species formed from the carbene is a dicyclopropylmethyl free radical. Those products in Scheme II that are numbered and that are associated with yield estimates provide ample evidence for the intermediacy of such a radical.

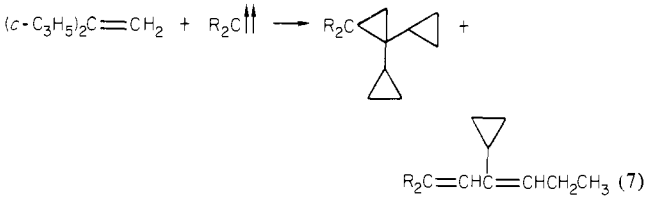
Decomposition of **4** in $CHCl_3$ was relatively clean, yielding primarily methyl acetate and 1,1,1-trichloro-2,2-dicyclopropylethane (**16**) (eq 5). Surprisingly, products of cyclopropyl ring

$$\mathbf{4} \xrightarrow[79.5\ °C]{CHCl_3} \underset{(84)}{CH_3CO_2CH_3} + \underset{\mathbf{16}\ (77\%)}{(c\text{-}C_3H_5)_2CHCCl_3} \qquad (5)$$

opening were minor or absent (no vinyl signals in the NMR spectrum). Since there is no reason to expect that the rate constant for ring opening of the dicyclopropylmethyl radical is smaller than that of the chlorodicyclopropylmethyl radical, the radical pair mechanism in eq 6 can be ruled out as a major route to **16**. If

$$(c\text{-}C_3H_5)_2C\text{:} + HCCl_3 \rightarrow (c\text{-}C_3H_5)_2\dot{C}H\ \dot{C}Cl_3 \rightarrow \mathbf{16} \qquad (6)$$

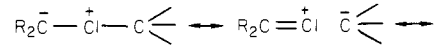
such a pair were on the reaction pathway, there ought to be products from ring opening of the dicyclopropylcarbinyl free radical. Such products, which might include 1-cyclopropyl-1-butene, 1,1,1-trichloro-2-cyclopropylpentane, and 5-trichloromethyl-3-heptene were not found. Since ring opening does occur in closely related radicals, such as chlorodicyclopropylmethyl (above, Scheme II) and in adducts from attack of triplet carbenes on 1,1-dicyclopropyl-ethylene[17] (eq 7), it seems to be necessary



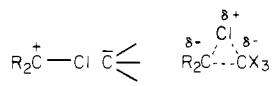
(7)

to postulate that dicyclopropylcarbinyl radicals are not involved in the chemistry of eq 5. Specifically ruled out is intersystem crossing to triplet dicyclopropyl carbene followed by selective H-abstraction from chloroform. The product of coupling, following initial attack by the carbene at chlorine of $CHCl_3$ to form a radical pair, may have been formed in very low yield (ca. 0.5%). The molecular weight, chlorine content (MS), and a singlet at δ 5.2 in the ^1H NMR spectrum were assigned tentatively to 1,2,2-trichloro-1,1-dicyclopropylethane, but a pure sample could not be obtained. The above evidence can be accommodated readily if it is assumed that the main reaction of dicyclopropyl carbenes with chloroform is a concerted insertion into the C–H bond.

A rationale for the very different behavior of chloroform and carbon tetrachloride is based on relative stabilities of the various potential intermediates or transition states. In a stepwise attack the carbene acts either as a Lewis acid or as a Lewis base, contributing structures for reaction at Cl of CCl_4 or $CHCl_3$ being **17** (an ylide) and **18** and **19** (ion pairs). Although cyclopropyl



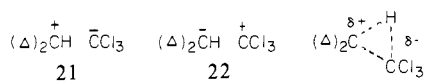
17 18



19 20

groups (R = c-C_3H_5) would tend to favor **18** ↔ **19**, those contributors are formally derived from nucleophilic attack by the carbene at chlorine. Since chlorine is the negative end of the C–Cl dipole, a transition state in which it accepts a pair of electrons could be of fairly high energy because of electron–electron repulsion. Ylide contributor **17**, on the other hand, is formally derived from nucleophilic attack by a Cl lone pair at the electron deficient site of the carbene. Since cyclopropyl substituents (R) can not stabilize the negative end of the resulting dipole conjugatively, there is no reason to expect that the transition state would be very **17**-like either. These arguments form a basis for rationalizing the observation that Cl-abstraction from $CHCl_3$ by singlet dicyclopropyl carbene is slow relative to C–H insertion. Concerted C-Cl insertion would probably involve similar charge separation (**20**), since bond making to Cl can be expected to run ahead of bond making to the CX_3 carbon, because of steric hindrance. Steric hindrance added to unfavorable electronic factors at the carbenic center may be sufficient to put the concerted mechanism out of reach in favor of the stepwise mechanism of reaction of carbenes with many chloro compounds.[10]

A different situation pertains in the case of attack at C–H rather than C–Cl of chloroform. Stepwise transfer of H to singlet dicyclopropyl carbene could involve transition states modeled by ion pairs **21** and **22**. Of these, only **21**, which is reached by



21 22 23

nucleophilic substitution at hydrogen, is reasonable from the point of view of charge stabilization. The transition state for reaching **21**, in contrast to that for **17** ↔ **19**, involves a favorable electrostatic interaction between the filled orbital of the carbene and

(12) Baron, W. J.; De Camp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, H. R.; Sohn, M. B. In "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, p 18.
(13) Ando, W.; Kondo, S.; Migita, T. *J. Am. Chem. Soc.* **1969**, *91*, 6516.
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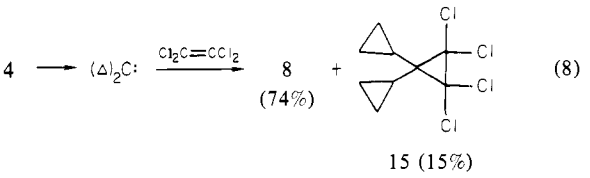
(17) Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6451.
(18) Heller, S. R.; Milne, G. W. H. EPA/NIH Mass Spectral Data Base, Vol. 1, U.S. Government Printing Office, Washington, DC, 1978, p 595.

the positive end of the H–C dipole.

Although the above model (**21**) is useful, it is very likely, in view of the feeble acidity of chloroform, that the real process is a concerted one rather than a two-step reaction through an ion pair. We suggest that insertion of singlet dicyclopropylcarbene into the CH bond of chloroform is a nonsynchronous concerted process, involving charge separation in the sense of **21** but with a geometry resembling **23**. Significant conjugative stabilization of positive charge by the cyclopropyl substituents may account for the present finding that dicyclopropylcarbene inserts into the C–H bond of chloroform whereas other singlet carbenes prefer to abstract chlorine instead.[10]

Finally, dicyclopropylcarbene from **4** can be trapped in a cycloaddition reaction with an alkene. Tetrachloroethylene (neat) intercepted about 15% of the carbene before it could undergo ring expansion to **8** (eq 8).

In summary, **4** appears to be the most convenient source of dicyclopropylcarbene that is currently available, for it is readily accessible and it decomposes under mild conditions in the absence of metallic or acid/base catalysts. The reaction of dicyclopropylcarbene with chloroform suggests that the carbene is relatively nucleophilic.



15 (15%) (8)

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Registry No. 4, 86310-10-3; **8**, 22693-18-1; **11**, 86310-11-4; **12**, 86310-12-5; **13**, 86310-13-6; **14**, 86310-14-7; **15**, 86310-15-8; **16**, 86310-16-9; $(c\text{-}C_3H_5)_2CO$, 1121-37-5; $H_2NNHCOCH_3$, 1068-57-1; $(c\text{-}C_3H_5)_2C{=}NNHCOCH_3$, 83313-96-6; $(c\text{-}C_3H_5)_2C{:}$, 86310-17-0; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; $Cl_2C{=}CCl_2$, 127-18-4.

Total Synthesis of (±)-Spiniferin-1, a Naturally Occurring 1,6-Methano[10]annulene

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Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received February 24, 1983*

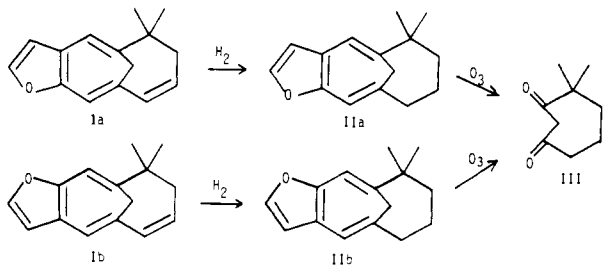
Abstract: Total syntheses of (±)-spiniferin-1 (Ia), a natural furanosesquiterpene with a 1,6-methano[10]annulene carbon skeleton, and the dihydro derivative IIa are described. A key transformation in each synthesis entails catalyzed electrocyclic ring opening of a methanonaphthalenone (**10** and **48**, with acid and base, respectively). For the dihydro compound IIa, completion of the synthesis was achieved, after Wittig homologation to the bis(enol ether) **13**, by acid-catalyzed furan cyclization. However, analogous cyclization of the dehydro counterpart, bis(enol ether) **57**, led to multiple decomposition products. The acid lability of spiniferin-1 and its synthetic precursors led to the examination of various base-promoted internal Wittig and aldol-type furan cyclizations. Specifically, the ester aldehyde **56** was found to give a mixture of (±)-spiniferin-1 (Ia), the furan ester **59**, and the furan acid **60** upon base treatment followed by acidification. Acid **60** afforded (±)-spiniferin-1 through Cu-promoted decarboxylation in quinoline.

In their extensive studies on marine natural products, Cimino et al. isolated an unstable furanosesquiterpene, spiniferin-1, from the sponge *Pleraplysilla spinifera*, found in the Bay of Naples.[1] The instability of spiniferin-1 made classical chemical investigation difficult. However, two key transformations, hydrogenation to a dihydro derivative and ozonolysis of this derivative to 4,4-dimethylcycloheptane-1,3-dione (III), provided the clues that, together with perceptive spectral analysis, proved instrumental to the ultimate structure assignment as Ia or the furano isomer Ib (Scheme I). The former was preferred on biogenetic grounds.

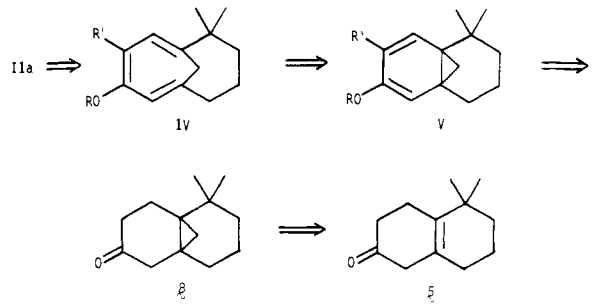
The formulation of spiniferin-1 as a substituted 1,6-methano[10]annulene, a substance conceived and elegantly synthesized by Vogel in his brilliant studies on Hückel aromaticity,[2] was profoundly interesting to us as a conceptual link between theoretical and natural products chemistry. For the present, spiniferin-1 represents the sole known sesquiterpene with this unusual carbon skeleton. While the proposed structure seemed fully consistent with the reported spectral data, we felt that rational chemical synthesis would provide desirable verification of both the carbon skeleton and the furan orientation.

We selected IIa, the favored structure for dihydrospiniferin-1,[1] as an initial synthetic target.[3] Our plan (Scheme II) employed a norcaradiene–cycloheptatriene-type electrocyclic rearrangement to introduce the methanoannulene structural unit.[4] An analogous rearrangement was used by Vogel in his efficient synthesis of the parent aromatic system.[2] Of course, such reactions are reversible,

Scheme I



Scheme II



[†] National Science Foundation predoctoral fellow, 1979–1982. The results described in this manuscript are recorded in: Conrow, R. E. Ph.D. Dissertation, submitted to Northwestern University, Evanston, IL, June 1983.

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