Photolysis of 3e.—A solution of 70 mg of **3e** in 50 ml of methanol was irradiated for 0.5 hr. After evaporation of the solvent, the resulting residue was recrystallized from methanol to give 80 mg of **8e** as colorless crystals: mp 145.5–146°; ir (KBr) 1750, 1730, 1230, 1200 cm^{-1}; *m/e* 340 (parent), 118.

Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.41; H, 5.74.

Photolysis of 3f.—A solution of 75 mg of **3f** in 50 ml of methanol was irradiated for 0.5 hr. After evaporation of the solvent, the resulting residue was subjected to silica gel chromatography and then fractional crystallization from ether to give 50 mg of **8f** and 25 mg of **8g**.

For the first, **8f**, the following was observed: mp 97–98° (benzene–hexane); ir (KBr) 1730, 1660 1210, 1170 cm^{-1}; *m/e* 312 (parent), 118.

Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.03; H, 6.44.

For the second, **8g**, the following was observed: mp 212–214° (petroleum ether); ir (KBr) 1730, 1110 cm^{-1}; *m/e* 314 (parent), 118.

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.88; H, 6.99.

Reaction of 2d with *N*-Phenylmaleimide.—A solution of 500 mg of **2d** and 775 mg of *N*-phenylmaleimide in 30 ml of toluene was refluxed for 9 hr. Evaporation of the solvent under the reduced pressure gave a pale yellow residue which was recrystallized from ethanol to give 560 mg of colorless solid. Glpc and nmr analyses showed it to be a mixture of endo adduct **15** and exo adduct in the ratio 2:1. Because of its low solubility, the purification was very difficult and only major product **15** was isolated as colorless crystals by fractional crystallization from ethanol: mp 213–215°; ir (KBr) 3400, 1780, 1700, 1670, 1380 cm^{-1}; nmr ($CDCl_3$) δ 3.46 (d, 1 H, J = 7.5 Hz), 3.62 (d, 1 H, J = 7.5 Hz), 4.10 (m, 1 H), 4.90 (s, 1 H, exchangeable by D_2O), 6.0–6.3 (m, 3 H), 6.55 (t, 1 H, J = 9.0 Hz), 7.0–7.5 (m, 5 H); *m/e* 295 (parent).

Anal. Calcd for $C_{17}H_{13}O_4N$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.01; H, 4.63; N, 4.75.

Photolysis of 14.—A solution of 106 mg of **14** in 50 ml of methanol was irradiated for 2 hr under the same conditions as above. The reaction mixture was analyzed by nmr and then chromatographed on a silica gel column using chloroform. The first fraction gave 10 mg of unconverted **14**. The second fraction gave 15 mg of photoproduct **16**: mp 134–135° (ethanol); ir (KBr) 3300, 1665, 1585 cm^{-1}; *m/e* 198 (parent).

Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.54; H, 5.13.

Photolysis of 15.—A suspension of 150 mg of **15** in 50 ml of methanol was irradiated for 1 hr. After removal of the solvent, the resulting residue was chromatographed using chloroform. The first fraction gave 10 mg of unconverted **15** and the second fraction gave 90 mg of diketone **17** as colorless crystals: mp 199–201° (benzene–ethanol); ir (KBr) 1780, 1740, 1710, 1695, 1500 cm^{-1}; *m/e* 295 (parent).

Anal. Calcd for $C_{17}H_{13}O_4N$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.39; H, 4.57; N, 4.62.

Registry No.—**1**, 573-57-9; **2a**, 539-80-0; **2b**, 6264-93-3; **2c**, 6422-12-4; **2d**, 533-75-5; **2e**, 33739-54-7; **2f**, 2161-40-2; **3a**, 38276-32-3; **3b**, 42150-82-3; **3c**, 42150-83-4; **3d**, 42150-84-5; **3e**, 42150-85-6; **3f**, 42150-86-7; **4c**, 42150-87-8; **5c**, 42150-88-9; **5e**, 42150-89-0; **5f**, 42150-90-3; **6f**, 42150-91-4; **8c**, 42150-92-5; **8e**, 42150-93-6; **8f**, 42150-94-7; **8g**, 42150-95-8; **9c**, 42150-96-9; **13**, 38276-37-8; **14**, 33655-59-3; **15**, 42150-99-2; *exo*-**15**, 42151-00-8; **16**, 5824-32-8; **17**, 42151-02-0; *N*-phenylmaleimide, 941-69-5.

Halogenated Ketenes. XXIV. Cycloaddition of Alkylhaloketenes and Methylenecycloalkanes. Spiro Compounds[1]

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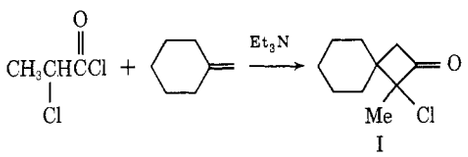
The cycloaddition of methylchloroketene with methylenecyclohexane, methylenecyclobutane, β-pinene, and 5-methylene-2-norbornene to yield the corresponding spiro[3.5] and spiro[3.3] ketones has been investigated. The cycloaddition of ethylchloroketene with methylenecyclobutane is also described. The spiro ketones are all readily reduced to the corresponding spiro alcohols. Some base-catalyzed rearrangement reactions are described including ring contractions to spiro[5.2] compounds.

A number of reports have appeared in recent years on the cycloaddition of ketenes and olefinic compounds. The majority of these reports have been concerned with the reactive cyclopentadiene and/or other activated olefins. Cycloadditions with methylenecycloalkanes has received little attention and in the scattered reports few details are given.[2-4]

We now report the cycloaddition of the reactive alkylhaloketenes and methylenecycloalkanes to yield [3.*n*] spiro ketones depending on the particular methylenecycloalkane employed. The spiro ketones and particularly the spiro alcohols undergo a base-catalyzed ring contraction reaction to yield other spiro compounds, thus providing an excellent general method for a wide variety of spiro compounds.

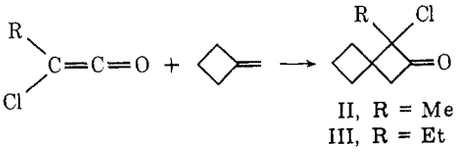
The *in situ* cycloaddition of methylchloroketene and methylenecyclohexane resulted in a 60% yield of the spiro[5.3]nonanone I. The optimum conditions



I

for effecting this cycloaddition are in refluxing hexane. A slow addition of acid halide to the amine and olefin in hexane are desirable to minimize the formation of the α-halovinyl ester.[5,6]

This *in situ* cycloaddition also occurs with methylenecyclobutane to yield the corresponding spiro[3.3]-heptanones in 30 and 35% yields, respectively (II and III). The yield is lower with this olefin because the



II, R = Me
III, R = Et

(1) Paper XXIII: W. T. Brady and G. A. Scherubel, *J. Amer. Chem. Soc.*, in press.

(2) P. R. Brook and J. G. Griffiths, *Chem. Commun.*, 1344 (1970).

(3) R. Maurin and M. Bertrand, *Bull. Soc. Chim. Fr.*, 998 (1970).

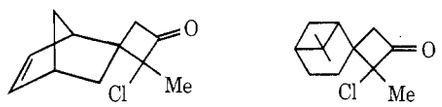
(4) J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970).

(5) R. Giger, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1466 (1968).

(6) W. T. Brady, F. H. Parry, III, R. Roe, Jr., E. F. Hoff, Jr., and L. Smith, *J. Org. Chem.*, **35**, 1515 (1970).

boiling point of the olefin dictates a lower reaction temperature. It was found desirable to isolate and distil these cycloadducts as soon after cycloaddition as possible because of side reactions which reduced the amount of cycloadducts isolated. The symmetrical nature of these three spiro compounds dictates only one isomer in each case.

The cycloadditions of methylchloroketene with 5-methylene-2-norbornene and β-pinene produce the following spiro[3.5] compounds in 65% yields (IV and V, respectively).



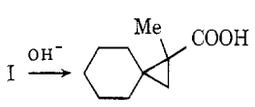
IV V

It is interesting to note that in the case of 5-methylene-2-norbornene two double bonds are available for cycloaddition with the ketene; yet cycloaddition occurs exclusively at the exo double bond, even though the strain is much greater in the internal double bond. This is a further indication that ketene olefin cycloadditions are in fact sterically controlled.[7]

Ethylchloroketene also undergoes cycloaddition with these two olefins; however, purification of the cycloadducts was difficult because of decomposition which occurs upon vacuum distillation.

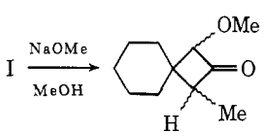
The *in situ* cycloaddition of dimethylketene with 5-methylene-2-norbornene in refluxing hexane was done in an effort to quantitatively compare this ketene with the alkylhaloketenes. The dimethylketene cycloadduct was produced as evidenced by ir and nmr spectra but in a yield of less than 10%. The cycloadduct was predominantly the spiro ketone resulting from cycloaddition with the exo double bond with some evidence of the other cycloadduct being present.

In an effort to effect a Favorskii-type ring contraction of I, this ketone was heated with aqueous base. Only a small amount of the ring-contracted acid was observed.[8,9]



VI

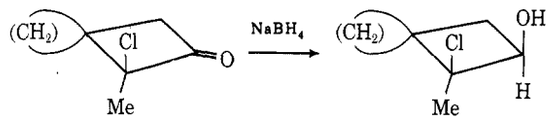
Treatment of I with NaOMe in methanol resulted in an allylic substitution through the enolate rather than ring contraction to produce the methoxy ketone VII. This is further evidence that only those halo-



VII

genated ketene–olefin cycloadducts will undergo the base-catalyzed ring contraction when the enol form is retarded, *i.e.*, cyclopentadiene adducts.[10]

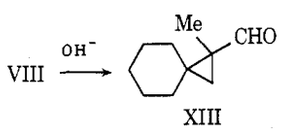
The sodium borohydride reduction of the five cycloadduct spiro ketones described above was effected in ethanol to give a quantitative or near-quantitative yield of the corresponding alcohols (VIII–XII). Of



VIII-XII

the two possible isomeric alcohols, only one was detected and this is believed to be the alcohol where the chloro and hydroxy substituents are cis. This is consistent with what Brook and Duke observed for the reduction of the cycloadducts of methylchloro- and chloroketene with cyclopentadiene.[6] The C–Cl dipole effect directs attack on the methyl side of the ketone, thus producing the alcohol shown.

1-Chloro-1-methylspiro[3.5]-2-nonanol (VIII) upon treatment with aqueous base underwent a ring contraction reaction in good yield to produce 1-methylspiro[2.5]octane-1-carboxaldehyde (XIII). Reduction



XIII

of the spiro ketone to the alcohol eliminates the undesirable enolization such that the allylic substitution reaction cannot occur and a smooth ring contraction takes place. The other spiro alcohols were also susceptible to this ring-contraction reaction. The spiro aldehydes produced are very sensitive to oxidation to the corresponding acids.

The following conclusions are drawn from this study.

(1) The cycloaddition of alkylhaloketenes with methylenecycloalkanes occurs in good yield under the appropriate conditions to yield spiro ketones. The halogenated ketenes appear to be much superior to alkylketenes in terms of yields of cycloadduct.

(2) These spiro ketones are not easily susceptible to base-catalyzed ring contraction reactions as are the cyclopentadiene adducts.

(3) Reduction of the spiro ketones to the corresponding alcohols and subsequent base-catalyzed ring contraction occurs smoothly to the spiro aldehydes, although these aldehydes are quite susceptible to oxidation.

(4) These cycloaddition and ring-contraction reactions represent an excellent general method for the preparation of various types of spiro compounds.

Experimental Section

Proton nmr spectra were recorded on Jeolco Minimar 60-MHz and Jeolco PS-100 nmr spectrometers employing tetramethylsilane as an internal standard and CCl_4 as the solvent. Vpc was performed on a F & M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with 10% SE-30 on acid-washed Chromosorb W (80–100). Hexane and triethylamine were distilled from sodium and stored over Linde type 4-A Molecular Sieve.

General Procedure for *in Situ* Alkylhaloketene–Methylenecycloalkane Cycloadditions.—To a stirred, refluxing solution of 1 mol of methylenecycloalkane and 1.5 mol of triethylamine in hexane was slowly added 1 mol of α-chloropropionyl chloride. After the addition was complete, the reaction mixture was stirred for an additional 2 hr. The amine salt was removed by filtration

(7) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **93**, 1662 (1971).
(8) P. R. Brook and A. J. Duke, *Chem. Commun.*, 652 (1970).
(9) W. T. Brady and J. P. Hieble, *J. Amer. Chem. Soc.*, **94**, 4278 (1972).
(10) W. T. Brady and J. P. Hieble, *J. Org. Chem.*, **36**, 2033 (1971).

and the filtrate was concentrated on a rotatory evaporator and vacuum distilled to yield the cycloadduct spiro ketones.

1-Chloro-1-methylspiro[3.5]-2-nonanone (I).—This cycloadduct distilled at 67–70° (0.6 mm) (60%): ir 1785 cm^{-1} (C=O); nmr δ 1.5 (m, 13 H, singlet of methyl protons is meshed in this multiplet with cyclohexane methylene protons) and 2.78 (s, 2 H).

Anal. Calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.04. Found: C, 64.21; H, 7.91.

1-Chloro-1-methylspiro[3.3]-2-heptanone (II).—This cycloadduct distilled at 55° (0.8 mm) (30%): ir 1800 cm^{-1} (C=O); nmr δ 1.58 (s, 3 H), 2.0 (m, 4 H), 2.5 (m, 2 H), and 3.25 (s, 2 H).

Anal. Calcd for $C_8H_{11}C$ O: C, 60.56; H, 6.94. Found: C, 60.32; H, 6.88.

Cycloadduct of Methylchloroketene and β-Pinene (V).—This cycloadduct distilled at 95–98° (0.25 mm) (60%): ir 1785 cm^{-1} (C=O); nmr δ 0.98 (2 s, 3 H), 1.25 (s, 3 H), 1.6 (s, 3 H), 2.0 (m, 8 H), and 3.0 (s, 2 H).

Anal. Calcd for $C_{13}H_{19}ClO$: C, 68.87; H, 8.39. Found: C, 68.73; H, 8.42.

Cycloadduct of Methylchloroketene and 5-Methylene-2-norbornene (IV).—This cycloadduct distilled at 76–78° (0.5 mm) (70%): ir 1785 cm^{-1} (C=O); nmr δ 1.5 (m, 7 H), 3.0 (m, 4 H), and 6.45 (m, 2 H).

Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.17; H, 6.61. Found: C, 66.92; H, 6.53.

1-Chloro-1-ethylspiro[3.3]-2-heptanone (III).—Distillation occurred at 60° (0.6 mm) (35%): ir 1800 cm^{-1} (C=O); nmr δ 1.05 (t, 3 H), 1.85 (q, 2 H), 2.2 (m, 6 H), and 3.18 (s, 2 H).

Anal. Calcd for $C_9H_{13}ClO$: C, 62.60; H, 7.53. Found. C, 62.42; H, 7.51.

Rearrangement of I (VI).—A 2.5-g (2.7 mmol) portion of I was treated with 50 ml of 15% aqueous NaOH solution at 70° with stirring for 2 hr. After acidification with dilute HCl, the mixture was extracted with CCl_4 and dried over anhydrous $CaCl_2$. Vacuum distillation afforded a colorless oil at 90–100° (0.2 mm) (10%): nmr δ 0.43 (d, 1 H), 0.8 (d, 1 H), 1.25 (s, 3 H), 1.5 (m, 10 H), and 11 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.59; H, 9.41.

Methoxy Substitution of I (VII).—A 5-g portion of I was treated with an excess of sodium methoxide in about 50 ml of methanol. An immediate precipitation of NaCl was observed. After removal of the salt by filtration and the solvent by evaporation, the substitution product was distilled at 60–62° (0.6 mm) to yield 3.4 g (70%): ir 1785 cm^{-1} (C=O); nmr δ 1.2 (d, 3 H), 1.5 (m, 10 H), 2.6 (m, 1 H), 3.4 (m, 3 H), and 4.05 (s 2, 1 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.52; H, 9.89. Found: C, 72.34; H, 9.73.

General Procedure for Reduction of Spiro Ketones.—To a stirred solution of 0.1 mol of the spiro ketone in 100 ml of absolute ethanol was slowly added at room temperature sodium borohydride until all the cycloadduct had been reduced. The course of the reduction was followed by vpc analysis. After the reduction was complete, the solvent was removed under reduced pressure and the residue was acidified and extracted with CCl_4. Upon distillation, a quantitative yield of the corresponding alcohol was obtained. Nmr and vpc analysis indicated that only one isomer was produced.

1-Chloro-1-methylspiro[3.5]-2-nonanol (VIII).—This spiro alcohol distilled at 62–63° (0.6 mm): ir 3500 cm^{-1} (OH); nmr δ 1.5 (m, 15 H; there is a singlet out of this multiplet at 1.6 which corresponds to the methyl protons), 3.4 (s, 1 H), and 4.0 (t, 1 H).

1-Chloro-1-methylspiro[3.3]-2-heptanol (IX).—Distillation occurred at 43–45° (0.6 mm): ir 3500 cm^{-1} (OH); nmr δ 1.45 (s, 3 H), 1.8 (m, 8 H), 3.4 (s, 1 H), and 3.65 (t, 1 H).

Anal. Calcd for $C_8H_{13}ClO$: C, 59.81; H, 8.09. Found: C, 59.72; H, 8.12.

Reduction of III (X).—This alcohol distilled at 85–87° (0.25 mm): ir 3500 cm^{-1} (OH); nmr δ 2.88 (s, 1 H of OH), other protons are in multiplet.

Reduction of IV (XI).—This spiro alcohol distilled at 70–72° (0.6 mm): ir 3500 cm^{-1} (OH); nmr δ 2.88 (s, 1 H), 3.75 (m, 2 H), and 6.45 (m, 2 H).

1 Chloro-1-ethylspiro[3.3]-2-heptanol (XII).—Distillation occurred at 51° (1.0 mm): ir 3500 cm^{-1} (OH); nmr δ 1.0 (t, 3 H), 2.0 (m, 10 H), 2.84 (s, 1 H), and 2.6 (t, 1 H).

1-Methylspiro[2.5]octane-1-carboxaldehyde (XIII).—A 5-g portion of the spiro alcohol VIII was treated with 50 ml of 15% aqueous NaOH solution at 70° with stirring for 2–3 hr. The ring-contracted product was extracted with CCl_4 and the extract was dried over anhydrous $CaCl_2$. Vacuum distillation afforded 2.8 g (70%) of the spiro aldehyde at 52–55° (0.5 mm): ir 1705 cm^{-1} (C=O); nmr δ 0.65 and 1.0 (2 d, 2 H), 1.25 (s, 3 H), 1.5 (m, 10 H), and 9.22 (s, 1 H).

This aldehyde was very susceptible to oxidation and did not give an acceptable elemental analyses for this reason. Consequently, the aldehyde was oxidized to the corresponding acid as described below.

1-Methylspiro[2.5]octane-1-carboxylic Acid (XIV).—A 0.5-g portion of XIII was suspended in 20 ml of dilute NaOH solution and treated dropwise at room temperature with a saturated aqueous potassium permanganate solution until the permanganate color persisted. After acidification of the basic reaction mixture, the acid was extracted with CCl_4. The extract was dried and the solvent was evaporated to yield an acid which was identical with VI.

Acknowledgments.—The authors wish to express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

Registry No.—I, 42200-05-5; II, 42077-46-3; III, 42077-47-4; IV, 42077-48-5; V, 42077-49-6; VI, 42077-50-9; VII, 42077-51-0; VIII, 42077-52-1; IX, 42077-53-2; XI, 42077-54-3; XII, 42077-55-4; XIII, 42077-56-5; methylchloroketene, 7623-09-8; β-pinene, 127-91-3; 5-methylene-2-norbornene, 694-91-7.