The solution was evaporated to dryness *in vacuo*. The residue was recrystallized from acetone–ether to yield **30** (0.95 g, 3.9 mmoles), mp >340°.

Anal. Calcd for $C_{12}H_{20}O_2ClN$: C, 58.65; H, 8.20; Cl, 14.43. Found: C, 58.52; H, 8.25; Cl, 14.47.

Registry No.—**3**, 2534-80-7; **5**, 5549-04-2; ethyl 4-methylcyclohexa-1,3-diene-1-carboxylate, 14233-91-1; **6**, 14233-92-2; **8**, 5605-09-4; **9**, 14233-94-4; **10**, 14233-95-5; **11**, 14233-96-6; **12**, 14233-97-7; **13**, 14233-98-8; **16**, 1659-95-6; **17**, 1659-67-2; **18**, 14234-01-6; **19**, 1659-71-8; **21**, 14234-03-8; **22**, 14234-04-9; **23**, 14234-05-0; **24**, 14234-06-1; **25**, 14320-56-0; **26**, 14234-07-2; **27**, 14234-08-3; **28**, 14234-09-4; **29a**, 14234-10-7; **29b**, 14234-11-8; **30**, 14320-23-1; **30a**, 14234-12-9.

The Preparation of Bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1′-cyclopentane

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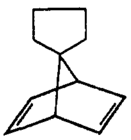
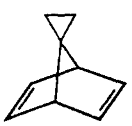
The preparation of bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1′-cyclopentane by the Hofmann and amine oxide routes is described. Unlike the parent bicycloheptadiene, the N-oxide gave the better yield. The eliminations are compared with the earlier preparations of norbornadiene.

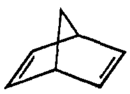
As part of a study of silver ion complexes of bicyclic olefins,[2] it became desirable to prepare the title compound **1** as an example of a diene in which the top sides of the π bonds were effectively blocked. The only member of the 7-spiro-substituted bicyclo[2.2.1]heptadiene series that has been reported[3] is bicyclo[2.2.1]-hepta-2,5-diene-7-spiro-1′-cyclopropane (**2**). This diene presents complications for metal complex studies because the cyclopropyl group is itself potentially capable of complexing[4] and its unique geometry orients the hindering hydrogen atoms up and away from the center of the π bond.



1



2



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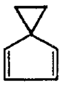

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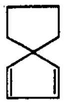

5

The route to the cyclopropyl diene **2** was by way of a Diels–Alder reaction between spiro[2,4]hepta-1,3-diene (**4**) and 1,2-dichloroethene.[3] Unfortunately, the precursor cyclopentadiene **5** for the preparation of **1** undergoes a preferential self Diels–Alder reaction at the high temperatures required for reaction with poor dienophiles like 1,2-dichloroethene. This limitation focused our attention on better dienophiles like acrylic acid derivatives and thence to the Cope[5] synthesis of the parent diene **3**. In that study, cyclopentadiene was adducted with methyl acrylate and the ester function then converted to both the amine oxide and a quaternary ammonium iodide group. Cope observed that the *exo*-amine oxide gave a 32% yield of diene **3** while the *endo* isomer gave only a 1.4% yield. Similarly the *exo*-ammonium iodide went in 58% yield while the *endo*-quaternary iodide gave only 3.1% of the diene. In the present case, the bulk of the spirocyclopentyl substituent promised to make the preparation of either *exo* isomer difficult with consequent low yields of **1**.

The Diels–Alder reaction of diene **5** with methyl acrylate went slowly at room temperature to give a mixture of *exo* and *endo* adducts in 77% yield.[3b] The *endo–exo* ratio was about 99:1 and an attempt to increase the amount of *exo* isomer by equilibration with sodium methoxide in methanol (17 hr under reflux) did not alter the ratio to any practical extent.[6] Because of the ready availability of the *endo* isomer, its chemistry was explored.[7]

The *endo* ester was readily converted to hydrazine **7** and thence by the Curtius reaction to carbamate **8**, which could be reduced in good yield to the secondary amine, **9**. This amine was methylated by the Clark–Eschweiler technique to give the tertiary amine **10** in an over-all yield from **5** of 35% (Scheme I). The methohydroxide **11** was prepared from the methiodide with silver oxide. Following the conditions employed by Cope, pyrolysis of **11** gave an isolated 10% yield of **1**.

Cram has reported[8] that the Cope elimination takes place at room temperature for many N-oxides when dry tetrahydrofuran is used as the solvent. In the present case these mild conditions failed for the N-oxide **12** and it was only by pyrolysis of the diene at 320° that elimination occurred. The diene was formed in surprisingly[9] high yield (53% by analytical glpc) and even after isolation in pure form by preparative glpc the yield was 22%.

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[1] (a) Taken from the Ph.D. dissertation submitted by G. Whitney in partial fulfillment of the Cornell Graduate School requirements, 1966; (b) G. C. W. would like to acknowledge a predoctoral NIH fellowship for 1964–1966.

[2] C. F. Wilcox, M. F. Wilcox, G. Whitney, and R. Craig, unpublished results.

[3] (a) K. Alder, H. Ache, and F. H. Block, *Ber.*, **93**, 1988 (1960); (b) C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 4258 (1961).

[4] Cyclopropane rings are widely noted for their ability to interact with protons and developing carbonium ions. The electron affinity of Ag^+ is close to that of C^+, thereby making it a potential contender for the electrons of the cyclopropane ring bonds.

[5] A. C. Cope, E. Ciganek, and N. A. LeBel, *J. Am. Chem. Soc.*, **81**, 2799 (1959).

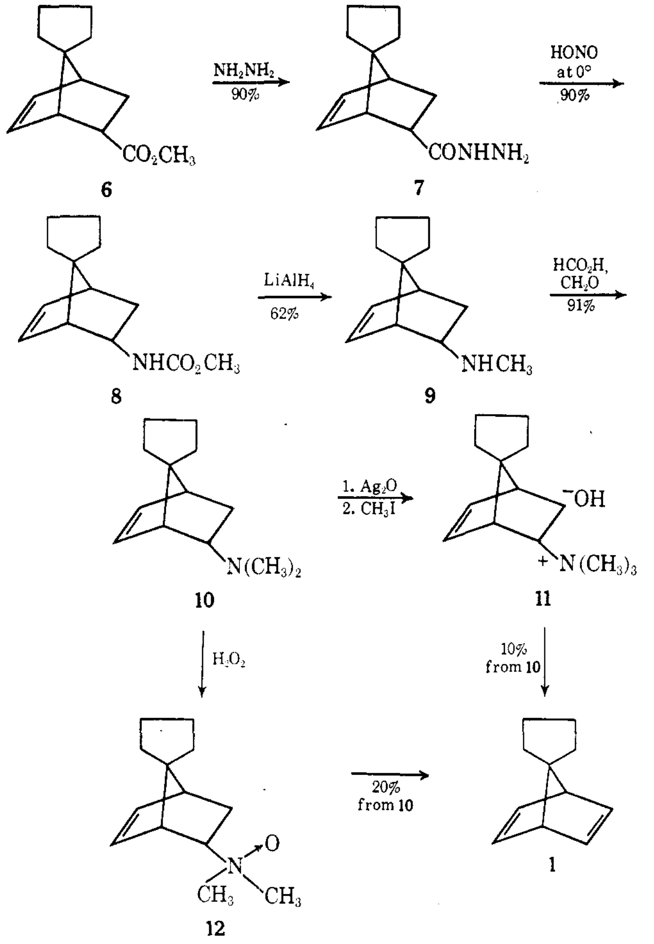
[6] Whether this negative result reflects an extremely large *exo–endo* ratio or a slow equilibration was not determined. The question was not pursued because of the difficulty found in separating the mixture by distillation as well as the unexpectedly high yields obtained with the *endo* isomer.

[7] The interfering bulk of the spirocyclopentane ring might well have given poor yields in the pyrolysis of the *exo*-amine oxide. The expectation for the *exo*-ammonium salt is less clear.

[8] D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[9] In comparing the present results with those of Cope, *et al.*, it might be noted that their yields are based on analytical glpc before isolation.

SCHEME I



The diene was characterized in part by its correct CH analysis as well as by its strong infrared absorption at 13.6 μ, characteristic of *cis*-disubstituted olefins in this bicyclic system.[10] Indirect chemical evidence was provided by the lack of reaction with bromine in carbon tetrachloride solution as expected for a [2.2.1]-bicyclic olefin hindered on the *exo* side.

The ultraviolet absorption spectrum of **1** in isooctane included a plateau at 240 mμ (log ϵ 2.178) and shoulders at 220 (3.17) and 207 (3.23). This pattern is very similar to that observed for the[3b,11] related bicyclic dienes **2** and **3**. The ^{1}H nmr spectrum of **1** showed four olefinic protons in a multiplet[12] centered at 6.52 ppm, two bridgehead protons in a multiplet at 3.12 ppm, and an asymmetric multiplet of relative area eight at 1.51 ppm for the methylene protons.[13] The positions of the olefinic and bridgehead protons of **2** and **3** are reasonably similar.

While the present work was undertaken for preparative reasons, it is worthwhile to consider the results to see if they have any mechanistic implications. This is particularly true because the high yield of diene from the *endo*-amine oxide might seem to be at variance with the mechanistic interpretation of Cope, *et al.*[5] These workers in discussing the poor yields of diene **3** obtained by pyrolysis of the *endo* isomers suggested that in both transition states from *endo* materials the functional groups were coplanar with one of the β hydrogens leading to an increase in steric repulsion by the 5,6-double bond relative to the ground state. With the relatively unhindered *exo* substituents, this enhancement of steric strain was proposed to be less significant. These results were contrasted with those of Grob,[14] who prepared bicyclo[2.2.2]octa-2,5-diene (**13**) in good yield by pyrolysis of both the *endo* N-oxide and the *endo*-quaternary salt. Models suggest that a coplanar transition state could be achieved more readily with the [2.2.2] system. The strikingly good yield of diene **1** from the *endo* N-oxide might be explained similarly[15] by proposing that the bulky spiro ring compressed against the *exo* C_2 and C_3 hydrogens forces the *endo* substituents to become more coplanar and raises the ground-state energy. The same argument could be applied to the quaternary ammonium salt if it were proceeding through a cisoid transition state. Cope had tentatively suggested an ylide mechanism for the formation of **3** from the ammonium salt.[16] Subsequent work[17] has shown that the ylide path can give as good yields of olefin with sterically constrained systems as the more normal *trans* path does with flexible systems. Banthorpe has suggested that the ylide path dominates in Hoffmann pyrolysis.[18] The alternative of a concerted *cis* E2 elimination seems unlikely in view of the great difficulty of *endo-cis* elimination observed in the closely related dihalonorbornane systems.[19] The present results are thus consistent with the original suggestion of a *cis* elimination proceeding through an ylide intermediate.[19a]

In summary, it has been shown that a [2.2.1]bicycloheptadiene with a bulky substituent at the 7 position can be prepared in good yield by pyrolytic elimination of an *endo*-amine oxide. Increased co-

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(10) (a) C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961); (b) K. Nakanishi, "Infrared Absorption Spectroscopy—Practical," Holden-Day, Inc., San Francisco, Calif., 1962.

(11) C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

(12) The appearance of this multiplet is very similar to that reported (and verified) for norbornadiene: P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); F. S. Mortimer, *J. Mol. Spectry.*, **3**, 528 (1959); K. Tori, R. Muneyuki, and N. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

(13) Nmr spectra of AA'A''A'''BB'B''B''' are not necessarily symmetrical. For examples see tetrahydrofuran and tetrahydrothiophene, N.M.R. Spectra Catalog, Varian Associates, Inc., Palo Alto, Calif., 1963. Another example is cyclopentanone which has a superficial band shape closely resembling the high-field portion of **1**. The asymmetry of the simpler AA'A'XX'X'' system has been discussed by R. G. Jones, R. C. Hirst, and H. J. Bernstein, *Can. J. Chem.*, **43**, 683 (1965). The situation in AA'A''A'''XX'X''C''' systems, R. G. Jones and S. M. Walker, *Mol. Phys.*, **10**, 363 (1966), is more complex and cannot be discussed in the systematic manner used for the six-spin case.

(14) C. A. Grob, H. King, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(15) A referee has noted that the good yield of diene **1** compared with diene **3** might simply reflect the relative ease of polymerization of **3**. The present emphasis on the ease of formation of **1** was taken because under nearly identical reaction conditions the *exo* starting materials gave good yields (32 and 58%) of **1** (total recovery of nonpolymeric material of 52 and 72%). Moreover, in the parallel reactions to form norbornene (where polymerization is not a problem) the total yields and distribution of products from both *exo* and *endo* starting materials were quite similar to those of the diene. It is possible that this particular parallelism of four pairs of reactions is fortuitous and that comparison of the *endo* reactions with the *exo* reactions is misleading. It is hoped that measurement of relative reaction rates with adequate control reactions can be determined to clarify this point.

(16) A. C. Cope and D. L. Ross, *J. Am. Chem. Soc.*, **83**, 3854 (1961); A. C. Cope and A. S. Mehta, *ibid.*, **85**, 1949 (1963).

(17) A. C. Cope and A. S. Mehta, *ibid.*, **85**, 1949 (1963).

(18) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., Amsterdam, The Netherlands, 1963, p 104.

(19) N. A. LeBel, P. D. Beirne, and P. M. Subramanian, *J. Am. Chem. Soc.*, **86**, 4144 (1964).

(19a) NOTE ADDED IN PROOF.—J. Coke and M. Cooke, Jr. (*ibid.*, **89**, 2779 (1967)) have shown recently that pyrolysis of the *exo* quaternary ammonium hydroxide of norbornane gives about 6% ylide elimination and 94% *cis* E2 elimination.

planarity of the transition state is suggested for the marked improvement of yield relative to the unsubstituted case.

Experimental Section

endo-**2-Carbomethoxybicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane** (6).—Spiro[4.4]nona-1,3-diene[20] (70 g, 0.58 mole) was added to a solution of 59.3 g (0.69 mole) of freshly distilled methyl acrylate in 150 ml of anhydrous diethyl ether and the reaction mixture was sealed under nitrogen. After 12 days at room temperature, the solvent was removed in a rotatory evaporator and the residue was fractionally distilled through a 40-cm glass spiral column to give 86.1 g (77.5%) of product, bp 112° (2 mm) (lit.[10a] bp 90° (1.7 mm)). Analysis of the product by glpc on a 4% Carbowax 20 M column at 130° indicated that the material was 98% *endo* ester **3** and less than 1% *exo* ester with about 1% diene dimer. The infrared spectrum of a sample purified by preparative glpc corresponded with the known material and also had a consistent ^{1}H nmr spectrum.

endo-**2-Carboxybicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane Hydrazide** (**7**).—A solution of 85 g (0.41 mole) of 98% pure ester **3** and 74.7 g (1.27 moles) of 85% hydrazine hydrate in 100 ml of 95% ethanol was heated under reflux for 18 hr. The mixture was evaporated to dryness on a rotatory evaporator heated with a steam bath. The solid residue was broken up and washed with water and pentane. After drying to constant weight, 95 g (90.5%) of crude **4** was obtained, mp 90–93°. A small sample was recrystallized twice from benzene and melted at 98–100°.

Methyl *endo*-**N-2-Bicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane Carbamate** (**8**).—To a cold solution of 30 g of concentrated hydrochloric acid in 290 ml of water was added 62 g (0.301 mole) of crude hydrazide. After dilution with 290 ml of ether, the solution was cooled to 0° and a solution of 21 g (0.304 mole) of sodium nitrate in 50 ml of water was added dropwise with stirring over a 35-min period. The reaction mixture was maintained at 0° during the addition by adding small chips of Dry Ice. Stirring was continued at 0° for 40 min after the addition had been completed. The clear, slightly yellow ether layer was separated and the water layer washed twice with 90 ml of cold ether. After the combined ether extracts had been washed with dilute aqueous sodium bicarbonate and dried over calcium chloride, 150 ml of absolute methanol was added and the ether removed by fractional distillation through a 30-cm glass helices column. The decomposition of the azide, which commenced during the distillation, was completed by heating the methanol solution under reflux for 14 hr. Evaporation of the solution to constant weight gave 59.5 g (90% based on carbamate) of a crude, viscous, orange oil which could not be crystallized from either hexane or benzene.

endo-**2-Methylaminobicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane** (**9**).—A solution of 59.5 g (*ca.* 0.27 mole) of crude **8** in 225 ml of ether was added dropwise to a stirred suspension of 27 g (0.71 mole) of lithium aluminum hydride in 540 ml of ether. The addition, adjusted so as to maintain gentle reflux, required 80 min, after which the solution was stirred for an additional 30 min and then heated under reflux for 21 hr. The excess hydride was decomposed by careful dropwise addition of 30 ml of water, 30 ml of 15% aqueous sodium hydroxide, and 80 ml of water. The white suspension was stirred for 1 hr and filtered; the filter was cake washed with ether. The combined ether extracts were washed four times with a total of 280 ml of 10% sulfuric acid. The acid layer was basified with sodium hydroxide pellets and extracted with two 100-ml portions of ether. After the ether solution had been dried overnight with potassium hydroxide pellets, it was concentrated in a rototary evaporator and the residue was fractionally distilled through a 40-cm spiral tantalum wire column to give 29.5 g (62%) of **9** as a colorless, fishy smelling liquid, bp 86° (5 mm). Analysis by glpc on a 4% Carbowax 20 M on Fluorpak column at 160° indicated greater than 99% purity. The infrared spectrum contained a bond at 2.9 μ (NH).

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.30; H, 10.70; N, 7.84.

endo-**2-Dimethylaminobicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane** (**10**).—To 44 g of 90% formic acid was added slowly, with cooling, 29.4 g (0.165 mole) of monomethylamine **9** followed by 33 g of 37% aqueous formaldehyde. The solution was heated with stirring under reflux for 10 hr. During the final 15 min of heating, vigorous gas evolution occurred. The solution was cooled and 36 ml of concentrated hydrochloric acid was added slowly with external cooling. After concentration of the solution in a rotatory evaporator, the light orange residue was mixed with 100 ml of ice water and the amine extracted into ether, aided by the addition of solid sodium hydroxide. The aqueous layer was extracted again with ether, and the combined ether extracts, after being dried over potassium hydroxide, were concentrated in the rotatory evaporator. The residue was fractionally distilled through a 40-cm spiral tantalum wire column to give 28.7 g (91%) of **10** as a fishy smelling liquid, bp 72.5° (1 mm). Analysis by glpc on a 4% Carbowax 20 M on Fluorpak column at 160 showed only one peak. The infrared spectrum no longer had a bond at 2.9 μ (NH).

Anal. Calcd for $C_{13}H_{21}N$: C, 81.61; H, 10.06; N, 7.32. Found: C, 81.30; H, 10.94; N, 7.53.

endo-**2-Dimethylaminobicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane Methiodide.**—To a solution of 27.5 g (0.144 mole) of dimethylamine **10** in 275 ml of anhydrous ether was added 44 g (0.31 mole) of freshly distilled methyl iodide. Within 15 min the reaction mixture solidified to a white gel. After being allowed to stand at room temperature for 24 hr in the dark, the precipitate was collected by filtration and washed with fresh ether. The yield of crude methiodide was 46.5 g (97%), mp 271–274 dec. An analytical sample was prepared by two recrystallizations from ether–ethanol and melted at 273–275° dec.

Anal. Calcd for $C_{14}H_{24}NI$: C, 50.45; H, 7.26; N, 4.20; I, 38.08. Found: C, 50.07; H, 7.25; N, 4.32; I, 38.20.

endo-**2-Dimethylaminobicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane Methohydroxide** (**11**).—Fresh silver oxide was prepared by adding a solution of 0.3 mole of silver nitrate in 50 ml of water to a solution of 0.6 mole of sodium hydroxide in 75 ml of water. The brownish black precipitate was filtered, washed with small portions of water until the filtrate was neutral, then washed twice with small portions of methanol, and finally dried by suction filtration.

A solution of 46 g (0.138 mole) of methiodide in 200 ml of 50% methanol–water was added, with stirring, to a suspension of the freshly prepared silver oxide in 200 ml of 50% methanol–water. After being stirred for 21 hr at room temperature, the mixture was filtered and the salts washed with a few milliliters of methanol. The solution was concentrated in a rotatory evaporator at 50° and 25 mm to give 42 g of crude **11** as a viscous light yellow oil. The crude product was used without further purification.

Pyrolysis of Methohydroxide 11.—In a small flask fitted with a capillary nitrogen inlet and attached to a short-path distillation head leading to two traps cooled in a Dry Ice bath was placed 42 g of the crude methohydroxide **11**. With nitrogen bubbling through the methohydroxide and the system evacuated to a *ca.* 25-mm pressure, the pyrolysis flask was heated with an oil bath at a rate of 2°/min. At 130° and continuing to 150° vigorous bubbling was observed. After bubbling had ceased, the oil bath was heated to 170° and the pressure decreased to 1 mm for 10 min. The liquid in the traps was dissolved in pentane and the solution washed twice with cold 10% sulfuric acid and then with water until the washings were neutral. Analysis of the dried pentane solution by glpc on a 5% Carbowax 20 M column at 90° showed only one peak other than the solvent peak. After the solvent had been removed in a rotatory evaporatory, 21 g. (*ca.* 10%) of pure **1**, n^{20}_{D} 1.4995, was isolated by preparative glpc on a 20 ft × $^3/_8$ in. Carbowax column. The ^{1}H nmr spectrum showed multiplets at 6.52 (four protons), 3.12 (two protons), and 1.51 ppm (eight protons). The ultraviolet absorption spectrum included bonds at 240 mμ (plateau, log ε 2.248), 220 (sh, 3.17), and 208 (sh, 3.23).

Anal. Calcd for $C_{11}H_{14}$: C, 90.25; H, 9.65. Found: C, 90.14; H, 9.65.

From the residue in the pyrolysis flask and the acid washings of the pentane solutions of **1** could be isolated 12.5 g of 90% pure **10** corresponding to a recovery of 43%.

endo-**2-Dimethylaminobicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane N-Oxide** (**12**).—To a cooled solution of 5 g (0.026 mole) of **10** in 10 ml of methanol was added drop an wise 9 g of 30% hydrogen peroxide. The solution was stirred for additional 1 hr in an ice bath and then allowed to sit at room temperature for 24 hr. The excess hydrogen peroxide was carefully decomposed by addition of platinum black portionwise to the cooled solution over a 30-min period while it was stirred under a nitrogen at-

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[20] R. B. Turner, W. R. Meador, and R. F. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

mosphere. After the bubbling had ceased, the solution was stirred for an additional 3 hr and then permitted to warm to room temperature. The platinum black was removed by filtration and washed with a few milliliters of 50% methanol–water. The solution and washing were evaporated to a constant weight using a rotatory evaporator and a steam bath to give 3.9 g of crude **12** as a thick, light orange oil that solidified upon standing at room temperature. Final drying of the crude N-oxide was accomplished in a vacuum desiccator containing silica gel. The crude product melted at 35–37°. The picrate of **12**, after three crystallizations from 95% ethanol, melted at 161–162°.

Anal. Calcd for $C_{19}H_{24}N_4O_8$: C, 52.29; H, 5.54; N, 12.83. Found: C, 52.27; H, 5.34; N, 12.30.

Pyrolysis of N-Oxide 12.—The pyrolysis tube was a 250 × 22 mm Pyrex tube wound with a nichrome wire heater and filled to a height of 80 mm with $^3/_8$-in. glass helices. The tube was mounted vertically and a short Liebig condenser attached to the top. A dropping funnel with a nitrogen inlet was connected to the condenser. The bottom end of the tube opened directly into a flask that had an outlet leading to a second trap. Both traps were cooled in a Dry Ice bath.

A solution of 3.85 g (0.0185 mole) of crude **12** in 40 ml of freshly dried and distilled tetrahydrofuran was dried further by addition of 3 g of Linde 4A Molecular Sieve pellets. After 3 hr in contact with the sieves, the solution was filtered through glass wool and dripped (10 drops/sec) into the pyrolysis chamber, which was maintained at 320°. After addition of 25 ml of pentane to the pyrolysate, the solution was washed with 50 ml of water and the water layer was extracted with 25 ml of fresh pentane. The combined pentane extracts were washed twice with 15 ml of cold 10% sulfuric acid and then with small portions of water until the washings were neutral. Concentration of the dried (magnesium sulfate) pentane solution in a rotatory evaporator gave 1.7 g of product, which was *ca.* 85% pure according to glpc analysis on a 4% Carbowax 20 M column. Preparative glpc on a 20% Carbowax 20 column gave 0.5 g (22%) of product, bp 56° (7 mm). The amine was recovered in 17% yield as described under the pyrolysis of **11**.

Registry No.—**1**, 6572-54-9; **7**, 13619-10-8; **6**, 13619-06-2; **9**, 13619-07-3; **10**, 13619-08-4; **11**, 13619-09-5; **12**, 13618-84-3; **12**, picrate, 13618-85-4; *endo*-2-dimethylaminolucyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane methiodide, 13618-86-5; **8**, 13619-11-9.

Cyclopropanes from Reactions of Ethyl (Dimethylsulfuranylidene)acetate with α,β-Unsaturated Compounds

GEORGE B. PAYNE

Shell Development Company, Emeryville, California

Received May 4, 1967

Ethyl (dimethylsulfuranylidene)acetate has been isolated in 90–95% yield as an analytically pure liquid and stored successfully for several weeks at −10°; it decomposed slowly at room temperature. Reaction of the ylide with a variety of α,β-unsaturated esters, ketones, aldehydes, and nitriles readily afforded cyclopropyl compounds in yields of 40–90%.

Recent publications concerned with several different resonance-stabilized sulfonium ylides have covered their preparation and spectral properties, but relatively few of their chemical reactions have been described.[1] Most recently, the preparation and properties of a number of sulfonium and oxosulfonium carbalkoxymethylides were reported.[2] Here again, the emphasis was on synthesis of new ylides rather than on their utilization as chemical intermediates.

Ethyl (dimethylsulfuranylidene)acetate (**1**, EDSA) was recently prepared by the reaction of the requisite sulfonium halide with sodium hydride (NaH) in tetrahydrofuran (THF), and its reaction *in situ* with Schiff bases was described.[1a] In later reports, nuclear magnetic resonance (nmr) and infrared spectral data were recorded.[1b]

$$^-X(CH_3)_2S^+CH_2CO_2C_2H_5 \xrightarrow[\text{THF}]{\text{NaH}} \underset{\textbf{1}}{(CH_3)_2S{=}CHCO_2C_2H_5}$$

Owing to its ease of preparation (by a new procedure described below), as well as to the potential utility of its derivatives, EDSA has undergone independent studies in these laboratories. We are reporting here a general synthesis of cyclopropyl derivatives by reaction of EDSA with a variety of α,β-unsaturated compounds.

Preparation of EDSA.—Treatment of a vigorously stirred chloroform solution of carbethoxymethyl dimethylsulfonium bromide with saturated potassium carbonate solution containing 1 molar equiv of sodium hydroxide afforded EDSA as an analytically pure residue in 90–95% yield. The reaction required 15 min at 10–20° and the product was isolated by vacuum removal of chloroform from the dried organic layer. EDSA was best stored at −10°; there it suffered little change during 1-month's time. At room temperature EDSA deteriorated gradually, and the nature of its decomposition is discussed below.

Exposure to moisture caused rapid conversion of EDSA to the inner salt (**2**). For this reason, it was

$$(CH_3)_2S{=}CHCO_2C_2H_5 + H_2O \longrightarrow \underset{\textbf{2}}{(CH_3)_2S^+CH_2COO^-} + C_2H_5OH$$

important to use anhydrous reagents in reactions involving EDSA. Indeed, the successful isolation of this ylide from the water-containing reaction mixture used in its preparation must be attributed to its great solubility in chloroform relative to saturated aqueous potassium carbonate.

Summary of Results.—Reaction of EDSA with α,β-unsaturated systems has generally led to substituted cyclopropanes. The mechanism undoubtedly

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