the time period of 60–180 s of reaction time.

Acknowledgment. This work was supported in part by grants from the National Science Foundation and from the National Institutes of Health.

Appendix

The following method was used to estimate the rate of appearance of the sulfenimidyl radical when styrene was included in the reaction mixture. The observed rate of radical appearance, R_{obsd}, is equal to the total rate of radical appearance, R_T, from the reaction of the sulfenimide and peroxide (eq 9) less the rate of radical disappearance, R_D, due to addition of the radical to styrene (eq 6). (See eq 20.) Since we are dealing with short reaction times and

$$R_{obsd} = R_T - R_D \quad (20)$$

initial rates, these rates can be replaced with the appropriate radical concentration (eq 21). The rate of sulfenimidyl radical disappearance via addition to styrene, R_D, is given by eq 22.

$$[(PhS)_2N\cdot]_{obsd} = [(PhS)_2N\cdot]_T - [(PhS)_2N\cdot]_D \quad (21)$$

$$R_D = k_6[(PhS)_2N\cdot]_{obsd}[\text{styrene}] \quad (22)$$

At short times t, that portion of the sulfenimidyl radical concentration which has disappeared by way of addition to styrene is given by eq 23. Combining eq 21 and 23 gives

$$[(PhS)_2N\cdot]_D = k_6(t)[(PhS)_2N\cdot]_{obsd}[\text{styrene}] \quad (23)$$

eq 24, where the radical concentration at time t that has

$$[(PhS)_2N]_T = (1 + k_6(t)[\text{styrene}])[(PhS)_2N]_{obsd} \quad (24)$$

appeared as a result of the sulfenimide/peroxide reaction is expressed in terms of the observed radical concentration at time t. These corrected radical concentrations are then used to determine the corrected rates of radical appearance that are given in parentheses in Table III.

Registry No. 1, 24364-84-9; benzoyl peroxide, 94-36-0; benzenesulfenyl chloride, 931-59-9; dibenzenesulfenimide-*N*-*d*, 73680-07-6; benzoic acid, 65-85-0; diphenyl disulfide, 882-33-7.

Cyclopropanones. Formation of Vinylcyclopropanols and Their Rearrangement to Cyclobutanones

Harry H. Wasserman,* Michael J. Hearn,[1] and Robert E. Cochoy

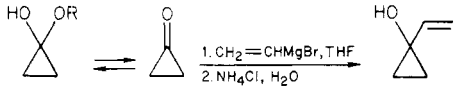
Department of Chemistry, Yale University, Sterling Chemistry Laboratory, New Haven, Connecticut 06520

Received February 25, 1980

Vinylcyclopropanols, formed by the addition of vinylmagnesium bromide to the ethyl hemiketal of cyclopropanone, may be converted to cyclobutanone derivatives on reaction with various electrophiles. The ring enlargement of 1-vinyl-2-methylcyclopropanol takes place by preferential migration of the more highly substituted carbon atom.

Cyclopropanones, among the most reactive carbonyl compounds in organic chemistry, have previously found limited use in synthesis partly because of difficulties in the preparation and handling of such energetic systems.[2] However, when trapped in the form of addition products which can yield the three-membered ketone in situ, cyclopropanone can be a participant in a number of useful chemical transformations including cyclobutanone and β-lactam formation.[2]

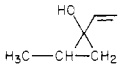
Among the cyclopropanone precursors has been the ethyl hemiketal (**1a**), which can be formed on addition of



1a, R = Et
b, R = Me
c, R = Ph

ethyl alcohol to solutions of cyclopropanone resulting from the addition of ketene to diazomethane. In previous work[3] we have found that such alcohol addition products (1) are in equilibrium with the free ketone in solution and undergo nucleophilic attack by carbanionic reagents. For example, reduction of **1a** to cyclopropanol takes place with lithium aluminum hydride, and reactions of **1a** with Grignard reagents lead to 1-substituted cyclopropanol derivatives.[4-6]

Table I. Vinylcyclopropanols from Cyclopropanones[a]

cyclopropanol	yield, %
 **2**	65
 **3**	65
 **4**	68

[a] All cyclopropanols were further characterized as the corresponding acetates, formed by treatment of the alcohol with 1 equiv of ethylmagnesium bromide followed by acetyl chloride.

(1) Department of Chemistry, Wellesley College, Wellesley, MA 02181.

(2) For reviews, see (a) N. J. Turro, *Acc. Chem. Res.*, **2**, 25 (1969); (b) H. H. Wasserman, G. M. Clark and P. C. Turley, *Fortsch. Chem. Forsch.*, **47**, 73 (1974); (c) B. M. Trost, *Acc. Chem. Res.*, **7**, 85 (1974); (d) J. M. Conia and M. J. Robson, *Angew. Chem., Int. Ed. Engl.*, **14**, 473 (1975).

(3) H. H. Wasserman, M. J. Hearn, B. Haveaux, and M. Thyes, *J. Org. Chem.* **41**, 153 (1976); H. H. Wasserman and E. Glazer, *J. Org. Chem.*, **40**, 1505 (1975); H. H. Wasserman, E. A. Glazer, and M. J. Hearn, *Tetrahedron Lett.*, 4855 (1973); H. H. Wasserman, H. W. Adickes, and O. Espejo de Ochoa, *J. Am. Chem. Soc.*, **93**, 5586 (1971).

(4) D. C. Clagett, Ph.D. Thesis, Yale University, New Haven, CT, 1966.

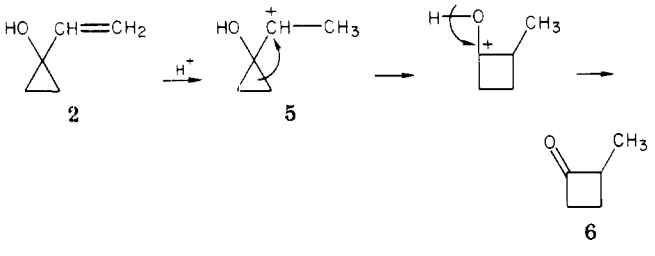
(5) H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Am. Chem. Soc.*, **91**, 2375 (1969)..

0022-3263/80/1945-2874$01.00/0

We now describe details of our studies on the chemistry of 1-vinylcyclopropanols prepared by this route. These reactive alcohols have recently become more readily available since an alternative method has been reported for the formation of **1a** which does not require use of diazomethane. The ethyl hemiketal can now be prepared easily in a two-step sequence from ethyl β-chloropropionate.[7]

In a typical nucleophilic addition to the carbonyl group, **1a** is introduced slowly to a refluxing solution of vinylmagnesium bromide in tetrahydrofuran. After being heated for a short period, the reaction is worked up with saturated aqueous ammonium chloride, forming 1-vinylcyclopropanol (**2**) in 65% yield. Vinylcyclopropanols formed by addition of Grignard reagents to cyclopropanone are listed in Table I. [a]All cyclopropanols were further characterized as the corresponding acetates, formed by treatment of the alcohol with 1 equiv of ethylmagnesium bromide followed by acetyl chloride.

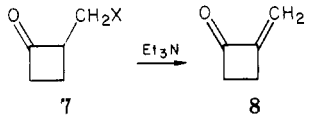
Vinylcyclopropanol (**2**) undergoes ready ring expansion with a variety of electrophilic reagents to form cyclobutanones. With dry hydrogen bromide gas in methylene chloride, it can be converted cleanly to 2-methylcyclobutanone (**6**) (83%). Similar results are obtained with



2 **5** **6**

p-toluenesulfonic acid (65%) and cold concentrated sulfuric acid (42%). Use of perchloric acid (0.4 M as an 80% aqueous acetone solution) leads to some ring cleavage, yielding ethyl vinyl ketone (20%) in addition to the ring-expanded product (20%). The ring expansion most probably takes place through **5** which, as a cyclopropylcarbinyl carbonium ion, readily rearranges to the cyclobutyl ion and then undergoes proton loss.[5]

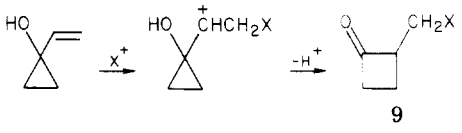
Other electrophilic species such as Cl^+ and OH^+ bring about the same type of ring expansion. Thus, dropwise addition of an alcohol-free chloroform solution of *tert*-butyl hypochlorite to a solution of **2** in chloroform in the dark at 0 °C afforded 2-(chloromethyl)cyclobutanone (**7**, X = Cl, 81%). Treatment of the latter in dry tetrahydrofuran



7 **8**

solution with 1 equiv of triethylamine produced 2-methylenecyclobutanone (**8**) in 50% yield, identical in all respects with the material reported by Muehlstaedt and Meinhold.[8] The reaction of an ethereal solution of **2** with an equivalent amount of perbenzoic acid in ether yielded 2-(hydroxymethyl)cyclobutanone (**9**, X = OH, 32%). With trioxymethylene and dibenzylamine hydrochloride in refluxing ethanol, 1-vinylcyclopropanol underwent a Mannich type of reaction to yield the corresponding 2-(2-(dibenzylamino)ethyl)cyclobutanone (**9**, X = $CH_2N(CH_2Ph)_2$, 60%). Table II summarizes the cyclobutanone derivatives formed by reaction of 1-vinylcyclopropanol with various electrophilic reagents.

Table II. Cyclobutanones from 1-Vinylcyclopropanol

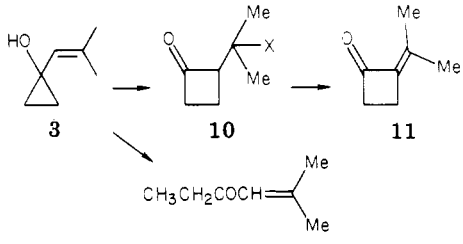


9

electrophilic reagent, X =	yield, %
H	83,[a] 42,[b] 20[c]
Cl	81
Br	45
OH	32
$CH_2N(CH_2Ph)_2$	60

[a] Dry HBr gas in methylene chloride. [b] Concentrated sulfuric acid. [c] 0.4 M perchloric acid in 80% aqueous acetone.

1-Isobutenylcyclopropanol (**3**) was prepared in 76% yield from the reaction of isobutenylmagnesium bromide with cyclopropanone ethyl hemiketal in refluxing tetrahydrofuran. Treatment of **3** with *tert*-butyl hypochlorite in chloroform at 0 °C resulted in ring enlargement, forming 2-(2-chloro-2-propyl)cyclobutanone (**10**, X = Cl, 80%).



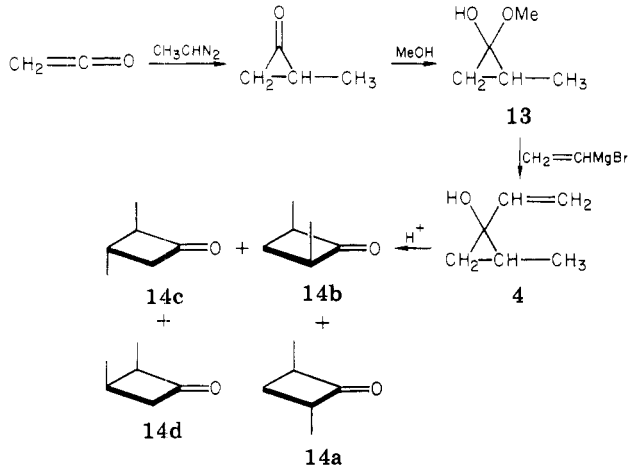
3 **10** **11**

12

The latter could be readily dehydrohalogenated with triethylamine in tetrahydrofuran to give 2-isopropylidenecyclobutanone (**11**) (70%).[9] When *m*-chloroperbenzoic acid was allowed to react with **3** in chloroform in the cold, 2-(2-hydroxy-2-propyl)cyclobutanone (**10**, X = OH, 65%) was obtained. With proton donors as electrophiles, however, opening of the cyclopropane ring was the predominant reaction, leading to 5-methyl-4-hexen-3-one (**12**) and products resulting from addition to this species. The latter observation is in accord with the findings of other workers[10] who noted that highly substituted vinylcyclopropanols tend to undergo ring-opening reactions in strongly acidic media.

In order to learn more about the migrating species in the vinylcyclopropanol–cyclobutanone rearrangement, we studied the ring enlargement of the methyl-substituted cyclopropane derivative (**4**). The latter was prepared in a two-step sequence starting with the addition of ketene to 1 equiv of diazoethane in methylene chloride at −78 °C. Addition of excess methanol to the reaction mixture followed by removal of solvent yielded the hemiketal **13** (41%) showing the expected spectroscopic properties.[11] This 2-methyl-1-methoxycyclopropanol was then added dropwise to a stirred refluxing solution of vinylmagnesium bromide in dry THF to yield 1-vinyl-2-methylcyclopropanol (**4**) showing a hydroxyl absorption in the infrared at 3350 cm^{-1} and three vinyl protons at δ 5–6 in the NMR.

(6) H. H. Wasserman and D. C. Clagett, *J. Am. Chem. Soc.*, **88**, 5368 (1966).
(7) K. Rühlmann, *Synthesis*, 236 (1971); J. Salaün, *J. Org. Chem.*, **41**, 1237 (1976).
(8) von M. Muehlstaedt and H. Meinhold, *J. Prakt. Chem.*, **309**, 162 (1968).
(9) J.-M. Conia and J.-P. Sandre, *Bull. Soc. Chim. Fr.*, **744** (1963).
(10) F. Bourelle-Wargnier, *Tetrahedron Lett.*, 1589 (1974).
(11) W. Hammond, Ph.D. Thesis, Columbia University, New York, NY 1966.



This vinylcyclopropanol derivative was further characterized as the acetate.

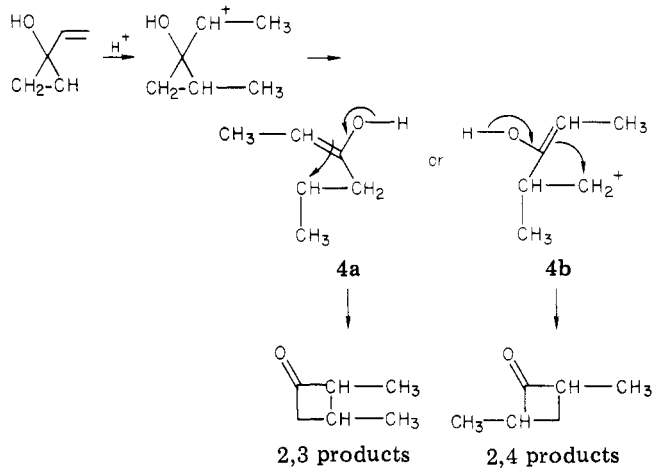
The vinyl carbinol 4 was recovered unchanged after heating at 110 °C for 17 h in dry base-washed pyrolysis tubes. However, when treated with concentrated sulfuric acid at 0 °C, rearrangement took place (40%) within 5 min, giving a mixture of dimethylcyclobutanones. The distribution of the dimethylcyclobutanones (**14a–d**) was the following: **14a**, 2,4-trans (4%); **14b**, 2,4-cis (26%); **14c**, 2,3-trans (24%); **14d**, 2,3-cis (46%).

The acid-catalyzed ring expansion took a different course in a nonpolar solvent. Thus, when 2-methyl-1-vinylcyclopropanol (4) was treated with dry HBr in methylene chloride at 0 °C for 5 min, only the 2,3-dimethylcyclobutanone derivatives (**14c,d**) were formed (83%) in a trans/cis ratio (**14c:14d**) of 3:1. Authentic samples of the dimethylcyclobutanone isomers **14a–d** were prepared according to the procedure of Turro and Gagosian,[12] employing the reaction of ketene with 2 equiv of diazoethane, in order to establish the structures of the reaction products. These cyclobutanones were then used for comparison (GC, NMR, IR) with the products obtained by the above acid-catalyzed ring expansion of the vinylmethylcyclopropanol (4).

In control runs with the individual cyclobutanone isomers, the following results were obtained. With hydrogen bromide in methylene chloride, the 2,3-cis isomer (**14d**) was converted to a mixture of 2,3-trans (**14c**, 73%) and 2,3-cis isomers (27%), with no detectable 2,4 material. With hydrogen bromide in methylene chloride, 2,3-trans was converted essentially to the same mixture of 2,3-trans (77%) and 2,3-cis (23%), with no 2,4 material. With sulfuric acid, 2,3-cis produced only a very small amount of 2,3-trans and no 2,4 material. With sulfuric acid, 2,3-trans remained totally unchanged. Neither 2,4-trans (**14a**) nor 2,4-cis (**14b**) produced any 2,3 material when treated with hydrogen bromide in methylene chloride. With sulfuric acid, 2,4-trans produced only a very small amount of 2,4-cis and no 2,3 material. With sulfuric acid, 2,4-cis showed no significant isomerization to the trans and gave no 2,3 material.

In Scheme I, showing the development of positive charge on the migrating carbon atoms (**4a** and **4b**), 2,4-dimethyl-substituted products are derived from the migration of the less substituted carbon (**4b**), while 2,3-dimethyl-substituted products result from the migration of the methyl-substituted atom (**4a**). Separate control experiments were run on each of the individual isomeric cyclobutanones to determine behavior under pertinent

Scheme I



conditions. The control experiments verified the following points: (1) Under all of the acidic conditions employed, the 2,3- and 2,4-isomers do not interconvert. (2) Starting from either 2,3-isomer, cis–trans isomerization occurs in the HBr/methylene chloride medium and results in the formation of products in the ratio (trans:cis) 75:25.[12] (3) Cis–trans isomerization is not significant in the sulfuric acid medium.

That 2,3-dimethyl-substituted products should be favored in the acid-catalyzed rearrangement is consistent with a preferred migration of the more highly substituted carbon atom.[13] If the ring expansion is pictured as shown in Scheme I, one would expect that the predominant products in a given medium would be those derived from the more stable accommodation of the positive charge in the carbonium ion intermediates. The ability of the reaction medium to stabilize the charged intermediates appears to be an important factor in determining the products formed, and the observed solvent effects can be explained on this basis. In concentrated sulfuric acid, the carbonium ions which are formed, whether they have primary or secondary character, are solvated by a solvent of high dielectric constant (ϵ = 100). This solvent stabilization helps to lower the energy of both primary and secondary carbonium ions and results in the formation of both 2,4- and 2,3-dimethylcyclobutanones. On the other hand, in methylene chloride, a solvent of very much lower dielectric constant (ϵ = 9), the carbonium ions formed by reaction of 4 with dry hydrogen bromide would not be expected to receive appreciable stabilization from the nonpolar medium. The extra inductive release of electrons from the methyl group would thus become more significant in stabilizing the secondary carbonium ion relative to the primary ion. Thus, the 2,3-dimethyl isomers are formed as the exclusive products.

Experimental Section

Melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 237, 337, 421 or 700A spectrophotometer as solutions in carbon tetrachloride or as otherwise specified. Nuclear magnetic resonance spectra were obtained at ambient temperature with a Varian Model A60 or Model A60-A (60 MHz) spectrometer or otherwise with a JEOLCO Minimar 100 (100 MHz) or Brüker 270 (270 MHz) spectrometer as indicated. Chemical shifts are reported in parts per million with tetramethylsilane as the internal standard and $CDCl_3$ as the solvent unless otherwise noted.

(12) N. J. Turro and R. Gagosian, *J. Am. Chem. Soc.*, **92**, 2036 (1970).

(13) Related observations in the peracid oxidation of methylenecyclopropanes are found in the work of J. K. Crandall and W. W. Conover, *J. Org. Chem.*, **43**, 3533 (1978).

Microanalyses were performed by Dr. P. Rittner of Olin Matheson Chemical Co., New Haven, CT, Galbraith Laboratories, Knoxville, TN, and Alfred Bernhardt, Muhlheim, Germany. Mass spectra were recorded on either a Hitachi Perkin-Elmer Model RMU-6 spectrometer, a CEC Model 21-103 spectrometer, courtesy of Dr. D. Friedland, or an AEI Model MS-9 instrument, courtesy of Dr. W. McMurray.

Gas chromatographic analyses and sample preparations were performed with an Aerograph Model A90-P3 instrument, using a 10 ft × 0.375 in. 20% Dow 710 silicon oil column packed on 70–80 mesh Anakrom AB, with a helium flow rate of 175 mL/min, or under the conditions specified in the individual experiments. Sample purity checks were made on a Waters Associates Model ALC-100 analytical chromatography apparatus.

Dry tetrahydrofuran for Grignard reactions was prepared by distilling commercial tetrahydrofuran (Fisher Certified Reagent) from lithium aluminum hydride and storing it over sodium metal. *tert*-Butyl hypochlorite was distilled prior to use. The distilled material was sealed in ampules under nitrogen and kept in the dark at 0 °C until used. Alcohol-free chloroform was prepared by passing commercial chloroform (Corco Reagent Grade) through a column (26 × 2.8 cm) of neutral Woelm alumina (activity I) and storing over anhydrous calcium chloride (8 mesh).

Cyclopropanone Ethyl Hemiketal (1a). For the preparation of diazomethane, *N*-nitroso-*N*-methylurea (32.0 g, 0.32 mol) was added in several portions over 30 min to an ice-cooled magnetically stirred mixture of 125 mL of 40% aqueous potassium hydroxide and 238 mL of ether. When all of the urea had dissolved, the mixture was cooled to −78 °C in dry ice–acetone to freeze the aqueous phase. The bright yellow ethereal layer was slowly decanted into a flask containing potassium hydroxide pellets and was stored at 0 °C under anhydrous conditions until required. The diazomethane solution was 0.64 M according to benzoic acid titration. Ketene was bubbled through a fritted-glass bubbler into 200 mL of methylene chloride in a 500-mL three-necked, round-bottomed flask equipped with a calcium chloride drying tube and a nitrogen bubbler. The reaction vessel was kept at −78 °C during the addition of ketene (17 min at 7.4 mmol/min, 126 mmol). After the formation of the ketene solution, the diazomethane solution was added dropwise over 30 min at −78 °C with rapid stirring by a magnetic stirring bar (186 mL of 0.64 M solution, 119 mmol of diazomethane). The mixture was stirred as 20 mL of absolute ethyl alcohol was added at −78 °C. After an additional 20 min, the solution was washed with 350 mL of saturated sodium bicarbonate. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporator to give 5.01 g (41%) of very clean material (bp 60–62 °C, 20 mmHg), uncontaminated by propionic ester. The material was identified by comparison of its IR and NMR spectra with those of an authentic sample: IR (liquid film) 3595, 3400, 3100, 3020 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (s, 4 H), 1.15 (t, 3 H), 3.70 (q, 2 H), 5.7 (s, 1 H).

1-Vinylcyclopropanol (2). Magnesium metal turnings (6.25 g, 0.26 mol) were placed within a 250-mL three-necked, round-bottomed flask which was equipped with a 125-mL dropping funnel, a magnetic stirrer, and a reflux condenser fitted with a calcium chloride drying tube. The apparatus was flamed and purged with dry nitrogen as it cooled. Dry tetrahydrofuran (55 mL) was poured into the flask, and several crystals of iodine were added. Vinyl bromide was conveniently obtained in pure form as the liquid (bp 16 °C, 750 mmHg) by condensation of the commercial bottled gas in a dry ice condenser. The dropping funnel was charged with vinyl bromide (17 mL, 28.6 g, 0.267 mol) and 40 mL of tetrahydrofuran. This solution (10 mL) was added in one portion to the reaction flask with gentle warming and mild agitation to start the formation of the Grignard reagent. The remainder of the vinyl bromide solution was dropped in at a rate sufficient to maintain refluxing. The solution was then heated at reflux for an additional 25 min. At the end of this time, 8.58 g (84.1 mmol) of distilled cyclopropanone ethyl hemiketal in 25 mL of tetrahydrofuran was added dropwise at reflux. The mixture was heated for another 0.5 h, cooled, and poured rapidly into saturated aqueous ammonium chloride (175 mL). The organic layer was drawn off. The aqueous layer was extracted with ether (3 × 100 mL). The combined organic phases were dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the remaining material was distilled under vacuum in a short-path apparatus (bp 35–45 °C, 20 mmHg). 1-Vinylcyclopropanol was identified on the basis of comparison of its IR and NMR spectra with those previously noted:[5] IR (liquid film) 3400, 3100, 3020, 1640, 1420, 1300 cm^{-1}; NMR ($CDCl_3$) δ 0.79 (m, 4 H), 4.45 (s, 1 H), 4.85–5.85 (m, 3 H).

1-Vinylcyclopropyl Acetate. 1-Vinylcyclopropanol was acetylated by using a procedure developed by Barber.[14]

An ethereal solution of ethylmagnesium bromide from magnesium turnings (0.94 g, 39 mmol) and ethyl bromide (4.25 g, 39 mmol) was prepared in a 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a 50-mL dropping funnel, and a reflux condenser fitted with a drying tube. 1-Vinylcyclopropanol (3.00 g, 35.8 mmol) in ether (25 mL) was then added dropwise followed immediately by acetyl chloride (3.21 g, 41 mmol) in ether (25 mL). The solution was then poured into water (40 mL). The ether layer was separated, washed with several portions of saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The solvent was removed (rotovac) to yield crude 1-vinylcyclopropyl acetate (3.48 g, 27.6 mmol, 77%) which was purified by preparative GLC (column temperature 85 °C); IR ν_{max} 3100, 3020, 3000, 1760, 1645, 1420, 1370, 1225 cm^{-1}; NMR δ 5.95–5.50 (m, 1 H), 5.05–4.70 (m, 2 H), 1.92 (s, 3 H), 0.92 (m, 4 H).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.41; H, 8.00.

2-(Bromomethyl)cyclobutanone (7, X = Br). In a 250-mL conical flask, 1-vinylcyclopropanol (2.12 g, 0.252 mol) and 75 mL of ether were brought to 0 °C through the use of an ice–salt bath. Bromine was added dropwise with magnetic stirring until a faint red color persisted. The solution was washed quickly with aqueous sodium thiosulfate solution to discharge the slight excess of bromine and dried over magnesium sulfate. The ether was removed by distillation at room pressure. The residue was distilled in vacuo to give 2-(bromomethyl)cyclobutanone (1.85 g, 45%), bp 85 °C, 30 mmHg. Further purification was accomplished by vapor-phase chromatography with a 12 ft × 1.4 in. 9% SE-30 column packed on Anakrom A (column temperature 110 °C, helium flow rate 60 cm/min): IR (liquid film) 3000, 2965, 2940, 2875, 1780, 1440, 1400, 1320, 1225, 1190, 1150, 1060, 910 cm^{-1}; NMR ($CDCl_3$) δ 1.75–2.50 (m, 2 H), 2.85–3.25 (m, 2 H), 3.45–4.00 (m, 3 H); 2,4-dinitrophenylhydrazone, mp 137 °C dec.

Anal. Calcd for C_5H_7BrO: C, 36.85; H, 4.33. Found: C, 36.55; H, 4.20.

2-Methylcyclobutanone (6). Reaction of 1-Vinylcyclopropanol with Dry HBr in Methylene Chloride. 1-Vinylcyclopropanol (200 mg, 2.38 mmol) was dissolved in methylene chloride (25 mL) and brought to 0 °C. Dry HBr gas was bubbled through the solution for 2 min. The reaction was allowed to stand for 5 min in the cold, poured into saturated sodium bicarbonate solution (10 mL), and extracted into methylene chloride (2 × 10 mL). The extract was dried over anhydrous magnesium sulfate and the solvent removed under vacuum at 25 °C to give 2-methylcyclobutanone (83%). A pure sample of 2-methylcyclobutanone was obtained by preparative GLC (column temperature 140 °C): IR ν_{max} 1785, 1090, 1030 cm^{-1}; NMR δ 3.50–1.30 (m, 5 H), 1.15 (d, J = 7 Hz, 3 H).

Anal. Calcd for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.20; H, 9.68.

Reaction of 1-Vinylcyclopropanol with Sulfuric Acid. 1-Vinylcyclopropanol (0.60 g, 7.1 mmol) was added dropwise with stirring to concentrated sulfuric acid (4 mL) at 0 °C. The reaction mixture immediately darkened. After being stirred 10 min at 0 °C, the solution was poured into ice water (40 mL) and extracted with ether (4 × 15 mL). The combined ether extracts were neutralized with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The ether was then removed by distillation to yield 2-methylcyclobutanone (0.25 g, 3.0 mmol, 42%). No starting material or ethyl vinyl ketone was present.

Reaction of 1-Vinylcyclopropanol with *p*-Toluenesulfonic Acid in Methylene Chloride. Treatment of 1-vinylcyclopropanol (100 mg, 1.19 mmol) in methylene chloride (20 mL) at 0 °C with *p*-toluenesulfonic acid (25 mg) was followed by stirring for 5 min

(14) E. Barber, Ph.D. Thesis, Yale University, New Haven, CT, 1969.

and workup as noted above to yield 2-methylcyclobutanone (65%) and ethyl vinyl ketone (18%), identical in all respects with authentic samples.

Reaction of 1-Vinylcyclopropanol with Perchloric Acid. 1-Vinylcyclopropanol (200 mg) was allowed to stir at room temperature with perchloric acid (10 mL, 0.4 M as an 80% aqueous acetone solution). Workup gave 2-methylcyclobutanone (20%) and ethyl vinyl ketone (20%). No starting material was recovered.

2-(Chloromethyl)cyclobutanone (7, X = Cl). Reaction of 1-Vinylcyclopropanol with *tert*-Butyl Hypochlorite in Chloroform at 0 °C. Distilled *tert*-butyl hypochlorite (3 mL) in alcohol-free chloroform (4 mL) was added dropwise, with stirring, to a solution of 1-vinylcyclopropanol (1.27 g, 15 mmol) in alcohol-free chloroform (6 mL). The reaction was run in a black-taped flask at 0 °C in a dark room. During the addition of *tert*-butyl hypochlorite, the temperature of the solution rose to a maximum of 35 °C and then dropped. The solution was stirred for an additional 45 min at 5–10 °C. The solvent was then removed (rotovac) in a black-taped flask. Care was taken to insure removal of all unreacted *tert*-butyl hypochlorite before final distillation. The residue was then distilled (short-path apparatus) to yield 2-(chloromethyl)cyclobutanone (1.45 g, 12.2 mmol, 81%), bp 68–70 °C (14 mm), as a colorless liquid which rapidly discolors upon standing. A sample of 2-(chloromethyl)cyclobutanone was further purified by preparative GLC (15 ft, 5% SE-30 on Anakrom A, 110 °C): IR ν_{max} 1790, 1430, 1390, 1320, 1275, 1075 cm^{-1}; NMR δ 3.90–3.50 (m, 3 H), 3.30–2.80 (m, 2 H), 2.50–1.70 (m, 2 H).

Anal. Calcd for C_5H_7ClO: C, 50.63; H, 5.95; Cl, 29.92. Found: C, 50.79; H, 6.04; Cl, 29.69.

2-Methylenecyclobutanone (8). Reaction of 2-(Chloromethyl)cyclobutanone with Triethylamine. Distilled 2-(chloromethyl)cyclobutanone (2.45 g, 20 mmol) in tetrahydrofuran (20 mL) was added to a 50-mL, three-necked, round-bottomed flask fitted with a magnetic stirrer, a 25-mL dropping funnel, and a reflex condenser. Triethylamine (2.45 g, 24 mmol) in tetrahydrofuran (15 mL) was added dropwise at ambient temperature with stirring. The solution was then heated at reflux for 2 h, cooled, and filtered to remove the precipitated triethylamine hydrochloride. The filtrate was washed once with water (~10 mL) and the aqueous layer washed twice with ether (2 × 10 mL). The combined organic phases were dried over anhydrous magnesium sulfate and distilled to a head temperature of ~70 °C. The light yellow pot residue (3.10 g) consisted of tetrahydrofuran (~72%) and 2-methylenecyclobutanone (~0.87 g, 10.7 mmol, 50% overall). A portion of the crude solution was purified by GLC (column temperature 100 °C) to give pure 2-methylenecyclobutanone as a colorless liquid that resinifies at room temperature: IR ν_{max} ($CHCl_3$) 1755, 1655, 1390, 1215, 1150, 1060, 945 cm^{-1}; NMR δ 5.62 (m, 1 H), 4.99 (m, 1 H), 3.14–2.38 (m, 4 H); UV λ_{max} (CH_3CN) 226 μm (ϵ 7600), 233 (sh); mass spectrum, *m/e* 82 (parent).

Anal. Calcd for C_5H_6O: C, 73.15; H, 7.37, Found: C, 72.87; H, 7.16.

2-(Hydroxymethyl)cyclobutanone (9, X = OH). Reaction of 1-Vinylcyclopropanol with Perbenzoic Acid. An ethereal solution of perbenzoic acid (40 mL, containing 33 mmol of perbenzoic acid) was added dropwise at ambient temperature to a stirred solution of 1-vinylcyclopropanol (2.52 g, 30 mmol) in ether (25 mL). The solution was allowed to stir at ambient temperature for 12 h. The reaction mixture was then transferred to a dropping funnel and added slowly to a suspension of sodium hydride (2.5 g, 55% in mineral oil) in ether (50 mL). Excess sodium hydride was then destroyed with absolute ethanol (~5 mL) and the resulting sodium salts were filtered. The salts were washed with several portions of 50:50 ether/ethanol solution. The filtrate and washings were then combined, concentrated (rotovac), and distilled (short-path apparatus) to yield crude 2-(hydroxymethyl)cyclobutanone (0.95 g, 9.5 mmol, 32%), bp 100–105 °C (5 mm). A portion of the crude product was further purified by GLC (column temperature 155 °C): IR ν_{max} 3480, 1780, 1460, 1390, 1265, 1080 cm^{-1}; NMR δ 4.10–3.20 (m, 4 H), 3.15–2.75 (m, 2 H), 2.35–1.70 (m, 2 H).

Acetylation of 2-(Hydroxymethyl)cyclobutanone. Ketene was bubbled through a cold solution (0 °C) of 2-(hydroxymethyl)cyclobutanone (0.55 g, 5.5 mmol) in anhydrous ether (15 mL) at a moderate rate for 1 h. The ether was then removed (rotovac) to yield crude 2-(acetoxymethyl)cyclobutanone (0.50 g, 3.5 mmol, 64%). The crude product was purified by preparative GLC (7 ft, 16% QF-1 on 70–80 mesh Anakrom ABS, 175 °C): IR ν_{max} 1790, 1750, 1385, 1370, 1240, 1080, 1050 cm^{-1}; NMR δ 4.20 (d, J = 5 Hz, 2 H), 3.90–3.30 (m, 1 H), 3.25–2.88 (m, 2 H), 2.50–1.50 (m, 2 H), 2.00 (s, 3 H).

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.80; H, 7.00.

2-(2-(Dibenzylamino)ethyl)cyclobutanone (9, X = $CH_2N(CH_2Ph)_2$). 1-Vinylcyclopropanol (1.0 g, 12 mmol) in 2 mL of absolute ethanol was added to a stirred solution of trioxymethylene (1.0 g, 11 mmol) and dibenzylamine hydrochloride (1.7 g, 7 mmol) in refluxing absolute ethyl alcohol (10 mL). The mixture was stirred at reflux for 5 h, concentrated, and worked up in the usual way to yield 2-(2-(dibenzylamino)ethyl)cyclobutanone (60%): mp 80.5–82 °C; IR ν_{max} 1780 cm^{-1}; NMR δ 7.20 (s, 10 H), 3.45 (s, 4 H), 3.3–2.4 (m, 5 H), 2.0–1.4 (m, 4 H).

Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.95; H, 7.89; N, 4.77.

1-Isobutenylcyclopropanol (3). Isobutenyl bromide was prepared and purified according to the method of Braude and Timmons.[15] In an apparatus similar to that used in the preparation of 1-vinylcyclopropanol (2), magnesium metal (7.2 g, 0.30 mol) in dry THF (60 mL) was allowed to react with isobutenyl bromide (2 g) with mechanical stirring until reaction commenced. The remaining bromide (total, 37 g, 0.274 mol) in 50 mL of THF was then added dropwise under mild reflux. After the solution was heated for 10 min at reflux, cyclopropanone ethyl hemiketal (10.2 g, 95% pure, 0.10 mol) in 40 mL of THF was added dropwise. After 1 h at reflux, the reaction mixture was worked up as described for the preparation of 1-vinylcyclopropanol. Distillation of the crude product yielded 8.5 g of 1-isobutenylcyclopropanol, (76%, 93% purity), bp 65–70 °C (18 mm), along with a small amount of 1,1-diisobutenylphenol. The crude cyclopropanol could be purified by preparative GLC (column temperature 110 °C): IR (liquid film) ν_{max} 3310, 3080, 1670, 1620, 1450, 1380, 1225, 1020 cm^{-1}; NMR δ 5.33 (m, J = 1.5 Hz, 1 H), 3.20 (s, 1 H), 1.80 (d, J = 1.5 Hz, 3 H), 1.65 (d, J = 1.5 Hz, 3 H), 0.65 (m, 4 H). The product was further characterized by conversion to the acetate, as described below. For large-scale preparative purposes, it was found convenient to use the 1-isobutenylcyclopropanol as a 93% pure product.[16]

1-Isobutenylcyclopropyl Acetate. To an ethereal solution of ethylmagnesium bromide, prepared from magnesium turnings (0.27 g, 11 mmol) and ethyl bromide (1.20 g, 11 mmol), was added 1-isobutenylcyclopropanol (0.76 g, 6.8 mmol) in ether (10 mL) followed by acetyl chloride (0.86 g, 11 mmol) in ether (5 mL). The reaction mixture was then poured into water (~15 mL) and extracted first with saturated sodium bicarbonate solution and then with saturated ammonium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated (rotovac) to yield crude 1-isobutenylcyclopropyl acetate (~1.0 g, 6.4 mmol, 95%). A portion of the crude acetate was purified by preparative GLC (column temperature 150 °C): IR ν_{max} 3080, 1750, 1670, 1450, 1370, 1250, 1200 cm^{-1}; NMR δ 5.60 (m, J = 1.5 Hz, 1 H), 1.82 (s, 3 H), 1.77 (d, J = 1.5 Hz, 3 H), 1.69 (d, J = 1.5 Hz, 3 H), 0.82 (m, 4 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.20; H, 9.12.

Reaction of 1-Isobutenylcyclopropanol with Perchloric Acid. An 80% aqueous acetone solution which was approximately 0.4 M in perchloric acid was prepared by diluting 5.7 mL of 70% perchloric acid to 20 mL with water and mixing with 80 mL of acetone.

To 1-isobutenylcyclopropanol (2.80 g, 25 mmol) was added 40 mL of the above acid solution, and the solution was stirred and heated at reflux for 11 h. The dark solution lightened when neutralized with saturated sodium bicarbonate solution. The excess acetone was then distilled (760 mm). The aqueous residue was then extracted several times with ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. The ether was removed by distillation, leaving a residue (4.15 g) which, by preparative GLC (column temperature 118 °C), gave mesityl

(15) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2000 (1950).
(16) R. Cochoy, Ph.D. Thesis, Yale University, New Haven, CT, 1969.

oxide and 5-methyl-4-hexen-3-one (identical with commercially available products), as well as 5-hydroxy-5-methyl-3-hexanone (0.40 g, 3 mmol, 12%): IR (liquid film) ν_{max} 3490, 1700, 1460, 1375, 1315, 1160, 1110 cm^{-1}; NMR δ 3.40 (s, 1 H), 2.50 (s, 2 H), 2.40 (q, 2 H), 1.18 (s, 6 H), 1.02 (t, 3 H); mass spectrum, m/e 112 (p − 18, loss of water).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.88; H, 10.61.

2-(2-Chloro-2-propyl)cyclobutanone (10, X = Cl). Reaction of 1-Isobutenylcyclopropanol with *tert*-Butyl Hypochlorite at 0 °C. Distilled *tert*-butyl hypochlorite (3.5 mL) in alcohol-free chloroform (20 mL) was added dropwise at 0 °C to a solution of 1-isobutenylcyclopropanol (1.60 g, 14.3 mmol) in alcohol-free chloroform (15 mL). After addition was complete, the solution was allowed to warm to room temperature and stirred for an additional 45 min. The solvent was then removed (rotovac), and the residue was distilled (short-path apparatus) to yield crude 2-(2-chloro-2-propyl)cyclobutanone (1.70 g, 11.5 mmol, 80%), bp 60–65 °C (5 mm). A sample of 2-(2-chloro-2-propyl)cyclobutanone was further purified by preparative GLC (7 ft, 16% QF-1 on 70–80 mesh Anakrom ABS, 85 °C): IR ν_{max} 1785, 1460, 1390, 1375, 1300, 1210, 1080 cm^{-1}; NMR δ 3.50 (t, 1 H), 2.89 (m, 2 H), 2.20 (m, 2 H), 1.62 (s, 3 H), 1.58 (s, 3 H).

Anal. Calcd for $C_7H_{11}ClO$: C, 57.32; H, 7.75; Cl, 24.20. Found: C, 57.57; H, 7.64; Cl, 24.47.

2-Isopropylidenecyclobutanone (11). Reaction of 2-(Chloro-2-propyl)cyclobutanone with Triethylamine. Distilled 2-(2-chloro-2-propyl)cyclobutanone (2.0 g, 13.6 mmol) in tetrahydrofuran (15 mL) was added to a 50-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a 25-mL dropping funnel, and a reflux condenser. Triethylamine (2.70 g, 27 mmol) in tetrahydrofuran (10 mL) was added dropwise at ambient temperature with stirring. The solution was then heated at reflux for 3 h, cooled in an ice bath, and filtered to remove the precipitated triethylamine hydrochloride. The solvent was then distilled (760 mm) to a head temperature of 68 °C. Distillation (short-path apparatus) of the remaining liquid (4.4 g) provided almost pure 2-isopropylidenecyclobutanone (1.04 g, 9.5 mmol, 70%), bp 63–68 °C (15 mm), as a colorless liquid stable at room temperature. A portion of the distillate was further purified by GLC (column temperature 138 °C): IR ν_{max} ($CHCl_3$) 1745, 1670, 1430, 1390, 1370, 1095, 1010 cm^{-1}; NMR δ 2.90–2.20 (m, 4 H), 2.02 (t, 3 H), 1.71 (s, 3 H); UV λ_{max} (CH_3CN) 249 μm (ϵ 10 700) [lit.[9] λ_{max} (EtOH) 249–250 μm (ϵ 9950)].

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.27; H, 8.95.

2-(2-Hydroxy-2-propyl)cyclobutanone (10, X = OH). Reaction of 1-Isobutenylcyclopropanol with *m*-Chloroperbenzoic Acid. To a stirred solution of 1-isobutenylcyclopropanol (2.50 g, 22 mmol) in chloroform (14 mL) cooled to 0 °C in an ice–salt bath was added dropwise, with stirring, *m*-chloroperbenzoic acid (5.60 g, 89% assay, 29 mmol) in chloroform (56 mL). The solution was warmed to room temperature with stirring for 12 h. After the solution was cooled in an ice bath, the precipitated *m*-chlorobenzoic acid was removed by filtration (Buchner). The filtrate was washed once with a saturated solution of sodium sulfite and several times with a saturated solution of sodium bicarbonate. The organic phase was separated and the aqueous washings were extracted several times with ether. The ether washings were combined with the chloroform phase and dried over anhydrous magnesium sulfate. After the solvent (rotovac) was removed, a portion of the crude residue was purified by preparative GLC (column temperature 140 °C) to yield 2-(2-hydroxy-2-propyl)-cyclobutanone (1.83 g, 14.2 mmol, 65%): IR ν_{max} 3620, 3500, 1780, 1465, 1375, 1210, 1080, 945 cm^{-1}; NMR δ 3.45–2.70 (m, 3 H), 2.58 (s, 1 H), 2.21–1.78 (m, 2 H), 1.28 (s, 3 H), 1.16 (s, 3 H).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.70; H, 9.19.

Methylcyclopropanone Methyl Hemiketal (13). Nitrosoethylurea (17 g) was added in small portions to a rapidly stirred mixture of ether (150 mL) and 40% KOH (100 mL) at 0 °C. The aqueous layer became viscous and white, while the ether layer turned reddish orange. The aqueous layer was frozen out at −78 °C, and the ether portion was decanted into a flask containing some KOH pellets in order to dry. A 5-mL aliquot was withdrawn and reacted with a weighed excess of benzoic acid (673 mg, 5.51 mmol) in ether (5 mL). The benzoic acid solution was titrated with standard NaOH solution (43.5 mL of 0.1 N solution, 4.35 mmol), and the molarity of the diazoethane solution was obtained (0.23 M). Ketene was generated and doubly distilled before use. The ketene was bubbled into a methylene chloride solution (200 mL) at −78 °C for 16 min. The diazoethane solution (125 mL, 28.8 mmol) was then added dropwise with rapid stirring. After the addition was complete, the cold reaction mixture was placed under vacuum for 2.25 h, in the presence of a slow bleed of dry nitrogen gas from a capillary tube below the surface of the liquid. After evacuation, a large excess of methanol (50 mL) was added, and the solvent was removed on the rotary evaporator below room temperature to give the hemiketal (41%), possessing all of the spectroscopic properties previously noted for the compound.[11] In a similar way, the ethyl hemiketal could be prepared from methylcyclopropanone and ethanol. The ethyl hemiketal underwent conversion to the methyl hemiketal upon standing at room temperature in excess methanol. The methyl hemiketal could be distilled (bp 61–66 °C, 18 mmHg) to afford virtually pure material.

1-Vinyl-2-methylcyclopropanol (4). Magnesium metal (1.21 g, 49.7 mmol, 70–80 mesh) was added to a 50-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen line, a 25-mL dropping funnel, and a reflux condenser. After the apparatus was flame dried, some tetrahydrofuran (10 mL) and a few crystals of iodine were added. The dropping funnel was charged with vinyl bromide (5.35 g, 8.15 mL, 49.7 mmol) dissolved in cold tetrahydrofuran (10 mL), and a small portion of this solution was then added at such a rate that gentle refluxing was observed. After complete addition, refluxing was continued for 30 min. Then a solution of methylcyclopropanone methyl hemiketal (2.20 g, 21.6 mmol) in tetrahydrofuran (10 mL) was added dropwise at reflux. The solution was refluxed and stirred for a further 20 min and then poured into saturated aqueous ammonium chloride solution (100 mL). The organic layer was drawn off, and the aqueous layer was extracted with ether (2 × 100 mL). The combined organic phases were dried over anhydrous magnesium sulfate, and the solvent was removed on the rotary evaporator to yield a yellow oil, which was further purified by distillation at 48–50 °C (16 mmHg): yield 68% by NMR; IR (liquid film) 3350, 3080, 3000, 2960, 2930, 2870, 1635, 1450, 1380, 1280, 1220, 1160, 1100, 1065, 1030, 1000, 900, 870, 790, 720 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.6–1.35 (complex multiplets, 6 H), 4.0 (br, 1 H), 5.0–6.0 (vinyl pattern, 3 H). The vinyl carbinol was further characterized as the acetate.

1-Vinyl-2-methylcyclopropyl Acetate. A solution of ethylmagnesium bromide in ether was prepared from magnesium metal (0.114 g, 4.70 mmol, 70–80 mesh) and bromoethane (0.511 g, 4.70 mmol) in a 50-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a dropping funnel, and a nitrogen line. After complete addition of the bromoethane, the solution was refluxed for 40 min. Then 1-vinyl-2-methylcyclopropanol (0.400 g, 4.08 mmol) was added dropwise at reflux, followed immediately by the addition of acetyl chloride (0.358 g, 4.70 mmol). After being stirred at reflux for several minutes, the reaction was poured into 50 mL of saturated aqueous sodium chloride solution. The ether layer was drawn off, and the aqueous layer was extracted with 50 mL of ether. The combined organic layers were dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed by concentration under vacuum to give a light yellow oil (51%). The product was further purified by vapor-phase chromatography on a 10 ft × $^3/_8$ in. 20% 1,2,3-tris(β-cyanoethoxy)propane column packed on Chromosorb P (flow rate 60 mL of He/min, column temperature 70 °C): IR (liquid film) 3080, 3000, 2960, 2930, 2870, 1750, 1640, 1440, 1370, 1240, 1220, 1200, 1100, 1020, 990, 950, 900 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.6–1.21 (complex pattern from which emerges at 1.21 a br s), 2.23 (s, 3 H), 5.15–6.20 (vinyl pattern, 3 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.75; H, 8.62.

Collection of the product peak under the conditions noted above followed by reinjection of the sample on the same column indicated only one peak.

Thermal Behavior of 1-Vinyl-2-methylcyclopropanol. The thermal stability of the vinyl carbinol was tested by placing a sample of the compound in a dry tube which had been previously

washed with concentrated ammonium hydroxide solution; the tube was sealed under vacuum and placed in an oil bath at 110 °C for 17 h. Analysis by NMR and IR showed recovery of the starting material intact.

Reaction of 1-Vinyl-2-methylcyclopropanol with Sulfuric Acid. To concentrated sulfuric acid (5 mL) at 0 °C was added dropwise with stirring 1-vinyl-2-methylcyclopropanol (75 mg in 75 mL of tetrahydrofuran). Stirring at 0 °C was continued for 5 min, and the mixture was poured into ice water (40 mL) and extracted with ether (4 × 25 mL). The ether phase was washed with saturated sodium bicarbonate solution (20 mL) and dried over anhydrous magnesium sulfate. Removal of the solvent at room temperature under vacuum gave the mixture of dimethylcyclobutanone isomers (20 mg, 40% overall), which was analyzed by VPC on a 10 ft × $^3/_8$ in. 20% 1,2,3-tris(β-cyanoethoxy)propane column packed on Chromosorb P (column temperature 70 °C, flow rate 60 mL of He/min). Authentic samples of the cyclobutanone isomers were synthesized according to a known method.[12] These samples were then used for comparison purposes with the products of the present experiment. The percentage of products was the following: 2,4-trans (4%), 2,4-cis (26%), 2,3-trans (24%), 2,3-cis (46%).

Reaction of 1-Vinyl-2-methylcyclopropanol with Dry HBr in Methylene Chloride. The vinyl carbinol (99 mg in 89 mg of tetrahydrofuran) was dissolved in methylene chloride (25 mL) and brought to 0 °C with an ice–water bath. Dry HBr gas from the commercial source was bubbled through the solution for 2 min. The reaction was then allowed to stand for 5 min in the cold, poured into saturated sodium bicarbonate solution (10 mL), and extracted with methylene chloride (2 × 10 mL). After the solution was dried over anhydrous magnesium sulfate, the solvent was removed under vacuum at room temperature to yield the isomeric dimethylcyclobutanones (83% overall). The compounds were analyzed by VPC as before, showing formation of 2,3-trans (75%) and 2,3-cis (25%). The other isomers were not observed. In separate control runs done on the individual isomers, the following results were obtained. With hydrogen bromide in methylene chloride, 2,3-cis went to a mixture of 2,3-trans (73%) and 2,3-cis (27%), with no 2,4 material. With hydrogen bromide in methylene chloride, 2,3-trans went to 2,3-trans (77%) and 2,3-cis (23%), with no 2,4 material. With sulfuric acid, 2,3-cis produced only a very small amount of 2,3-trans and no 2,4 material. With sulfuric acid, 2,3-trans remained totally unchanged. Neither 2,4-trans nor 2,4-cis produced any 2,3 material at all when treated with hydrogen bromide in methylene chloride. With sulfuric acid, 2,4-trans produced only a very small amount of 2,4-cis and no 2,3 material at all. With sulfuric acid, 2,4-cis underwent no significant isomerization to the trans form and gave no 2,3 material.

Acknowledgment. This work was supported by Grant GM-07874 from the National Institutes of Health.

Registry No. 1a, 13837-45-1; **2**, 22935-31-5; **2** acetate ester, 73680-08-7; **3**, 73680-09-8; **3** acetate ester, 73680-10-1; **4**, 73680-11-2; **4** acetate ester, 73680-12-3; **6**, 1517-15-3; **7** (X = Br), 73680-13-4; **7** (X = Br) 2,4-dinitrophenylhydrazone, 73680-14-5; **7** (X = Cl), 22935-33-7; **8**, 17714-43-1; **9** (X = OH), 23107-52-0; **9** (X = OAc), 73680-15-6; **9** (X = $CH_2N(CH_2Ph)_2$), 22935-34-8; **10** (X = Cl), 73680-16-7; **10** (X = OH), 73680-17-8; **11**, 24186-34-3; **13**, 19995-72-3; **14a**, 1604-99-5; **14b**, 1605-00-1; **14c**, 1942-42-3; **14d**, 28113-36-2; cyclopropanone, 5009-27-8; 2-methylcyclopropane, 19995-71-2; vinyl bromide, 593-60-2; ethyl vinyl ketone, 1629-58-9; ketene, 463-51-4; dibenzylamine hydrochloride, 20455-68-9; isobutenyl bromide, 3017-69-4; 5-hydroxy-5-methyl-3-hexanone, 59356-91-1.

Tetranitroethylene. In Situ Formation and Diels–Alder Reactions[1]

T. Scott Griffin and Kurt Baum*

Fluorochem Inc., Azusa, California 91702

Received March 20, 1980

The reaction of hexanitroethane with dienes gave the Diels–Alder adducts of tetranitroethylene. Thus, the reaction in refluxing benzene of hexanitroethane with anthracene gave 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene. Similarly, 9-methylanthracene and 9,10-dimethylanthracene gave 9-methyl-11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene and 9,10-dimethyl-11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene, respectively. Cyclopentadiene reacted with hexanitroethane in methylene chloride at −10 °C to give 5,5,6,6-tetranitro-2-norbornene. Reaction of the anthracene adduct of tetranitroethylene with sodium iodide gave the sodium salt of 12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one, which was protonated with acetic acid to give the corresponding nitro ketone. Treatment of the sodium salt with chlorine and bromine gave 12-chloro-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one and 12-bromo-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one, respectively.

Olefins highly substituted with electron-withdrawing substituents have been of general interest since the first synthesis of tetracyanoethylene[2] led to a broad area of useful reactions.[3] Tetranitroethylene remains an unknown extreme example of this class of compounds.[4] The existence of the unstable olefin 1,1-dinitroethylene has been demonstrated by trapping experiments,[5] and, more recently, the isolation and characterization of 1,2-dinitroethylene has been reported.[6] We now report the in situ preparation of tetranitroethylene as evidenced by its trapping as Diels–Alder adducts.

Mixing hexanitroethane[7] with an excess of anthracene in benzene gave a transient violet coloration that disappeared upon heating. Heating the solution at reflux resulted in the evolution of nitrogen oxides and the precipitation of a 63% yield of a white solid that was identified

(1) This work was supported by the U.S. Army Research Office.

(2) Cairns, T. L.; Carboni, R. A.; Coffman, D. D.; Engelhardt, V. A.; Heckert, R. E.; Little, E. L.; McGeer, E. G.; McKusick, B. C.; Middleton, W. J.; Scribner, R. M.; Theobald, C. W.; Winberg, H. E. *J. Am. Chem. Soc.* **1958**, *80*, 2775.

(3) For reviews see: (a) Dhar, D. N. *Chem. Rev.* **1967**, *67*, 611; (b) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1133; (c) *Ibid.*; 1975; Vol. 5, p 647.

(4) The compound was claimed in a patent (Gilliland, W. L. U.S. Patent 3 257 470, 1966) without structure proof and the work could not be repeated: Nielsen, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.* **1979**, *44*, 1181.

(5) (a) Frankel, M. B. *J. Org. Chem.* **1958**, *23*, 813. (b) Zeldin, L.; Schechter, H. S. *J. Am. Chem. Soc.* **1957**, *79*, 4708. (c) Gold, M. H.; Hamel, E. E.; Klager, K. *J. Org. Chem.* **1957**, *22*, 1665. (d) Winters, L. J.; McEwen, W. E. *Tetrahedron* **1963**, *19*, Suppl. 1, 49. (e) Ungnade, H. E.; Kissenger, L. W. *J. Org. Chem.* **1966**, *31*, 369.

(6) Lipina, E. S.; Pavlova, F. Z.; Perekalin, V. V. *Zh. Org. Khim.* **1969**, *5*, 1312.

(7) Borgardt, F. B.; Seeler, A. K.; Noble, P., Jr. *J. Org. Chem.* **1966**, *31*, 2806.

0022-3263/80/1945-2880$01.00/0