by comparing its ir spectrum with that of an authentic sample.

Authentic **2a** was prepared by treating the known *endo*-norcarane-7-carboxylic acid[6,7] with diazomethane. The resulting ester analyzed correctly for $C_9H_{14}O_2$. Authentic 7-carbomethoxynorcarane displayed an absorption band in its ir spectrum at 1734 cm^{-1} as did **2a**. Its nmr spectrum exhibited absorptions at 3.58 ppm (3 protons, singlet) and 0.8–2.1 ppm (11 protons, multiplet).

When **1a** is treated with a 10% solution of potassium *tert*-butoxide in dimethyl sulfoxide,[2] *exo*-7-phenylnorcarane (**1b**) is obtained, which, after work-up and distillation, resulted in a sample of **1b** which was 97% pure. When **1b** was treated in turn with ozone, hydrogen peroxide,[5] and diazomethane, it furnished a 24% yield of *exo*-7-carbomethoxynorcarane (**2b**) and a 13% yield of methyl benzoate. The products were separated by preparative gas chromatography employing a 20% Carbowax 1500 column. Methyl benzoate was identified as before. Compound **2b** was identified as *exo*-7-carbomethoxynorcarane on the basis of a correct elemental analysis and by comparing its ir spectrum (1728 cm^{-1}, ester carbonyl) with that of an authentic sample.

Authentic *exo*-7-carbomethoxynorcarane was prepared in the same manner as its endo isomer. Authentic *exo*-7-carbomethoxynorcarane exhibits nmr absorptions at 3.57 ppm (3 protons, singlet) and 1.0–2.3 ppm (11 protons, multiplet). These data indicate that **1a** and **1b** are indeed the endo and exo isomers, respectively, of 7-phenylnorcarane, and are in complete agreement with the conclusions reached by Closs, Jensen, and Ledlie. We are presently investigating the ozonization of other bicyclo[*n*.1.0] systems as a function of structure and reaction temperature.

Experimental Section

An F & M gas chromatograph, Model 810, equipped with a 7 ft by 0.25 in. 20% Carbowax 1500 column operated at 125°, was employed for separation of methyl benzoate from *exo*-7-carbomethoxynorcarane. A 6 ft by 0.25 in. 30% SE-30 column was operated at 160° to achieve separation of methyl benzoate and *endo*-7-carbomethoxynorcarane. Ir spectra were obtained using a Beckman Model 10 grating ir spectrophotometer with potassium bromide cells. Nmr spectra were recorded in carbon tetrachloride with a Varian A-60 spectrometer employing tetramethylsilane as an internal reference. A Welsbach ozonator, Model T-816, generating a stream of 3% ozone at a flow of 1 l./min was used for all ozonolyses. The elemental analyses were performed by M-H-W Laboratories, Garden City, Mich. All boiling points are uncorrected.

Ozonolysis[5] of *endo*-7-Phenylnorcarane (1a).—A stream of 3% ozone was bubbled through a 250-ml gas wash bottle containing a magnetically stirred mixture of 2.0 g of **1a** (99% pure) in 100 ml of 95% acetic acid until a test in water showed no turbidity. The time required for this reaction when carried out at 25° was 2.5 hr. After completion of the reaction, 10 ml of 30% hydrogen peroxide was added, and the solution was allowed to stir at room temperature overnight. The mixture was then heated in an oil bath at 95° for 4 hr, the acetic acid removed by vacuum distillation, and the residue extracted four times with 5-ml portions of hot hexane. Evaporation of the hexane furnished 0.92 g of a mixture of two acids. These acids were treated with diazomethane and the resulting esters were separated by preparative gas chromatography employing a 6 ft by 0.25 in. column containing 30% SE-30 on Chromosorb P operated at 160°. The faster eluting compound (**3**) was proven to be methyl benzoate by comparison of its ir and nmr spectra with reference spectra. The slower eluting compound, **2a**, was collected and found to have ir and nmr spectra identical with those of an authentic sample of *endo*-7-carbomethoxynorcarane (see below). The yield of esters **2a** and **3** based on **1a** was 14 and 20%, respectively. The yields were calculated by comparing the area found under the vpc curves with those obtained from standard samples.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.21; H, 9.20.

Ozonolysis of *exo*-7-Phenylnorcarane (1b).—Ozonolysis of **1b** was carried out in exactly the same manner described for **1a**. A yield of 0.72 g of a mixture of two acids was obtained. These acids were treated with diazomethane and the resulting esters were separated by preparative gas chromatography employing a 7 ft by 0.25 in. column containing 20% Carbowax 1500 on Chromosorb P operated at 125°. The faster eluting compound (**3**) was proven to be methyl benzoate by comparison of its ir and nmr spectra with reference spectra. The slower eluting compound, **2b**, was collected and found to have ir and nmr spectra identical with those of an authentic sample of *exo*-7-carbomethoxynorcarane (see below). The yield of esters **2b** and **3** based on **1b** was 24 and 13%, respectively. The yields were calculated by comparing the area found under the vpc curves with those obtained from standard samples.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.16; H, 9.19.

***exo*-7-Carbomethoxynorcarane (2b).**—*exo*-Norcarane-7-carboxylic acid[6] was methylated by dissolving 5 g of the acid in 50 ml of ether and treating the solution with an excess of diazomethane.[8] The solution was allowed to stand in the dark for 30 min. The unreacted diazomethane was treated with a dilute solution of acetic acid in ether. The ether was evaporated and the residue distilled *in vacuo* to give 4.31 g (78%) of **2b**, bp 99° (15 mm), $n^{28}D$ 1.4700.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.30; H, 9.23.

***endo*-7-Carbomethoxynorcarane (2a).**—*endo*-Norcarane-7-carboxylic acid[6] was methylated in the same manner as its exo isomer except that only 0.4 g of the acid was used, and the reaction was allowed to stand in the dark for 2.5 hr after the diazomethane was added. A yield of 0.36 g (71%) of **2a**, bp 95° (15 mm), was isolated.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.03; H, 9.12.

Registry No.—**1a**, 10503-37-4; **1b**, 10503-36-3; **2a**, 36744-58-8; **2b**, 36744-59-9; **3**, 93-58-3.

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Cycloaddition Reactions of Vinylketene Thioacetals

FRANCIS A. CAREY* AND A. S. COURT

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22903

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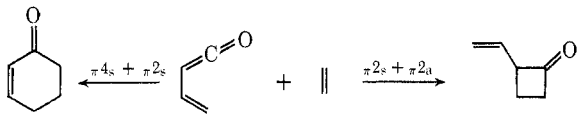
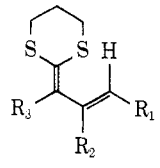
The relative unavailability of vinylketenes from readily available precursors coupled with their tendency to ring close has precluded their use in synthesis. An obvious application would be in cyclohexenone synthesis by Diels–Alder addition of olefins to a vinylketene, but here an additional complication arises in that vinylcyclobutanones could arise by a $_{\pi}2_s + {}_{\pi}2_a$ process in competition with the desired $_{\pi}4_s + {}_{\pi}2_s$ process.[1]

(1) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 163–168.



A solution to these problems can be found in the now-familiar approach of using stable reagents which bear the critical functionality masked in a fashion which permits the required reactions to occur.[2] In the work described here the vinylketene equivalents employed are unsaturated ketene thioacetals (vinylketene thioacetals) **1a–c**.



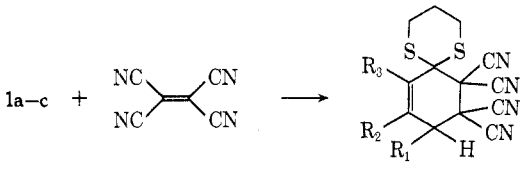
1

	R_1	R_2	R_3
a	CH_3	CH_3	H
b	Ph	H	H
c	$-(CH_2)_4-$		CH_3

These vinylketene thioacetals retain the diene system necessary for the 4 + 2 cycloaddition while the expected adducts of such reactions can be converted to cyclohexenones by a variety of hydrolytic methods.[3] Previous work on simple ketene thioacetals did not indicate a tendency toward 2 + 2 cycloaddition;[4] so vinylcyclobutanone formation as a competing process should be unimportant.

The compounds studied were all prepared by the recently developed method employing addition of 2-lithio-2-trimethylsilyl-1,3-dithiane to α,β-unsaturated aldehydes and ketones.[5] Addition occurs exclusively at the carbonyl group and elimination of Me_3SiOLi is spontaneous under the reaction conditions to afford good yields of **1a–c**. Compound **1c** was prepared from 1-acetylcyclohexene in 87% yield while **1a** (from tiglaldehyde) and **1b** (from cinnamaldehyde) were available from previous studies.

The first dienophile examined toward cycloaddition to **1a–c** was tetracyanoethylene (TCNE). Each of the vinylketene thioacetals reacted with TCNE in methylene chloride at room temperature within minutes to afford the corresponding 4 + 2 adducts **2a–c** in good yield (71–83%).



2a–c

The nmr spectra of the adducts fully supported their formulation as 4 + 2 cycloaddition products. In particular, the presence in the nmr spectrum of **2a** of signals for an allylic methyl group (δ 1.90) and a vinyl proton (δ 5.60) is consistent with the assigned structure.

(2) E. J. Corey, B. W. Erickson, and R. Noyori, *J. Amer. Chem. Soc.*, **93**, 1724 (1971), and references cited therein.

(3) E. J. Corey and B. W. Erickson, *J. Org. Chem.*, **36**, 3553 (1971); E. Vedejs and P. L. Fuchs, *ibid.*, **36**, 366 (1971).

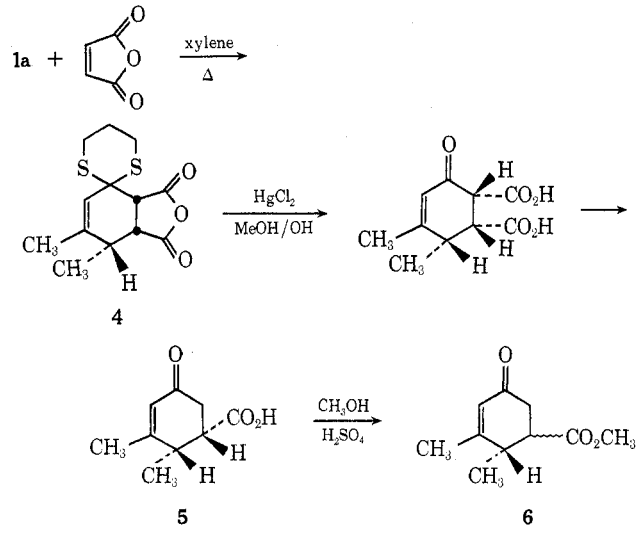
(4) F. A. Carey and J. R. Neergaard, *ibid.*, **36**, 2731 (1971).

(5) F. A. Carey and A. S. Court, *ibid.*, **37**, 1926 (1972); D. Seebach, B. T. Grobel, A. K. Beck, M. Braun, and K. H. Geiss, *Angew. Chem., Int. Ed. Engl.*, **11**, 443 (1972).

It was considered to be of interest to ascertain the effect of the sulfur substituents on reactivity in 4 + 2 cycloadditions, since it was not obvious whether they should activate the diene by electron release from the lone pairs or deactivate it by stabilization of the diene through d_π–p_π overlap.[6] Destabilization of the required s-cis conformation by the sulfur substituents should also retard the rate of cycloaddition.[7] To determine the relative importance of these various factors a competition reaction was carried out in which the vinylketene thioacetal **1b** was allowed to compete with *trans*-1-phenylbutadiene (**3**) for a deficiency of TCNE. One equivalent of TCNE was added to a solution containing 1 equiv of **1b** and 1 equiv of **3** in methylene chloride at 25°. The product which was isolated was exclusively **2b** and was formed in 87% yield. In a similar competition study between **1c** and 2,3-dimethyl-1,3-butadiene, 0.5 equiv of TCNE was added to a dichloromethane solution containing 1 equiv of each diene. Again the only adduct detected was that from the vinylketene thioacetal.

The implications from these experiments are, at least toward highly electrophilic olefins, that sulfur substituents on the diene activate the diene toward Diels–Alder cycloaddition to a substantial degree.[8]

Development of the desired cyclohexenone synthesis proceeded in a direct fashion using **1a** as the substrate and maleic anhydride as the dienophile. Refluxing a xylene solution of **1a** and maleic anhydride for 3 hr and evaporating the solvent afforded the crystalline adduct **4** in 60% yield. Hydrolysis of the dithioacetal protecting group was effected with mercuric chloride in 90% aqueous methanol at reflux for 15 hr. Under these conditions the initial product, a β-keto acid, underwent decarboxylation to yield **5**. Since it was determined by nmr that the crude product of the hydrolysis–decarboxylation was a mixture of **5** and its methyl ester **6**, the entire mixture was esterified to **6** in methanol containing a catalytic amount of sulfuric acid. The desired cyclohexenonecarboxylic ester was isolated as a mixture of epimers in 58% overall yield from **4**.



(6) For a review of reactivity in Diels–Alder reactions see J. Sauer, *ibid.*, **6**, 16 (1967).

(7) C. A. Stewart, *J. Org. Chem.*, **28**, 3320 (1963).

(8) Diels–Alder addition of olefins to a dienyl sulfide has recently been reported: D. A. Evans, C. A. Bryan, and C. L. Sims, *J. Amer. Chem. Soc.*, **94**, 2891 (1972).

Less reactive dienophiles such as diethyl maleate, diphenylacetylene, and *p*-benzoquinone did not react with **1a**. Of the three vinylketene thioacetals examined in this study **1a** was the only one to give an adduct with maleic anhydride. Failure of **1b** and **1c** to react with maleic anhydride is presumably due to electronic and steric effects, respectively.

Experimental Section

Nmr spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$ and chemical shifts are reported in parts per million (δ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr discs for solids and pressed films for liquids. Melting points are corrected and were determined on a Thomas-Hoover apparatus. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing potential of 70 eV.

Microanalyses were performed by Alfred Bernhardt, Engelskirchen, West Germany.

Vinylketene thioacetals **1a** and **1b** were previously reported, while 2-[1-methyl-1-(1-cyclohexenyl)]methylene-1,3-dithiane (**1c**) was prepared in 87% yield from 1-acetyl-1-cyclohexene according to the general procedure described in ref 5.

The analytical sample was obtained by preparative tlc to yield **1c** as a colorless liquid: nmr ($CDCl_3$) δ 1.4–1.8 (m, 4), 1.9 (s, 3, CH_3C=), 1.9–2.2 (m, 6), 2.6–3.0 (q, 4, SCH_2), 5.34 (m, 1, vinyl H).

Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01. Found: C, 63.74; H, 7.89.

General Procedure for Reactions of 1a–c with Tetracyanoethylene.—Tetracyanoethylene was added to an equal molar amount of the vinylketene thioacetal in methylene chloride (3 ml per 2 mmol of **1**) at 25° and the solution was stirred for 15–30 min and evaporated.

2a.—The residue obtained after evaporation was washed with ether to afford the pure adduct in 71% yield: mp 169–170°; nmr ($CDCl_3$) δ 1.60 (d, 3, J = 7 Hz, CH_3CH), 1.90 (s, 3, C=C), 2–4 (m, 7, SCH_2CH_2 and CH_3CH), 5.6 (br s, 1, C=CH).

Anal. Calcd for $C_{15}H_{14}N_4S_2$: C, 57.29; H, 4.48; S, 20.40. Found: C, 57.43; H, 4.35; S, 20.53.

2b.—Purified adduct, mp 183°, was obtained in 83% yield by washing the material remaining after evaporation with ether: nmr ($CDCl_3$) δ 4.40 (s, 1, PhCH), 6.0 (m, 2, HC=CH), 7.45 (s, 5, Ph); mass spectrum m/e (rel intensity) 326 (12), 234 (100), 160 (42).

The analytical sample, mp 183°, was obtained by recrystallization from ether. *Anal.* Calcd for $C_{19}H_{14}N_4S_2$: C, 62.95; H, 3.89; S, 17.70. Found: C, 62.76; H, 3.87; S, 17.90.

2c.—The crude product was purified by preparative tlc on silica gel using ether as the developing solvent to yield white crystals, mp 168–169° (72% yield). The nmr spectrum was characterized by three broad, complex multiplets at δ 1.6–2.4, 2.5–3.2, and 3.3–4 and a doublet (J = 1–2 Hz) at δ 1.99 assigned to the allylic methyl group; mass spectrum m/e (rel intensity) 354 (26), 179 (20), 106 (100), 91 (31).

Anal. Calcd for $C_{18}H_{18}N_4S_2$: C, 60.98; H, 5.12; S, 18.09. Found: C, 60.97; H, 5.20; S, 18.02.

An authentic sample of the adduct of TCNE and **3** was prepared in the same fashion as the adducts of **1** in 77% yield: mp 155°; nmr ($CDCl_3$) δ 3.2 (br, 2, allylic CH_2), 4.3 (br, 1, PhCH), 6.0 (s, 2, vinyl CH), 7.4 (s, 5, Ph).

Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90. Found: C, 74.22; H, 3.77.

Reaction of 1a with Maleic Anhydride.—A solution of 4.0 g (21.7 mmol) of **1a** and 2.1 g (21.5 mmol) of maleic anhydride in 50 ml of xylene was refluxed for 3 hr. The xylene solution was concentrated under vacuum. The crystalline adduct which resulted was filtered and washed with ether to yield 3.6 g (60%) of **4**: nmr ($CDCl_3$) δ 1.43 (d, 3, J = 7 Hz, CH_3CH), 1.87 (s, 3, CH_3C=), 1.9–2.2 (m, 2, SCH_2CH_2), 2.5–3.3 (m, 5, SCH_2 and CH_3CH), 3.5 (d, d, 1, J = 8, 5 Hz, HC=CO), 4.06 (d, 1, J = 8 HzHCC=O), 5.75 (br s, 1, C=CH).

The analytical sample was obtained by recrystallization from chloroform–ethanol, mp 114–115°.

Anal. Calcd for $C_{13}H_{16}O_3S_2$: C, 54.90; H, 5.67; S, 22.55. Found: C, 54.97; H, 5.46; S, 22.66.

Conversion of 4 to Methyl 2,3-Dimethyl-4-oxo-3-cyclohexenecarboxylate (6).—A solution of 500 mg (1.75 mmol) of **4** in 45 ml of methanol containing 5 ml of water and 1.05 g (3.9 mmol) of mercuric chloride was refluxed for 15 hr under nitrogen, cooled, and filtered through Celite. The Celite was washed thoroughly with methanol and the combined filtrates were evaporated. The residue (448 mg) exhibited peaks in the nmr at δ 3.7 attributable to a methyl ester and at 9.2 for the carboxylic acid. This product was taken up in 50 ml of methanol, several drops of sulfuric acid were added, and the solution was refluxed for 6 hr. The methanol was removed on the rotary evaporator and the product was taken up in methylene chloride. The solution was washed with water, dried ($MgSO_4$), filtered, and evaporated to yield 317 mg of **6**. The nmr spectrum of this product was identical with that of the purified product (190 mg, 58%) obtained by preparative tlc on silica gel with 75% ether–25% hexane. The nmr spectrum clearly showed that a mixture of epimers was present by the doubling of the $-OCH_3$ and CH_3CH signals: nmr ($CDCl_3$) δ 1.1 and 1.25 (2, d, J = 7 Hz, CH_3CH), 2.0 (2, d, CH_3C=C), 2.5–3 (m, CHC=O and CH_3CH), 3.70 and 3.75 (2, s, OCH_3), and 5.80 (br, s, vinyl H); mass spectrum m/e (rel intensity) 182 (18), 123 (100), 96 (65), 95 (28).

The analytical sample was obtained by preparative glpc on Carbowax at a column temperature of 200°.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.86; H, 7.72.

Registry No.—**1a**, 36744-60-2; **1b**, 36744-61-3; **1c**, 36736-49-9; **2a**, 36736-50-2; **2b**, 36736-51-3; **2c**, 36748-70-6; **3**–TCNE adduct, 36748-71-7; **4**, 36744-62-4; **6**, 36748-72-8.

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Ring Contraction in a Synthesis of 2-Piperazinemethanethiol[1]

JAMES R. PIPER,* LUCY MCCOMBS ROSE, AND THOMAS P. JOHNSTON

Kettering-Meyer Laboratory, Southern Research Institute, Birmingham, Alabama 35205

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The reaction of the disodium salt of *N*,*N*′-ethylenebis-*p*-toluenesulfonamide (**1**) with 2,3-dibromo-1-propanol has recently been shown to give hexahydro-1,4-bis(*p*-tolylsulfonyl)-1*H*-1,4-diazepin-6-ol[2] (**2**) instead of 1,4-bis(*p*-tolylsulfonyl)-2-piperazinemethanol (**4**) as originally reported[3] and subsequently assumed by other investigators.[4,5] The error was confirmed[2] by a comparison of **2** with an authentic sample of **4** (which was prepared from ethyl 1,4-dibenzyl-2-piperazinecarboxylate[6] in three steps). The intermediacy of *N*-2,3-epoxypropyl-*N*,*N*′-ethylenebis-*p*-toluenesulfonamide in the formation of **2** was suggested.[2] The firm identity of **2** cast considerable doubt on the structures of intermediates and products in the re-

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