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Silicon in Synthesis. 8.[1] Vinyltrimethylsilane, a Convenient Ethylene Equivalent for the Synthesis of Vinyl Aryl Sulfides, Vinyl Aryl Sulfoxides, Thiosilylketene Acetals, and Fused Cyclopentenones

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Vinyltrimethylsilane reacts with a variety of arylsulfenyl chlorides to give 2-chloro-1-(trimethylsilyl)ethyl aryl sulfide adducts **9–13**. These adducts can be converted into vinyl aryl sulfides and vinyl aryl sulfoxides, and for the case of 2-chloro-1-(trimethylsilyl)ethyl phenyl sulfide (**11**), treatment with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) gave 1-(trimethylsilyl)-1-(phenylthio)ethylene (**24**). α,β-Unsaturated acid chlorides react with vinyltrimethylsilane in the presence of stannic tetrachloride to give fused cyclopentenones. In all of the reactions described, vinyltrimethylsilane serves as a convenient ethylene equivalent.

Introduction

Despite the voluminous number of research publications during the past decade or so that have been concerned with the applications of organosilicon chemistry to synthesis,[2] there are relatively few simple available reagents based upon silicon chemistry that can be used to conduct useful synthetic transformations.[3] We have pursued a program of research that utilizes simple and readily available organosilicon reagents[4] to carry out synthetic transformations. Generally, the main purpose of this research has been to develop ways of making carbon–carbon bonds mediated by silicon reagents, but where appropriate the construction of carbon-heteroatom bonds is feasible. In this way organosilicon chemistry, and the reagents based upon this chemistry, can be available to the nonspecialist who is more concerned with carrying out a particular synthetic step in the most efficient way rather than with the detailed and fascinating nuances of silicon chemistry.

With this in mind we have examined the reactions of arylsulfenyl chlorides and α,β-unsaturated acid chlorides with vinyltrimethylsilane in an effort to synthesize vinyl aryl sulfides and fused cyclopentenones, respectively. Vinylsilanes[5] have recently found extensive use in organic synthesis;[6] notably their electrophilic chemistry has attracted the most attention.[7] The addition of an electrophile to a vinylsilane results in the buildup of electrophilic character β to the carbon–silicon bond.[8] Such a species **2a** is said to be stabilized either by bridging[9] or by so-called vertical stabilization (hyperconjugation).[10] The addition has the geometrical requirement that the electrophilic character of the β-position can enjoy stabilization only if the developing positive charge is contained in a $2p_z$ orbital that is in the same plane as the C–Si σ bond. This geometrical condition[11] imposes a severe limitation upon the

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(1) For previous papers in this series describing the development of organosilicon reagents in synthesis, see part 1, C. Burford, F. Cooke, E. Ehlinger, and P. D. Magnus, *J. Am. Chem. Soc.*, **99**, 4536 (1977); part 2, F. Cooke and P. D. Magnus, *J. Chem. Soc., Chem. Commun.*, 513 (1977); part 3, D. Ayalon Chass, E. Ehlinger and P. D. Magnus, *ibid.*, 772 (1977); part 4, P. D. Magnus and G. Roy, *ibid.*, 297 (1978); part 5, G. L. Bundy, F. Cooke, and P. D. Magnus, *ibid.*, 714 (1978); part 6, F. Cooke, J. Schwindeman, and P. D. Magnus, *Tetrahedron Lett.*, 1995 (1979); part 7, E. Ehlinger and P. D. Magnus, *J. Chem. Soc., Chem. Commun.*, 421 (1979).

(2) For the most recent and comprehensive review on organosilicon chemistry, see E. W. Colvin, *Chem. Soc. Rev.*, 7, 15 (1978). For a leading review covering general organosilicon chemistry and a detailed summary of the early literature, see C. Eaborn and R. W. Bott, "Organometallic Compounds of the Group IV Elements", Part I, A. G. MacDiarmid, Ed., Marcel Dekker, New York, 1968. For other leading review articles, see I. Fleming, *Chem. Ind.* (*London*), 449 (1975); S. S. Washburne, *J. Organomet. Chem.*, **83**, 155 (1974) and **123**, 1 (1976); R. F. Cunico, *ibid.*, **109**, 1 (1976); R. F. Hudrlik, "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., J. Organometallic Chem. Library, Vol. 1 and 2, Elsevier, Amsterdam, 1976; J. F. Klebe, *Adv. Org. Chem.*, 8, 97 (1972); L. Birkofer and A. Ritter, in "Newer Methods in Preparative Organic Chemistry", Vol. 5, W. Foerst, Ed., Academic Press, New York, 1968, p 221.

(3) The first general procedure that utilizes a simple silicon reagent is the Peterson olefination reaction: D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968). Many subsequent developments of the Peterson reaction have been described: T. H. Chan, W. Mychajlowskij, B. S. Ong, and D. N. Harpp, *J. Org. Chem.*, **43**, 1526 (1978); T. H. Chan, *Acc. Chem. Res.*, **10**, 442 (1977), and references cited therein.

(4) Petrarch Systems, Inc., Box 141, Levittown, PA 19059.

(5) For some recent methods of preparing vinylsilanes see G. Stork, M. E. Jung, E. Colvin, and Y. Noel, *J. Am. Chem. Soc.*, **96**, 3684 (1974); T. H. Chan, A. Baldassarre, and D. Massuda, *Synthesis*, 801, (1976); R. T. Taylor, C. R. Degenhardt, W. P. Melega, and L. A. Paquette, *Tetrahedron Lett.*, 159 (1977); A. R. Chamberlin, J. E. Stemke, and F. T. Bond, *J. Org. Chem.*, **43**, 147 (1978); M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *J. Organomet. Chem.*, **24**, 529 (1970). See also ref 2.

(6) Vinylsilanes are readily converted into α,β-epoxysilanes. See G. Stork and E. Colvin, *J. Am. Chem. Soc.*, **93**, 2080 (1971); G. Stork and M. E. Jung, *ibid.*, **96**, 3682 (1974). α-Lithiovinylsilanes, G. Stork and B. Ganem, *ibid.*, **95**, 6152 (1973); R. K. Boeckman and K. J. Bonza, *Tetrahedron Lett.*, 3365 (1974); B-Tn. Gröbel and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **13**, 83 (1974); *Chem. Ber.*, **110**, 852, 867 (1977). For addition of alkyllithiums to vinylsilanes see L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954) and *J. Am. Chem. Soc.*, **74**, 4582 (1952); P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1133 (1974); *J. Am. Chem. Soc.*, **97**, 1464 (1975); T. H. Chan and E. Chang, *J. Org. Chem.*, **39**, 3264 (1974).

(7) For leading references to the electrophilic chemistry of vinylsilanes, see J.-P. Pillot, J. Dunoques, and R. Calas, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **278**, 787, 789 (1974); *Bull. Soc. Chim. Fr.*, 2143 (1975); I. Fleming and A. Pearce, *J. Chem. Soc., Chem. Commun.*, 633 (1975); T. H. Chan, P. W. K. Lau, and W. Mychajlowskij, *Tetrahedron Lett.*, 3317 (1977); K. Utimoto, M. Kitai, and H. Nozaki, *ibid.*, 2825 (1975); T. H. Chan and W. Mychajlowskij, *ibid.*, 4439 (1976); T. H. Chan, W. Mychajlowskij, B. S. Ong, and D. N. Harpp, *J. Organomet. Chem.*, **107**, C1 (1976). For addition of chlorine and bromine to vinylsilanes, see R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 543 (1974); R. B. Miller and G. McGarvey, *J. Org. Chem.*, **43**, 4424 (1978); G. Zweifel and W. Lewis, *ibid.*, **43**, 2739 (1978). For 1,2-transposition of ketones via vinylsilanes, see W. E. Fristad, T. R. Bailey, and L. A. Paquette, *J. Org. Chem.*, **43**, 1620 (1978). For substituted vinylsilanes in Friedel-Crafts reaction, see W. E. Fristad, D. S. Dime, T. R. Bailey, and L. A. Paquette, *Tetrahedron Lett.*, 1999 (1979).

(8) For a review of the so-called β effect, see A. W. P. Jarvie, *Organomet. Chem. Rev., Sect. A*, **6**, 153 (1970); fluoride ion eliminations, R. F. Cunico and E. M. Dexheimer, *J. Am. Chem. Soc.*, **94**, 2868 (1972); R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 543 (1974).

(9) M. A. Cooke, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, **24**, 301 (1970); A. J. Bourne and A. W. P. Jarvie, *ibid.*, **24**, 335 (1970).

(10) T. G. Taylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Braun, *J. Am. Chem. Soc.*, **93**, 5713 (1971); T. G. Taylor, H. J. Berwin, J. Jetkunica, and M. L. Hall, *Pure Appl. Chem.*, **30**, 599 (1972).

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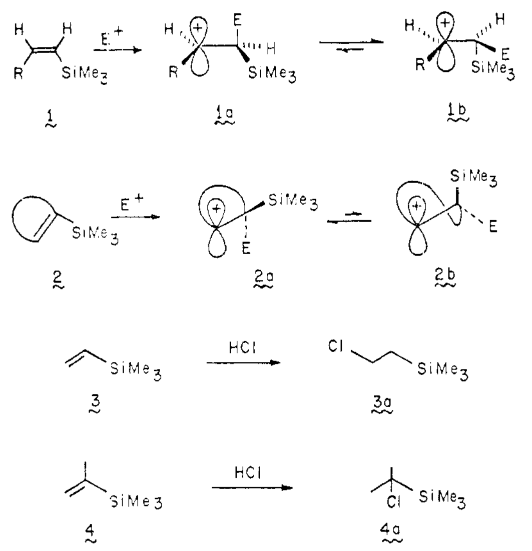
Scheme I[a]



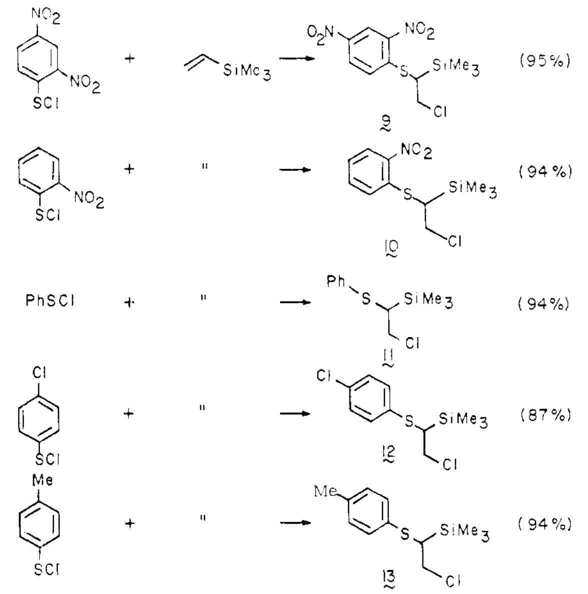
[a] For conformationally rigid systems or where the interconversion involves prohibitively high energy, then 2a will be the dominant species.

use of the β effect for stabilizing electrophilic additions to vinylsilanes. In acyclic systems there is usually no problem; as the incoming electrophile approaches the vinylsilane π system, rotation about the central carbon–carbon bond can take place to bring the β-carbonium ion into the same plane as the carbon–silicon bond[12] (**1** → **1a** ⇌ **1b**); but for cyclic vinylsilanes, particularly in conformationally rigid systems, it may be difficult, and in certain cases impossible, for the carbon–silicon bond to move into the same plane as the $2p_z$ orbital carrying the positive charge, **2** → **2a** ⇌ **2b**.

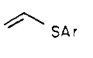
While the β effect has dominated much of the development of the synthetic usage of organosilicon chemistry and has been designated as a powerful effect, it is our view that the β effect is a delicate electronic stabilization that can be readily perturbed by relatively small steric and electronic changes. This view of the perturbation of the β effect by small electronic changes is substantiated by an observation made some years ago by Sommer and is shown in Scheme I.[13] Vinyltrimethylsilane (**3**) adds hydrogen chloride to give exclusively the β-chloro adduct **3a**, whereas isopropenyltrimethylsilane (**4**) adds hydrogen chloride to give the α-chloro adduct **4a**; the methyl group in **4** has completely overwhelmed the β effect.

As a consequence of these considerations we felt that the most effective use of vinylsilanes in synthesis, at least for reactions with electrophiles, would be to investigate the reactions of the readily available vinyltrimethylsilane (**3**) with various electrophiles. Vinyltrimethylsilane (**3**) (bp 55 °C; cf. ethylene, −104 °C) provides a convenient reagent that can function as an ethylene equivalent in electrophilic substitution reactions. In the first part of this paper we describe the use of vinyltrimethylsilane for the synthesis of vinyl aryl sulfides and various derivatives thereof.

Scheme II



Vinyl Aryl Sulfides and Derivatives. Vinyl aryl sulfides (**5**) have attracted considerable attention as interesting C_2 components in synthesis.[14] Similarly the oxidatively derived vinyl aryl sulfoxides (**6**) have shown potential in synthesis; in particular, vinyl phenyl sulfoxide (**6**, Ar = Ph) has been shown to function as a single-step acetylene equivalent in the Diels–Alder reaction.[15] Recently α-lithiovinyl phenyl sulfoxide (**7**) has been introduced as a reagent for a number of useful transformations.[16] Vinyl aryl sulfides are frequently prepared from the addition of an arylsulfenyl halide to an alkene, followed by the elimination of the elements of hydrogen halide.[17] Oxidation of the resulting vinyl aryl sulfide with *m*-chloroperbenzoic acid or sodium periodate[18] provides a route to vinyl aryl sulfoxides.



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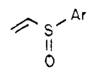

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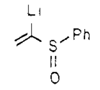

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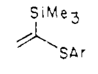

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Here we describe a new and convenient synthetic route to vinyl aryl sulfides (**5**), vinyl aryl sulfoxides (**6**), and

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(11) The geometrical constraints of the β effect have been subjected to some experimental verification. Evidence exists to support this theory. E. Ehlingler and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 421 (1979), show an example where to bring the C–Si bond into the same plane as the β-carbonium ion would cause a severe steric interaction between the $-SiMe_3$ group and an adamantyl group. Also, E. J. Thomas and G. H. Whitham, *ibid.*, 212 (1979), describe the addition of I-X to 1-trimethylsilylcyclohexene where the addition is a normal one, and apparently the $-SiMe_3$ cannot occupy an axial position and thus stabilize the β-carbonium ion. See also W. K. Musker and G. L. Larson, *J. Am. Chem. Soc.*, **91**, 514 (1969); P. F. Hudrlik, J. P. Arerleo, R. M. Schwartz, R. N. Misra, and R. J. Rona, *ibid.*, **97**, 1464 (1975); A. W. P. Jarvie, A. Holt, and J. Thompson, *J. Chem. Soc. B*, 852 (1969); T. G. Traylor, W. Henstein, and H. J. Berwin, *J. Am. Chem. Soc.*, **92**, 7476 (1970); C. Eaborn, F. Feichtmayr, M. Horn, and J. N. Murrell, *J. Organomet. Chem.*, **77**, 39 (1974).

(12) K. E. Koenig and W. P. Weber, *Tetrahedron Lett.*, 2533 (1973).

(13) L. H. Sommer, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

(14) K. Oshima, K. Shimoji, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **95**, 2694 (1973); I. Vlattas, L. D. Veechia, and A. D. Lee, *ibid.*, **98**, 2008 (1976); R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 990 (1976); T. Cohen, A. J. Mura, Jr., D. W. Skull, E. R. Fogel, R. J. Ruffner, and J. R. Falck, *J. Org. Chem.*, **41**, 3218 (1976); B. M. Trost, M. J. Crimmin, and D. Butler, *ibid.*, **43**, 4549 (1978); R. C. Cookson and P. J. Parson, *J. Chem. Soc., Chem. Commun.*, 821 (1978); B. Harirchian and P. D. Magnus, *ibid.*, 522 (1977); G. H. Posner and P.-W. Tang, *J. Org. Chem.*, **43**, 4131 (1978).

(15) L. A. Paquette, R. E. Moerck, B. Harirchian and P. D. Magnus, *J. Am. Chem. Soc.*, **100**, 1597 (1978).

(16) G. H. Posner, P.-W. Tang, and J. P. Mallamo, *Tetrahedron Lett.*, 3995 (1978).

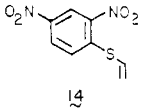
(17) For a recent and comprehensive paper describing the preparation of unsaturated aryl sulfides, sulfoxides, and sulfones, see P. B. Hopkins and P. L. Fuchs, *J. Org. Chem.*, **43**, 1208 (1978), and references cited therein; K. D. Grunderman and P. Holtmann, *Angew. Chem., Int. Ed. Engl.*, **7**, 668 (1966); W. Verboom, J. Meijer, and L. Brandsma, *Synthesis*, 577 (1978).

(18) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **53**, 2106 (1970). See also ref 17 and 19.

1-(trimethylsilyl)vinyl aryl sulfides (**8**).[19] Vinyltrimethylsilane (**3**) can be used in reactions with arylsulfenyl chlorides to give adducts that in subsequent reactions give ready access, both on a small and on a large scale, to the reagents **5**, **6**, and **8**.[20]

When arylsulfenyl chlorides, either generated in situ[17,21] or prepared in a separate reaction,[22] were treated with vinyltrimethylsilane in dichloromethane at −78 °C and the reaction mixture was allowed to warm to 20 °C, an extremely clean addition took place to give the adducts **9**, **10**, **11**, **12**, and **13**, in excellent yields (Scheme II). It should be noted that in all of these additions no elimination products, **5** or **8** (loss of Me_3SiCl or HCl, respectively), were detected. The adducts **9**–**13** would be expected to be labile with respect to the elimination of either Me_3SiCl or HCl since β-chloro sulfides are generally considered to be labile[23] and furthermore β-chloro silanes are also considered to be labile.[24,8] Surprisingly, the adducts **9**–**13** were remarkably stable. The crystalline adducts melted without decomposition, and in the case of **11**, distillation at 93 °C (11 mm) was not accompanied by any discernible decomposition.

Our first objective was to convert the adducts into the corresponding vinyl aryl sulfides and vinyl aryl sulfoxides. Solvolysis of **9** in 30% aqueous ethanol at 65 °C for 24 h gave the vinyl aryl sulfide **14** in excellent yield. Similarly, the 2-nitro adduct **10** was converted into the vinyl aryl sulfide **15** by heating in 30% aqueous ethanol at 50 °C for 48 h. Exposure of the adducts **11**, **12**, and **13** to the above ethanolysis conditions gave traces of the corresponding vinyl aryl sulfides, **16**, **17**, and **18**, respectively; the main products were the 2-ethoxy adducts **19** (Ar = Ph, *p*-Cl-C_6H_4–, and *p*-MeC_6H_4–).



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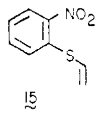

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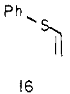

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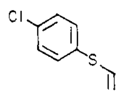

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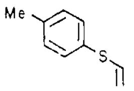

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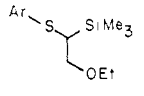

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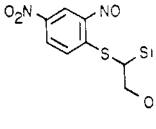
The 2,4-dinitro adduct **9** was treated with potassium fluoride dihydrate in dimethyl sulfoxide at 105 °C for 1 h to give the vinyl aryl sulfide **14** (83%). Silver trifluoroacetate reacted with **9** to give **14** in quantitative yield. The most convenient procedure for the preparation of **14** is to treat the adduct **9** with potassium fluoride (anhydrous) in dry tetrahydrofuran at 20 °C for 12 h. Application of this procedure to **10** gave **15** in near quantitative yield. The best procedure for the preparation of vinyl phenyl sulfide (**6**), vinyl *p*-chlorophenyl sulfide (**17**), and vinyl *p*-tolyl sulfide (**18**) is to treat the corresponding β-chloro adducts **11**, **12**, and **13** with potassium fluoride (anhydrous) in dry tetrahydrofuran at 20 °C, or potassium fluoride dihydrate in dimethyl sulfoxide at 70–100 °C.[8] In this way the vinyl aryl sulfides **16**, **17**, and **18** were obtained in 93, 99, and 90% yield, respectively. In general, the potassium fluoride dihydrate/dimethyl sulfoxide method is slightly superior.

Efforts to convert 2,4-dinitrophenylsulfenyl chloride and vinyltrimethylsilane directly into the vinyl sulfide **14** by using a procedure that involves treatment of 2,4-dinitrophenylsulfenyl chloride with silver trifluoroacetate followed by vinyltrimethylsilane gave only the 2-trifluoroacetoxy adduct **20** (77%).



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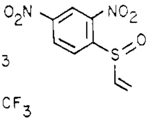

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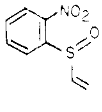

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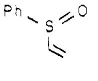

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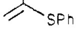
The vinyl aryl sulfides **14**–**16** were converted into the corresponding vinyl aryl sulfoxides **21**, **22**, and **23**, respectively, by oxidation with *m*-chloroperbenzoic acid in dichloromethane at room temperature. As expected, the nitroaryl vinyl sulfides were oxidized more slowly than the other sulfides. This sequence provides a quick and straightforward method for preparing vinyl aryl sulfoxides in three steps.

We found that we could effectively preclude one of these steps by reversing the order of the elimination–oxidation sequence. Oxidation of the adduct **9** in dichloromethane with *m*-chloroperbenzoic acid gave the sulfoxide **21** (95%) directly. Unfortunately application of this more direct method to the adducts **11**, **12**, and **13** gave complicated mixtures.

The current interest in ethylene thioacetals **24**[25] prompted us to attempt to eliminate the elements of hydrogen chloride from the adducts **9**–**13** to give 1-(trimethylsilyl)vinyl aryl sulfides (**8**). All attempts to eliminate hydrogen chloride, using a wide variety of bases, from the adducts **9** and **10** gave only intractable tars, whereas the adduct **11**, when treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN),[26] gave the required 1-(trimethylsilyl)-1-(phenylthio)ethylene **24** in good yield. Application of this procedure to **12** gave the required 1-(trimethylsilyl)vinyl aryl sulfide **25** along with small amounts of **17**. Compound **13** with DBU or DBN gave mainly **18** with traces of **26**. Deprotonation of **16** using LDA at −78 °C followed by trimethylsilyl chloride gave **24** in 97% yield.[19] Fortunately the most useful reagent from the above eliminations turns



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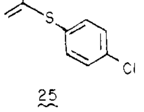

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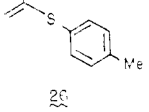

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(19) B-T. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 852, 867 (1977); B. Harirchian and P. D. Magnus, *J. Chem. Soc., Chem. Commun.*, 522 (1977); M. van der Leij and B. Zwanenberg, *Tetrahedron Lett.*, 3383 (1978).

(20) For the use of vinyltrimethylsilane as an ethylene equivalent in a preliminary communication of part of this work, see F. Cooke, J. Schwindeman, and P. D. Magnus, *Tetrahedron Lett.*, 1995 (1979).

(21) D. N. Harpp and P. Mathiaparanam, *J. Org. Chem.*, **37**, 1367 (1972).

(22) For references to the preparation of arylsulfenyl chlorides, see F. Kurzer and J. R. Powell, *Org. Synth.*, **4**, 934 (1963); T. Zincke and F. Farr, *Justus Liebigs Ann. Chem.*, **391**, 55 (1912); N. Kharasch, G. I. Gleason, and C. M. Buess, *J. Am. Chem. Soc.*, **72**, 1796 (1950). See also ref 17.

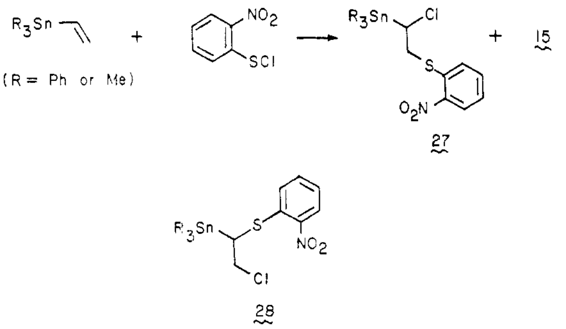
(23) G. H. Schmid and P. H. Fitzgerald, *J. Am. Chem. Soc.*, **93**, 2547 (1971).

(24) L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 485 (1946); L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, *ibid.*, **68**, 488 (1946).

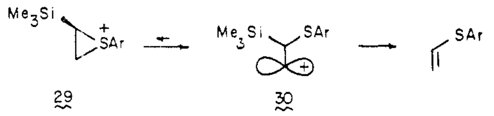
(25) See ref 19; D. Seebach, M. Kolb, and B-Th. Gröbel, *Chem. Ber.*, **106**, 2277 (1973); *Tetrahedron Lett.*, 3171 (1974); *Angew. Chem., Int. Ed. Engl.*, **12**, 69 (1973); D. Seebach, B-Th. Gröbel, A. K. Beck, M. Braun, and K-H. Geib, *Angew. Chem.*, **84**, 476 (1972); P. F. Jones and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 526 (1972); E. J. Corey and A. P. Kozikowski, *Tetrahedron Lett.*, 925 (1975); J. L. Herrman, J. E. Richman, P. J. Wepplo, and R. H. Schlessinger, *ibid.*, 4707 (1973); J. L. Herrman, G. R. Kieczykowski, R. F. Romant, P. J. Wepplo, and R. H. Schlessinger, *ibid.*, 4711 (1973); T. Oishi, H. Takechi, and Y. Bau, *Tetrahedron Lett.*, 3757 (1974).

(26) H. Oediger, F. Moller and Fiter, *Synthesis*, 591 (1972).

Scheme III



Scheme IV



out to be 24, which is the one that is most readily prepared. An initial description of the use of 24 as a reagent is shown later.

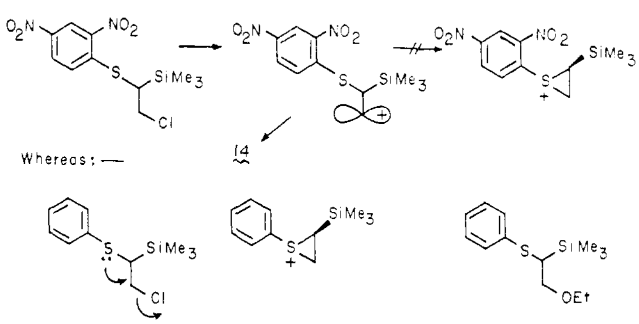
Discussion

Before discussing the mechanistic aspects of the synthetic procedures described above, we should note that the reaction of arylsulfenyl halides with vinyltriphenylstannane has been comprehensively studied[27] and should be compared with the results obtained here. Vinyltriphenylstannane and vinyltrimethylstannane react with 2-nitrophenylsulfenyl chloride to give the Markownikoff adduct **27** along with vinyl 2-nitrophenyl sulfide (**15**) as a minor product (Scheme III). The anti-Markownikoff adduct **28** was not isolated, although it is a probable precursor of **15**. The formation of the vinyl sulfide **15** is suggestive of the β elimination of the elements of triphenyl- or trimethylstannyl chloride, by analogy with β-halo silanes.[24] Presumably the stannyl group, especially the triphenylstannyl group, can tolerate the buildup of positive charge adjacent to itself since **27** is the major product.

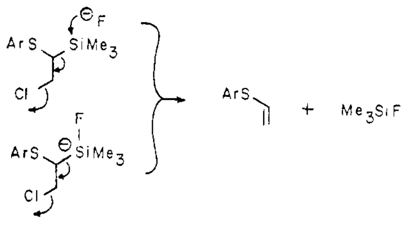
The reaction between vinyltrimethylsilane and arylsulfenyl chlorides to give the 2-chloro adducts **9**–**13** is best explained by the formation of the intermediate episulfonium ion **29** (Scheme IV).[28] Collapse of the episulfonium ion **29** to a vinyl aryl sulfide, in a concerted process, is precluded since the Si–C bond is orthogonal to the C–S bond. If there is any buildup of positive charge β to the trimethylsilyl group, as in **30**, and in the same plane as the C–Si bond, the trimethylsilyl group would be eliminated to give a vinyl sulfide.[29] In general we have observed that the so-called β effect is readily dominated by soft-polarizable heteroatoms.[29]

Solvolysis of the adducts **9** and **10** in aqueous ethanol gave the vinyl sulfides **14** and **15**, whereas the adducts **11**, **12**, and **13** gave the 2-ethoxy adducts **19** (Scheme V). Episulfonium ion participation in the 2,4-dinitro and 2-nitro adducts **9** and **10** is not so dominant as in the adducts **11**, **12**, and **13** since the electron-deficient nitroaryl groups inhibit the electron-donating ability of the attached sulfur atom. As a result, the β-chloro atom in the adducts **9** and

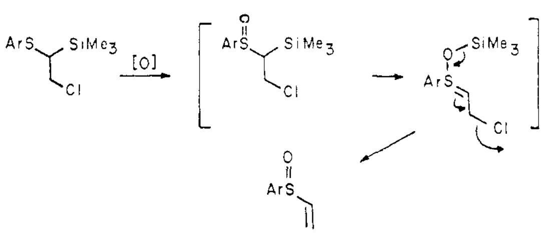
Scheme V



Scheme VI



Scheme VII



10 ionizes with little, if any, sulfonium ion formation, and the trimethylsilyl group can orient itself in the same plane as the developing β-carbonium ion. In this way the trimethylsilyl group is lost to give **14** and **15**. If sulfonium ion participation is prevalent, as in the cases of **11**, **12**, and **13**, the C–Si σ orbitals are orthogonal to the C–S σ orbitals; consequently the trimethylsilyl group is not lost, and the sulfonium ion is opened in a conventional S_N2 mode by ethanol to give the 2-ethoxy adducts **19**. The reaction of the β-chloro adducts with potassium fluoride operates by initial attack of the fluoride ion on the Si atom. The subsequent elimination of chloride ion to give the vinyl sulfides may be concerted with this process or involve a pentacoordinate Si intermediate. Either way the driving force is supplied by the extremely strong Si–F bond (Scheme VI).[30]

The direct oxidation of the 2-chloroethyl adduct **9** with *m*-chloroperbenzoic acid to give the vinyl sulfoxide **21** may be merely an oxidation to the 2-chloroethyl sulfoxide, followed by the elimination of the elements of trimethylsilyl chloride (Scheme VII). An attractive alternative involves the silyl-Pummerer rearrangement[31] which, in view of the conditions required to produce the vinyl sulfides (F^- or EtOH), is the preferred explanation.

Synthesis of Fused Cyclopentenones. The ability to conduct intermolecular Friedel–Crafts reactions with simple alkenes of low nucleophilicity, such as ethylene, is at best limited,[32] and in certain cases impossible.[33] For the

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[27] J. L. Wardell, *J. Chem. Soc., Dalton Trans.*, 1786 (1975); J. L. Wardell and S. Ahmed, *J. Organomet. Chem.*, **78**, 395 (1974).

[28] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964); N. A. Smit, M. Z. Krimer, and E. A. Vorobeva, *Tetrahedron Lett.*, 2451 (1975).

[29] See ref 8 and 24 and E. Ehlinger and P. D. Magnus, *J. Chem. Soc., Chem. Commun.*, 421 (1979).

[30] Si–F ca. 140 kcal mol^{-1}. E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements", Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, 1968.

[31] E. Vedejs and M. Mullins, *Tetrahedron Lett.*, 2017 (1975), and references cited therein. For the Se analogue, see H. J. Reich and S. K. Shah, *J. Org. Chem.*, **42**, 1773 (1977).

Scheme VIII

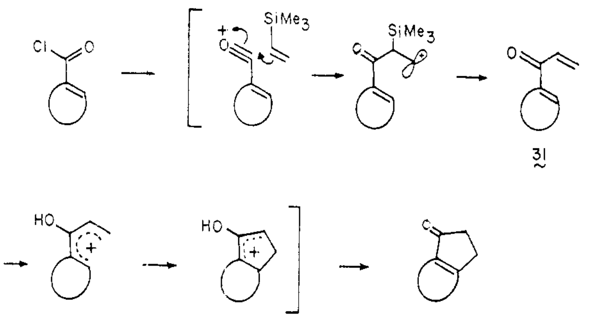
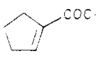
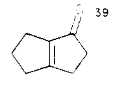
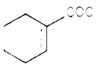
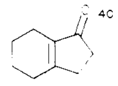
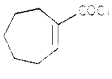
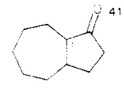
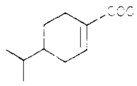
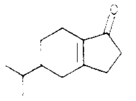
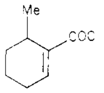
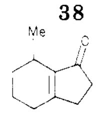
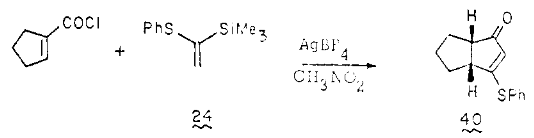


Table I

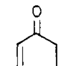
substrate	product	yield, %
	 35	52.5
	 36	46.0
	 37	32.0
	 38	56.0
	 39	63.5

reasons outlined in the first part of this paper, vinyltrimethylsilane should serve as an ethylene equivalent when reacted with α,β-unsaturated acid chlorides in the presence of a Lewis acid.[7,34] The above reaction should lead to a dienone **31**, which can enter into the Nazarov reaction[35] and thus provide a synthesis of certain cyclopentenones,[36] as shown in Scheme VIII. Of a number of Lewis acids examined ($AlCl_3$, $TiCl_4$, and BF_3), we found stannic tetrachloride to be the most effective in minimizing byproducts; in particular, the dienone **31** was readily transformed into the β-chloro adduct **32** when titanium tetrachloride was used.

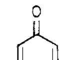
Scheme IX



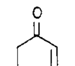
When the cyclic α,β-unsaturated acid chlorides listed in Table I were treated with vinyltrimethylsilane in the presence of stannic tetrachloride in dichloromethane, initially at −70 °C, and then warmed to 20 °C, a clean reaction took place to give the fused cyclopentenones listed. Acyclic α,β-unsaturated acid chlorides such as 3,3-dimethylacryloyl chloride gave mixtures of the β-chloro adduct **32** and the dienone **33**. No discernible amount of 4,4-dimethylcyclopentenone (**34**) could be detected. Other acyclic α,β-unsaturated acid chlorides such as cinnamoyl chloride and crotonyl chloride gave similar results. Consequently the reaction to make cyclopentenones is restricted to bicyclic systems in yields that average 50%. We have chosen substrates that are not highly substituted to avoid rearrangement reactions[37] that are so commonly associated with the Friedel–Crafts–Kondakov reaction.[38] In this way the bicyclo[*n*.3.0]enones listed below are available in a single-step procedure. In should be noted that previous routes to **35**, **36**, and **37** involve multistep and low overall yield procedures.[39-42] For the systems reported (**35**–**39**) we have not detected dienone intermediates **31**, although for the acyclic case above **33** was formed. No double bond isomers of **35**–**39** were observed in the crude products (NMR), and no angular methyl isomers of **39** were evident.



32



33



34

The two synthetic uses of vinyltrimethylsilane described here to prepare vinyl aryl sulfides, their derivatives, and fused cyclopentenones demonstrate the viability of using a simple silicon based reagent in synthesis. In conclusion, a brief mention is made of another reagent whose preparation is described here, namely 1-(trimethylsilyl)-1-(phenylthio)ethylene (**24**). Cyclopentenecarboxylic acid chloride in nitromethane at −70 °C was treated with silver

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(32) G. Olah in "Friedel–Crafts and Related Reactions", Vol. 3, Part 2, C. D. Nenitzescu and A. T. Balaban, Eds., Wiley, New York, 1963, p 1033; N. C. Deno and H. Chafetz, *J. Am. Chem. Soc.*, **74**, 3940 (1952); J. F. Norris and H. B. Couch, *ibid.*, **42**, 2329 (1920); T. Matsumoto, T. Nishida, and K. Hata, *J. Org. Chem.*, **23**, 106 (1958); H. T. Taylor, *J. Chem. Soc.*, 3922 (1958).

(33) A. P. Mesheryakov and L. V. Petrova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 98 (1950).

(34) For an extensive review of the Friedel–Crafts acylation of alkenes, see J. K. Groves, *Chem. Soc. Rev.*, 73 (1972).

(35) N. I. Nazarov and I. I. Zaretskaya, *Zh. Obshch. Khim.*, **27**, 693 (1957); I. N. Nazarov, *Usp. Khim.*, 18, 377 (1949); I. N. Nazarov and I. V. Torgov, *Bull. Acad. Sci. URSS Cl. Sci. Chim.*, 495 (1947); *Chem. Abstr.*, **42**, 7735 (1963); I. N. Nazarov and I. I. Zaretskaya, *ibid.*, 200 (1942); S. G. Matsoyan, M. G. Avetyan, and E. G. Darbinyan, *Izv. Akad. Nauk. Arm. SSR, Khim. Nauk.*, **17** (4) (1964); *Chem. Abstr.*, **45**, 6572 (1965); R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970; T. S. Sorensen, *J. Am. Chem. Soc.*, **89**, 3784 (1967); N. C. Deno, C. V. Pittman, Jr., and J. O. Turner, *ibid.*, **87**, 2153 (1965); G. Ohloff, K. H. Schulte, and E. Demole, *Helv. Chim. Acta*, **54**, 2813 (1971).

(36) For recent methods of cyclopentenone and cyclopentanone annulation, see M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, **99**, 5508 (1977), and references cited therein; B. M. Trost and D. E. Kelley, *ibid.*, **98**, 248 (1976); R. A. Ellison, *Synthesis*, 397 (1973); T. Hiyama, M. Shinoda, and H. Nozaki, *Tetrahedron Lett.*, 771 (1978); M. Karpf and A. S. Drieding, *Helv. Chim. Acta*, **59**, 1226 (1976); W. Hoffman and N. Muller, *Tetrahedron Lett.*, 3585 (1976); R. M. Jacobson, R. A. Raths, and J. H. McDonald, *J. Org. Chem.*, **42**, 2545 (1977); R. M. Jacobson and G. P. Lahm, *ibid.*, **44**, 462 (1979); G. A. MacAlpine, R. A. Raphael, A. Shaw, A. W. Taylor, and H-J. Wild, *J. Chem. Soc., Perkin Trans. 1*, 410 (1976).

(37) L. Otvos and H. Tudos, *Chem. Ind.* (*London*), 1140 (1960); L. Rand and R. J. Dolinski, *J. Org. Chem.*, 31, 3063 (1966). See also ref 34.

(38) I. L. Kondakov, *Russ. Phys. Chem. Soc.*, **24**, 309 (1892); *Bull. Soc. Chim. Fr.*, **7**, 576 (1892).

(39) H. Jones and H. T. Taylor, *J. Chem. Soc.*, 4017 (1959); S. Dev, *J. Indian Chem. Soc.*, **34**, 169 (1957); S. Dev and C. Rai, *ibid.*, 34, 266 (1957); S. B. Kulkarni and S. Dev, *Tetrahedron*, 545 (1968).

(40) S. Dev, *Chem. Ind.* (*London*), **32**, 255 (1955); D. W. Mathieson, *J. Chem. Soc.*, 177 (1951); 3248 (1953); W. S. Johnson, C. E. Davis, R. H. Hunt, and G. Stork, *J. Am. Chem. Soc.*, **70**, 3021 (1948); R. Bishop and W. Barker, *Tetrahedron Lett.*, 2375 (1973).

(41) G. Büchi and P. A. Plattner, *Helv. Chim. Acta*, **29**, 1608 (1946).

(42) References to the synthesis of cyclopentenones using inter- or intramolecular Friedel–Crafts reactions: G. Baddeley, H. T. Taylor, and W. Pickles, *J. Chem. Soc.*, 124 (1953); C.-K. Chuang, Y-L. Tien, C-M. Ma, *Ber.*, **69**, 1494 (1936); S. Dev, *J. Indian Chem. Soc.*, **33**, 703 (1956); J.-M. Conia and M.-L. Leriverend, *Tetrahedron Lett.*, 2101 (1968); G. J. Martin, C. Rabiller, and G. Malron, *ibid.*, 3131 (1970); G. J. Martin and G. Daviand, *Bull. Soc. Chim. Fr.*, 3098 (1970); R. Jacquier, M. Mousseron, and S. Boyer, *ibid.*, 1653 (1956); A. A. Schegolev, W. A. Smit, G. V. Roitburd, and V. F. Kucherov, *Tetrahedron Lett.*, 3373 (1974).

tetrafluoroborate, followed by **24** while the temperature was maintained at −70 °C, and then warmed to 20 °C to give **40** (Scheme IX). The development and synthetic potential of this new annulation procedure will be described in detail later.[43]

Experimental Section

Melting points were measured on a Fisher-Johns hot-stage melting point apparatus. All melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer 267 grating spectrometer as thin films for liquids and solutions in $CHCl_3$ for solids. Nuclear magnetic resonance (NMR) spectra were taken on an EM-360 60 MHz NMR spectrometer. Chemical shifts are reported in parts per million (δ) relative to Me_4Si (0.0 ppm) as an internal standard with $CDCl_3$ as solvent unless otherwise stated. Mass spectra were recorded on an A.E.I. MS-9 mass spectrometer.

All solvents were purified prior to use by standard techniques. Arylsulfenyl chlorides were prepared by standard methods.[17,21,22]

2-Chloro-1-(trimethylsilyl)ethyl 2,4-Dinitrophenyl Sulfide (9). To a cooled (−76 °C) suspension of 2,4-dinitrophenylsulfenyl chloride (2.34 g, 10.0 mmol) in dry dichloromethane (15 mL) was added trimethylvinylsilane (1.0 g), in dichloromethane (1.0 mL). The mixture was allowed to warm to 20 °C and stirred for 15 h. Evaporation and filtration of the residue through silica gel in dichloromethane gave the adduct **9** (3.18 g, 95.2%): mp 77–78.5 °C (from petroleum ether, bp 100–130 °C); ν_{max} 1610, 1465, 1345, 860, 745 cm^{-1}; NMR δ 2.80 (1 H, t, J = 6 Hz), 3.50 (1 H, d, J = 6 Hz), 3.65 (1 H, J = 6 Hz), 7.30 (1 H, d, J = 9 Hz), 8.09 (1 H, q, J = 9 Hz, 3 Hz), 8.70 (1 H, d, J = 3 Hz); the 9 H singlet of Me_3Si was used as a reference. Anal. Calcd for $C_{11}H_{15}N_2O_4ClSiS$: C, 39.45; H, 4.52; S, 9.57. Found: C, 39.36; H, 4.50; S, 9.56.

2-Chloro-1-(trimethylsilyl)ethyl 2-Nitrophenyl Sulfide (10). To a suspension of 2-nitrophenylsulfenyl chloride (1.896 g, 10 mmol) in dry dichloromethane (25 mL) at −76 °C was added vinyltrimethylsilane (1.00 g) in dry dichloromethane (1.0 mL). The mixture was allowed to warm to 20 °C and stirred for 20 h. The above mixture was evaporated under reduced pressure to approximately 5 mL and filtered through silica gel (2 × 14 cm), eluting with dichloromethane. Evaporation of the eluate gave a yellow residue that slowly crystallized, giving the adduct **10** (2.73 g, 94%): mp 36–37 °C (from petroleum ether, bp 100–130 °C), ν_{max} 1590, 1510, 1255, 853, 845, and 730 cm^{-1}; NMR δ 2.70 (1 H, dd, J = 6 Hz), 3.50 (2 H, dd, J = 6 Hz), 7.24–7.65 (3 H, m), 7.70 (1 H, d); the 9 H singlet of Me_3Si was used as a reference. Anal. Calcd for $C_{11}H_{16}NO_2SSiCl$: S, 11.06. Found: S, 11.28. M^+ calcd: 289.036. Found: 289.037.

2-Chloro-1-(trimethylsilyl)ethyl Phenyl Sulfide (11). To a solution of phenylsulfenyl chloride (1.44 g, 10 mmol) at −76 °C in dichloromethane (20 mL) was added vinyltrimethylsilane (1.00 g). The mixture was warmed to 20 °C and left for 15 h. The solution was evaporated, and the residue filtered through silica gel in dichloromethane. Evaporation gave an oil that was distilled to give the sulfide 11 (2.30 g, 94%): mp 36–38 °C; bp 93 °C (0.11 mm); ν_{max} 1580, 1480, 1438, 1250, 840, 730, 690 cm^{-1}; NMR δ 2.57 (1 H, t, J = 6 Hz), 3.51 (1 H, d, J = 6 Hz), 7.05 (5 H, m); the 9 H singlet of Me_3Si was used as a reference. Anal. Calcd for $C_{11}H_{17}SSiCl$: C, 54.09; H, 6.96. Found: C, 54.00; H, 6.84. This procedure is readily scaled up to 0.14 mol with no reduction in yield.

2-Chloro-1-(trimethylsilyl)ethyl 4-Chlorophenyl Sulfide (12). To a solution of *p*-chlorothiophenol (7.76 g, 53.7 mmol) in dry dichloromethane (10 mL) was added a suspension of *N*-chlorosuccinimide (7.14 g, 53.7 mmol) in dichloromethane (100 mL) at such a rate as to maintain reflux. The suspension was cooled to 20 °C, stirred for 1 h and then cooled to −78 °C, and treated with vinyltrimethylsilane (5.37 g) in dichloromethane (1.0 mL). The mixture was warmed to room temperature and held at this temperature for 2 h. Filtration and evaporation gave a yellow oil which was chromatographed over deactivated silica gel eluting with dichloromethane to give **12** (13.10 g, 87%): bp 118 °C (0.35 mm); ν_{max} 2960, 2900, 1580, 1260, 1100, 1020 and 850 cm^{-1}; NMR δ 2.47 (1 H, t, J = 6 Hz), 3.50 (2 H, d, J = 6 Hz), 7.07 (4 H, q); the 9 H singlet of Me_3Si was used as a reference. Anal. Calcd for $C_{11}H_{16}SiSCl_2$: C, 47.48; H, 5.75. Found: C, 47.35; H, 5.68.

2-Chloro-1-(trimethylsilyl)ethyl *p*-Tolyl Sulfide (13). *p*-Tolylsulfenyl chloride [prepared from *p*-thiocresol (6.67 g) and *N*-chlorosuccinimide (7.14 g)] in dichloromethane (110 mL) at −78 °C was treated with vinyltrimethylsilane (5.36 g). The mixture was warmed to 20 °C, stirred for 2 h, and then filtered. The filtrate was evaporated and the residue filtered through silica gel to give **13** (13.0 g, 94%): ν_{max} 2960, 1500, 1260, 1025, 855, 820 and 705 cm^{-1}; NMR δ 0.00 (9 H, s), 2.08 (3 H, s), 2.50 (1 H, t, J = 6 H), 3.52 (2 H, d, J = 6 Hz), 7.02 (4 H, q). Anal. Calcd for $C_{12}H_{19}SiSCl$: C, 55.53; H, 7.33. Found: C, 55.50; H, 7.28.

2,4-Dinitrophenyl Vinyl Sulfide (14). Compound **9** (0.870 g) in 30% aqueous ethanol (50 mL) was stirred at 65 °C for 24 h. The mixture was cooled and filtered to give the vinyl sulfide 14[27] (0.510 g, 87%): mp 72–74 °C (from methanol); ν_{max} 1585, 1450, 1340, 830, and 735 cm^{-1}; NMR δ 5.98 (1 H, d, J = 9 Hz), 6.00 (1 H, d, J = 17 Hz), 6.70 (1 H, dd, J = 9, 17 Hz), 7.65 (1 H, J = 9 Hz), 8.40 (1 H, q, J = 9 and 3 Hz), and 9.05 (1 H, J = 3 Hz); M^+ m/e calcd for $C_8H_6N_2O_4S$ 226.005, found 226.005.

The adduct **9** (1.0 g) in dimethyl sulfoxide (5 mL) was treated with potassium fluoride dihydrate (1.1 equiv) at room temperature. The brown solution was held at 105 °C for 1 h and then poured into water (10 mL)–dichloromethane (10 mL). The organic phase was washed with water (2 × 50 mL) and saturated aqueous sodium chloride (50 mL). The dichloromethane layer was dried ($MgSO_4$) and evaporated and the residue chromatographed over silica gel by eluting with dichloromethane to give the vinyl sulfide 14 (560 mg, 83%): mp 72–74 °C (from methanol).

Other procedures for the preparation of 2,4-dinitrophenyl vinyl sulfide (14) are as follows.

A suspension of the adduct **9** (1.0 g, 2.99 mmol) in methanol (15 mL) at 0 °C was treated with silver trifluoroacetate (0.659 g). The mixture was warmed to 20 °C and stirred for 12 h. The suspension was poured into water (50 mL)–dichloromethane (20 mL). The dichloromethane layer was washed with water (50 mL) and saturated aqueous sodium chloride solution (50 mL), dried ($MgSO_4$), and evaporated to give the vinyl sulfide **14** (0.676 g, 100%): mp 72–74 °C.

To a solution of the adduct **9** (1.0 g, 2.99 mmol) in dry tetrahydrofuran (15 mL) was added dry potassium fluoride (0.174 g). After 12 h at 20 °C the mixture was poured into water (50 mL)–dichloromethane (50 mL). The dichloromethane layer was washed with saturated aqueous sodium chloride (3 × 50 mL) and dried ($MgSO_4$). Evaporation of the dried extract gave the vinyl sulfide **14** (0.676 g, 100%).

2-Nitrophenyl Vinyl Sulfide (15). The adduct **10** (1.51 g) was suspended in 30% aqueous ethanol (80 mL) and held at 50 °C for 48 h. The mixture was evaporated and the residue dissolved in dichloromethane, washed with saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated. Distillation of the residue gave 2-nitrophenyl vinyl sulfide (**15**) (0.93 g, 98.6%): bp 110 °C (0.45 mm); mp 25.5–26 °C; ν_{max} 1587, 1565, 1515, 1340, 1305, 1250, 1105, 855, 780, 735 cm^{-1}; NMR δ 5.76 (1 H, d, J = 9 Hz), 5.84 (1 H, d, J = 17 Hz), 6.57 (1 H, dd, J = 9 and 17 Hz), 7.56–7.20 (3 H, m), 8.10 (1 H, d, J = 8 Hz); M^+ m/e calcd for $C_8H_7NO_2S$ 181.020, found 181.020.

Phenyl Vinyl Sulfide (16). To a solution of 2-chloro-1-(trimethylsilyl)ethyl phenyl sulfide (**11**) (1.00 g, 4.10 mmol) in dry tetrahydrofuran (5.0 mL) was added anhydrous potassium fluoride (0.238 g). The mixture was stirred at 20 °C for 12 h and the solvent removed by distillation. The residue was dissolved in ether (30 mL) and water (30 mL) added. The ether layer was washed with saturated aqueous sodium chloride solution (2 × 30 mL), dried ($MgSO_4$), and evaporated to give phenyl vinyl sulfide (**16**) (0.520 g, 93%): bp 92 °C (20 mm).[44] IR and NMR were in agreement with the literature.

***p*-Chlorophenyl Vinyl Sulfide (17).** To a solution of the

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[43] This represents a preliminary result, and a more detailed description of this reaction will be reported in due course.

[44] T. Okuyama, M. Masago, M. Nakada, and T. Fueno, *Tetrahedron*, 2379 (1977); C. C. Price and H. Morita, *J. Am. Chem. Soc.*, **75**, 4747 (1953); W. Verboom, J. Meijer, and L. Brandsma, *Synthesis*, 577 (1978); W. E. Parham, F. D. Blake, and D. R. Theissen, *J. Org. Chem.*, **27**, 2415 (1962); B. Belleau, *J. Med. Pharm. Chem.*, 1, 327 (1957).

adduct **12** (2.3 g) in dimethyl sulfoxide (15 mL) was added potassium fluoride dihydrate (674 mg). The above mixture was stirred at 20 °C for 4 h and then heated at 70 °C for 2.5 h. The mixture was cooled to 20 °C and poured into water (175 mL)–dichloromethane (75 mL). The organic layer was washed with water (4 × 100 mL) and saturated aqueous sodium chloride (75 mL), dried ($MgSO_4$), and evaporated to give a pale yellow oil which was distilled in vacuo to give **17**[44] (1.40 g, 99%): bp 92 °C (7.0 mm); NMR δ 5.30 (1 H, d, $J = 17$ Hz), 5.34 (1 H, d, $J = 10$ Hz), 6.5 (1 H, q, $J = 17$ and 10 Hz), 7.24 (4 H, s). Anal. Calcd for C_8H_7SCl: C, 56.14; H, 4.09. Found: C, 56.37; H, 4.20.

***p*-Tolyl Vinyl Sulfide (18).** To a solution of the adduct **13** (2.28 g, 8.8 mmol) in dimethyl sulfoxide (12 mL) was added potassium fluoride dihydrate (0.827 g) and the mixture slowly warmed to 100 °C. After 1 h at 100 °C the mixture was poured into water (75 mL)/dichloromethane (75 mL). The organic phase was washed with water (2 × 70 mL) and saturated aqueous sodium chloride solution (2 × 40 mL), dried (Na_2SO_4), and evaporated to give a pale yellow oil which was distilled in vacuo to give **18**[44] (1.19 g, 90%): bp 69–71 °C (4 mm); ν_{max} 3030, 2920, 1570, 1490, 1095, 1020, 960, 880 and 810 cm^{-1}; NMR δ 2.24 (3 H, s), 5.15 (1 H, d, $J = 9$ Hz), 5.20 (1 H, d, $J = 17$ Hz), 6.45 (1 H, q, $J = 17$ and 9 Hz). Anal. Calcd for $C_9H_{10}S$: C, 71.95; H, 6.71. Found: C, 71.94; H, 6.73.

2-(Trifluoroacetoxy)-1-(trimethylsilyl)ethyl 2,4-Dinitrophenyl Sulfide (20). To a cooled (–76 °C) suspension of 2,4-dinitrophenylsulfenyl chloride (2.34 g, 10.0 mmol) in dry dichloromethane (15 mL) was added silver trifluoroacetate (2.20 g). The mixture was stirred at –76 °C for 15 min and then treated with vinyltrimethylsilane (1.0 g) in dichloromethane (1 mL). The mixture was warmed to 20 °C and allowed to stir for 29 h. The suspension was filtered, and the filtrate evaporated under reduced pressure to give the adduct **20** (3.20 g, 77%): mp 78–80 °C (from petroleum ether, bp 100–130 °C); ν_{max} 1787, 1340, 1255, 1220, 1173, 1150, 853, 843, 835 and 740 cm^{-1}; NMR δ 2.80 (1 H, t, $J = 6$ Hz), 4.25 (1 H, q, $J = 6$ Hz), 7.30 (1 H, d, $J = 9$ Hz), 7.87 (1 H, dd, $J = 9$, 3 Hz), 8.60 (1 H, d, $J = 3$ Hz). Anal. Calcd for $C_{13}H_{15}N_2O_6F_3SiS$ C, 37.86; H, 3.67; S, 7.78. Found: C, 37.81; H, 3.68; S, 7.83.

2,4-Dinitrophenyl Vinyl Sulfoxide (21). 2-Chloro-1-(trimethylsilyl)ethyl 2,4-dinitrophenyl sulfide (**9**) (0.470 g, 1.41 mmol) in dry dichloromethane (15 mL) at 0 °C was treated with *m*-chloroperbenzoic acid (0.256 g). The mixture was stirred at 0 °C for 1 h and then at 20 °C for 1 h. After the reaction mixture was cooled to 0 °C, it was filtered and allowed to stand at –20 °C for 12 h. The mixture was filtered and the filtrate evaporated. The residue was crystallized from methanol to give the sulfoxide **21** (9.324 g, 95%): mp 92–94 °C; ν_{max} 3080, 3050, 1600, 1530, 1460, 1344, 1062, 1035, 835, 750, 740, and 680 cm^{-1}; NMR δ 5.83 (1 H, d, $J = 8.5$ Hz), 6.15 (1 H, d, $J = 16$ Hz), 6.87 (1 H, dd, $J = 8.5$ and 16 Hz), 8.2 (1 H, d, $J = 8.5$ Hz), 8.55 (1 H, dd, $J = 8.5$ and 2.0 Hz), 8.86 (1 H, d, $J = 2.0$ Hz); M$^+$, *m/e* calcd for $C_8H_6N_2O_5S$ 242.000, found 242.000.

To a solution of 2,4-dinitrophenyl vinyl sulfide (440 mg) in dry dichloromethane (15 mL) at –5 °C was added *m*-chloroperbenzoic acid (396 mg). After 1 h at –5 °C the mixture was warmed to 20 °C and 2 h later cooled to 0 °C and filtered. The filtrate was washed with saturated aqueous sodium carbonate solution (50 mL), aqueous sodium bisulfite solution (50 mL), and saturated aqueous sodium chloride solution (50 mL). The dried ($MgSO_4$) dichloromethane solution was evaporated to give the sulfoxide **21** (0.49 g, 100%): mp 92–94 °C.

2-Nitrophenyl Vinyl Sulfoxide (22). The vinyl sulfide **15** (0.91 g) in dichloromethane (15 mL) at 0 °C was treated with *m*-chloroperbenzoic acid (1.02 g). After the reaction mixture was stirred at 20 °C for 1 h, it was poured into saturated aqueous sodium carbonate. The dichloromethane layer was successively washed with saturated aqueous sodium bicarbonate (20 mL), sodium bisulfite (20 mL), and saturated aqueous sodium chloride solution (20 mL). The dichloromethane layer was dried ($MgSO_4$) and evaporated to give the sulfoxide **22** (0.81 g, 82%): mp 68–69 °C (from petroleum ether, bp 100–130 °C); ν_{max} 1590, 1530, 1075 cm^{-1}; NMR δ 5.40 (1 H, d, $J = 9$ Hz), 6.09 (1 H, d, $J = 16$ Hz), 6.70 (1 H, dd, $J = 9$ and 16 Hz), 7.10 (2 H, m), 7.80 (2 H, m). Anal. Calcd for $C_8H_7NO_3S$: C, 48.72; H, 3.58; N, 7.10. Found: C, 48.72; H, 3.58; N, 7.09.

Vinyl Phenyl Sulfoxide (23). Vinyl phenyl sulfide (**16**) (20.0 g) in dichloromethane (250 mL) at –78 °C was treated with a solution of *m*-chloroperbenzoic acid (25.4 g) in dichloromethane (100 mL) added dropwise over 0.5 h. The above mixture was poured into saturated aqueous sodium bicarbonate (300 mL) and extracted with dichloromethane (3 × 250 mL). The extract was washed with water (3 × 250 mL), dried ($MgSO_4$), and evaporated in vacuo to give **23** (93%):[17] bp 98 °C (0.6 mm); ν_{max} 3025, 1720, 1680, 1480, 1440, 1045, 750, 690 cm^{-1}; NMR δ 5.63–6.17 (2 H, m), 6.44–6.87 (1 H, m), and 7.10–7.55 (5 H, m).

1-(Trimethylsilyl)-1-(phenylthio)ethylene (24). 2-Chloro-1-(trimethylsilyl)ethyl phenyl sulfide (**11**) (3.0 g, 12.3 mmol) in dry ether (15 mL) at 0 °C was treated with DBN (1.52 g) in dry ether (1 mL). The mixture was stirred at 20 °C for 14 h and filtered, and the filtrate was washed with 5% aqueous hydrochloric acid (2 × 15 mL), saturated aqueous sodium bicarbonate (20 mL), and saturated aqueous sodium chloride (15 mL). The ether layer was dried ($MgSO_4$) and evaporated to give 1-(trimethylsilyl)-1-(phenylthio)ethylene (**24**) (2.36 g, 92%): bp 45 °C (0.025 mm); ν_{max} 3050, 2960, 1580, 1480, 1440, 1260, 1080, 1030, 840, 750, 680 cm^{-1}; NMR δ 0.10 (9 H, s), 5.20 (1 H, s), 5.40 (1 H, s), 7.0–7.3 (5 H, m). Anal. Calcd for $C_{11}H_{16}SSi$: C, 63.39; H, 7.73; S, 15.38; Si, 13.47. Found: C, 63.51; H, 7.87; S, 15.15; Si, 13.47.

1-(Trimethylsilyl)-1-(phenylthio)ethylene (**24**) is also readily prepared from vinyl phenyl sulfide (**16**) as follows: freshly distilled diisopropylamine (3.1 mL) was treated with *n*-butyllithium in hexane (10.5 mL, 2.1 M) at –78 °C under dry nitrogen. After the above slurry was stirred at –78 °C for 10 min, phenyl vinyl sulfide (3.0 g, 22 mmol) in dry tetrahydrofuran (10 mL) was added and the mixture stirred at –78 °C for 15 min. Trimethylchlorosilane (3.4 mL) was added and the mixture kept at –78 °C for 15 min and then quenched with saturated aqueous ammonium chloride solution (25 mL). Extraction with dichloromethane (3 × 50 mL), drying ($MgSO_4$), evaporation, and distillation gave **24** (97%).

1-(Trimethylsilyl)-1-(*p*-chlorophenylthio)ethylene (25). The adduct **12** (1.22 g, 4.37 mmol) in dry ether (15 mL) at 0 °C was treated with DBN (0.541 g). The mixture was stirred at 20 °C for 12 h and filtered and the filtrate washed with 5% aqueous hydrochloric acid (2 × 20 mL) and saturated aqueous sodium carbonate (20 mL). The dried ($MgSO_4$) organic phase was evaporated under vacuo to give **25** (0.85 g, 80.3%): NMR δ 5.05 (1 H, s), 5.30 (1 H, s), 7.10 (4 H, m). Small amounts (ca. 5%) of **17** were formed. Anal. Calcd for $C_{11}H_{15}SSiCl$: C, 54.54; H, 6.19. Found: C, 54.44; H, 6.15.

Bicyclo[3.3.0]-7-octen-1-one (35). Cyclopentene-1-carboxoyl chloride (12.00 g, 92 mmol)[45] and vinyltrimethylsilane (10.13 g, 101 mmol) in dry dichloromethane (100 mL) at –78 °C were warmed to –30 °C and then treated dropwise with stannic tetrachloride (26.35 g, 101 mmol). The temperature was maintained at –30 °C for 1 h, allowed to rise to room temperature, and then maintained at 25 °C until the ν_{max} 1695 cm^{-1} reached a maximum (6 h). The above mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic phase was washed with saturated aqueous sodium bicarbonate (100 mL), dried (Na_2SO_4), and evaporated in vacuo to give **35**[39] (5.90 g, 52.5%): bp 114–115 °C (13 mm); ν_{max} 2920, 2820, 1695, 1640, 1385 and 1025 cm^{-1}; NMR δ 2.82–2.15 (8 H, m), 2.15–1.6 (2 H, m); M$^+$ *m/e* calcd for $C_8H_{10}O$ 122.073, found 122.073, in agreement with literature values.

Bicyclo[4.3.0]-8-nonen-1-one (36). Cyclohexene-1-carboxoyl chloride (6.00 g, 42 mmol) and vinyltrimethylsilane (4.58 g, 46 mmol) in dry dichloromethane (40 mL) at –30 °C were treated dropwise with stannic tetrachloride (11.98 g, 46 mmol) at such a rate as to maintain the temperature at –30 °C. The above mixture was kept at –30 °C for 1 h, then allowed to warm to room temperature, and monitored as in the previous experiment. After 6 h the mixture was poured into water (50 mL) and extracted with dichloromethane (3 × 75 mL). The extract was washed with saturated aqueous sodium bicarbonate (50 mL), dried (Na_2SO_4),

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and evaporated in vacuo to give **36**[40] (2.67 g, 46%): bp 86–88 °C (0.3 mm); ν_{max} 2930, 2850, 1695, 1645, 1430, 1390, and 1270 cm^{-1}; NMR δ 2.65–1.85 (8 H, m) and 1.85–1.44 (4 H, m); M$^+$ m/e calcd for $C_9H_{12}O$ 136.089, found 136.089, in agreement with literature values.

Bicyclo[5.3.0]-9-decen-1-one (37). Cycloheptene-1-carboxoyl chloride (4.80 g, 30 mmol) and vinyltrimethylsilane (3.34 g, 34 mmol) were treated with stannic tetrachloride (8.43 g, 34 mmol) under the same conditions as above to give, after workup, **37**[41] (1.43 g, 32%): bp 91–94 °C (0.3 mm); ν_{max} 2900, 2840, 1685, 1635, 1438, 1190, and 1055 cm^{-1}; NMR δ 2.67–2.05 (8 H, m) and 2.05–1.15 (6 H, m); M$^+$ m/e calcd for $C_{10}H_{14}O$ 150.105, found 150.105, in agreement with literature values.

5-Isopropylbicyclo[4.3.0]-8-nonen-1-one (38). 4-Isopropylcyclohexene-1-carboxoyl chloride (4.00 g, 22 mmol) and vinyltrimethylsilane (2.51 g, 25 mmol) in dry dichloromethane (50 mL) at −30 °C were treated with stannic tetrachloride (6.50 g, 25 mL) under the same conditions as above to give, after workup, **38** (2.20 g, 56%): bp 110–112 °C (0.5 mm); ν_{max} 2960, 2920, 2870, 1700, 1650, 1395, and 1265 cm^{-1}; NMR δ 2.66–1.85 (8 H, m), 1.85–1.20 (4 H, m) and 0.90 (6 H, d, J = 7 Hz); M$^+$ m/e calcd for $C_{12}H_{18}O$ 178.136, found 178.136.

7-Methylbicyclo[4.3.0]-8-nonen-1-one (39). 6-Methylcyclohexene-1-carboxoyl chloride (5.70 g, 36 mmol) and vinyltrimethylsilane (4.10 g, 40 mmol) in dry dichloromethane (40 mL) at −30 °C were treated with stannic tetrachloride (10.68 g, 40 mmol) under the same conditions as above to give, after workup, **39** (3.43 g, 63.5%): bp 100–102 °C (0.5 mm); ν_{max} 2920, 2680, 1690, 1640, and 1390 cm^{-1}; NMR δ 2.70–2.00 (7 H, m), 2.00–1.30 (4 H, m) and 1.12 (3 H, d, J = 4.5 Hz); M$^+$ m/e calcd for $C_{10}H_{14}O$ 150.105, found 150.105. The above fused cyclopentenones were ≥95% pure (GLC).

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Registry No. **9**, 72610-19-6; **10**, 72610-20-9; **11**, 72610-21-0; **12**, 72610-22-1; **13**, 72610-23-2; **14**, 57682-85-6; **15**, 54848-82-7; **16**, 1822-73-7; **17**, 16411-16-8; **18**, 16336-54-2; **20**, 72622-64-1; **21**, 72622-65-2; **22**, 72622-66-3; **23**, 20451-53-0; **24**, 62762-20-3; **25**, 72622-67-4; **35**, 10515-92-1; **36**, 22118-00-9; **37**, 769-32-4; **38**, 72622-68-5; **39**, 67220-96-6; (2,4-dinitrophenyl)sulfenyl chloride, 528-76-7; trimethylvinylsilane, 754-05-2; (2-nitrophenyl)sulfenyl chloride, 7669-54-7; phenylsulfenyl chloride, 931-59-9; *p*-(chlorothio)phenol, 72622-69-6; *p*-tolylsulfenyl chloride, 933-00-6; cyclopentene-1-carboxoyl chloride, 59253-90-6; cyclohexene-1-carboxoyl chloride, 36278-22-5; cycloheptene-1-carboxoyl chloride, 72233-47-7; 4-isopropylcyclohexene-1-carboxoyl chloride, 72622-70-9; 6-methylcyclohexene-1-carboxoyl chloride, 72622-71-0; (4-chlorophenyl)sulfenyl chloride, 933-01-7.

Ozonolysis of Diphenylvinylene Carbonate. Synthesis and Thermolysis of Dibenzoyl Monoperoxycarbonate

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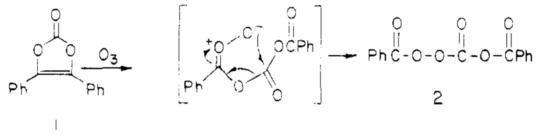
Dibenzoyl monoperoxycarbonate (2) was prepared by the reaction of diphenylvinylene carbonate (1) with ozone. The thermolysis of 2 in benzene gives products typical of the formation of benzoyloxy radicals. The reaction rate was investigated at different temperatures, and the activation parameters were determined ($\Delta H^{\ddagger}$ = 27.8 ± 1.2 kcal/mol, $\Delta S^{\ddagger}$ = 6.1 ± 3.5 eu). The thermolysis of 2 in the presence of the stable free radical galvinoxyl was investigated also. These experiments revealed that the fraction of radical escape from the solvent cage is 60 ± 5%.

Ozonolysis of sterically hindered olefins in some instances gives epoxides as well as ozonides and their derived products.[2] In contrast, our attempt to epoxidize the hindered olefin diphenylvinylene carbonate (1) with ozone gave the unusual rearranged peroxide dibenzoyl monoperoxycarbonate (2). Peroxycarbonate 2, to the best of our knowledge, is the first reported example of a diacyl monoperoxycarbonate. Its formation is simply understood in terms of intramolecular trapping of the intermediate carbonyl oxide proposed by Criegee to be formed in the normal ozonation of olefins.[3]



(1)

Peroxide 2 is related to benzoyl peroxide in that it can be prepared conceptually by inserting CO_2 between the carbonyl and phenyl groups of that well-known peroxide.[4] The products of the thermolysis of 2 in benzene are, in fact, similar to those obtained from the thermolysis of benzoyl peroxide.[5-7] However, the rate of reaction of 2 is significantly greater than that of benzoyl peroxide. The enthalpy and entropy of activation for the unimolecular decomposition of 2 suggest, moreover, that initial simultaneous two-bond cleavage occurs in this system.

Kiefer and Traylor[8] have concluded that formation of small molecules between the *tert*-butoxy radicals that result from the thermolysis of di-*tert*-butyl peroxide, di-*tert*-butyl hyponitrite, or di-*tert*-butyl peroxyoxalate decreases the ratio of in-cage to cage-escaped products. Comparison of benzoyl peroxide and 2 expands this study since a molecule of CO_2 is formed between the benzoyloxy radicals from 2.

Results and Discussion

Synthesis. The addition of excess ozone to a solution of diphenylvinylene carbonate in CH_2Cl_2 gives, upon evaporation of the solvent, a peroxidic, colorless solid. In CCl_4 solution this product exhibits strong IR absorptions at 1853 and 1787 cm^{-1}. Since no other diacyl monoperoxycarbonates have been reported, it is not possible to

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