

Cryochemical Synthesis and Molecular Energetics of Cyclopropanone and Some Related Compounds^{1a}

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Abstract: As a further illustration of the utility of cryogenic techniques in preparative chemistry, diazomethane and ketene were found to react smoothly at -145° in a solventless, liquid-phase process to yield cyclopropanone and possibly allene oxide. Cyclobutanone and cyclopentanone could also be produced depending upon the ratio of the reactants. Similarly, diazomethane reacted with ethylene at -145° to yield cyclopropane, cyclobutane, and cyclopentane. Reactivity at cryogenic temperatures increased with increasing ring strain. Mass spectral and critical potential measurements on cyclopropanone, cyclopropenone, cyclobutanone, cyclopropene, and cyclopropane are also reported. No energetic changes between cryogenic and room temperatures were observed for these species, and thus their chemistry is not influenced by rearrangement effects.

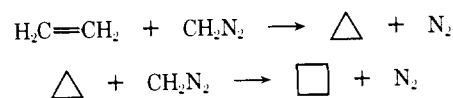
Cryochemistry is concerned with the synthesis, isolation, and characterization of compounds which have only a fleeting existence at higher temperatures because of their high instability or reactivity. If the activation energy for disappearance is small, we have only to make kT smaller and thereby freeze out an otherwise facile loss process. Clearly, the characterization of such species is severely constrained by their extreme thermal sensitivity.

Our primary characterization technique is cryogenic mass spectrometry² wherein one maintains the sample at its very low temperature until the instant of electron impact by arranging a refrigerated inlet system, the final cold port of which is grazed by the ionizing electron beam in the source. By controlled warming of a solid mixture, individual components can be sequentially distilled into the ion source depending on their relative volatility. Finally, by controlled energy electron impact, appearance potentials can be obtained from which it is possible to develop bond energies and heats of formation of these highly reactive or unstable molecules. From an operational point of view, this analytical technique limits research to those compounds that will exert a vapor pressure of the order of 10^{-4} Torr before its reactive loss, but this pressure could occur at any temperature down to about -218° . Thus the three analytical strata-gems of the cracking pattern, the appearance potentials, and the relative volatility are usually sufficient to separate, identify, and characterize products from cryoreaction experiments.

This particular study is concerned with an extension of cryochemical techniques to include the strained and reactive three-carbon ring compounds cyclopropanone, cyclopropenone, cyclopropane, and cyclopropene. Bond angles significantly reduced from normal values cause such molecules to be especially reactive at relatively low temperatures. Tentative evidence for the formation of cyclopropanone from the reaction of diazomethane and ketene at -70° is 40 years old,³ but the unequivocal characterization of the ketone from this reaction in dilute solution at -78° is much more recent.⁴ The ketone decomposes upon formation in the gas phase since its formation is at least 78 kcal/mol exoergic or 13 kcal/mol more than the minimum activation energy for the decomposition of cyclopropane.⁵ Thus decomposition into C_2H_4 and CO occurs before collisional quenching. Similarly, the energy released in the addition of CH_2 to C_2H_4 is greater than the activation energy for ring decomposition. The unsaturated ketone, cyclopropenone, has been recently isolated from the hydrolysis of dichlorocyclopropene at 0° ,⁶ and it is far less reactive than is cyclopropanone.

Experimental Section

Cyclopropanone was produced by allowing pure liquid ketene to contact pure liquid diazomethane at -145° .⁷ Although it was no problem in glass systems, the decomposition of diazomethane in our metal reactors resulted in little yield of the ketone. Cyclopropane was obtained from the reaction of diazomethane with ethylene, and cyclobutane was obtained from the subsequent reaction of another diazomethane with cyclopropane.⁸ In contrast to this cryo-



chemical behavior, diazomethane and ethylene yield propylene from their reaction at room temperature. Best yields of cyclopropanone occurred when using very pure reagents and with at least a five-fold excess of ketene. The ketone was produced as a white solid, nitrogen was evolved from the reactor and, after reaction, the excess ketene was easily removed by evaporation at -120° . The ratio of cyclopropanone to its only coproduct, cyclobutanone, was never higher than about unity but, with excess diazomethane, the larger ketone became the major product along with smaller amounts of cyclopentanone. The compounds from the cryoreactor and their temperatures of appearance were: ethylene (-170°), excess ketene (-140°), cyclopropanone (-90°), cyclobutanone (-70°), and cyclopentanone (-25°). Purification by simple distillation yielded about 90% cyclopropanone with the remainder being cyclobutanone.

The corresponding cyclic hydrocarbons were occasionally observed, though they were the dominant products when using a metal reactor. A new parent at m/e 56, but of much higher vapor pressure than cyclopropanone, was also occasionally observed, but no experiment revealed the conditions necessary for its formation. The mass spectrum now appeared at -130° rather than -90° , and it consisted of ion groups differing by 1 and 14 within and between groups, respectively. This was most likely the unknown allene oxide formed by methylene attack on the carbonyl rather than the olefin bond of ketene.

The mass spectral and energetic data that were observed at several temperatures when using our cryogenic inlet system attached to a Bendix Model 14-107 time-of-flight mass spectrometer are summarized in Table I.

A series of samples of cyclopropanone were "soaked" at -196° for weeks, at -90° for 30 min, and at room temperature for 60 min. The samples were thermostated such that no part of it could encounter any other temperature. Upon recooling to -196° , followed by slow warming, the reaction products were sequentially distilled through the low temperature inlet system and into the mass spectrometer. The cyclopropanone was indefinitely stable, somewhat polymerized, and totally polymerized in those respective experiments. In no experiment was there any evidence of decomposition, and the data of Table I are not compromised by that possibility.

Table I. Positive Ion^a Mass Spectra and Appearance Potentials of Small Ring Compounds at Low Temperatures

<i>m/e</i>	Cyclopropane 25°		Cyclopropene -140°		Cyclopropanone -90°			Cyclobutanone -70°			Cyclopropenone 25°	
	%	eV	%	eV	%	eV	eV	%	eV	eV	%	eV
70								20	9.6	9.4		
56					15	9.2	9.1					
55											3	
54											46	10.0 ± 0.3
53											13	
52											3	
42	100	10.3 10.2 ^b			15	10.0	9.9	100	10.6	11.0		
41	80							14				
40	29		60	9.7 9.95 ^c								
39	65		100	10.9				16				
38	14		36									
37	11		23									
29											4	
28	5	13.1			100	9.9	10.2	7	10.8	13.0	26	
27	36	13.5 13.4 ^b			35		12.9	12		14.1	4	
26	16	13.1 13.1 ^d	6		34		13.5	8			100	12.1 ± 0.4
25											18	
24											5	
18											12	
17											2	
15	5									15.7		
14	7	18.5 18.5 ^b	6				11.6	7		16.7	2	
13											6	21.8 ± 0.8

^a None of these cyclic compounds exhibited a negative ion spectrum, though OH⁻ from background water was visible. Precision in the appearance potentials is ±0.1 to 0.2 eV except for cyclopropenone. ^bF. H. Field, *J. Chem. Phys.*, 20, 1734 (1952). ^cReference 12. ^dJ. L. Franklin, P. M. Hierl, and D. A. Whan, *J. Chem. Phys.*, 47, 3148 (1967).

A fast flow furnace inlet system into a mass spectrometer is a common technique for observing short-lived free radicals produced in the furnace pyrolysis itself. Any rearrangement of cyclopropanone would have been revealed by our room temperature inlet experiments, wherein the "furnace" is now at room temperature. No significant differences in either the mass spectrum or the molecular energetics were observed with cyclopropanone, cyclopropene, or cyclobutanone.

In ordinary vacuum rack manipulations, the ketone could be transferred through glassware at room temperature with only minor loss if done quickly. A white polymer formed only where the solid cyclopropanone had been condensed, and thus it polymerized before it could become a mobile liquid. The polymer was thermally unstable near 200°, and it was soluble in benzene but insoluble in acetone, alcohol, and water at room temperature.

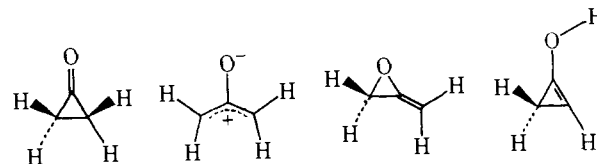
Cyclopropenone was made from the hydrolysis of dichlorocyclopropene.⁶ The compound polymerized and darkened rapidly at room temperature but more slowly when stored in the freezer at -35°. It is best handled as a solid well below its mp of -29°.

Discussion

Diazomethane is one of a very few reagents that is stable at room temperature and also readily reactive at cryogenic temperatures with no prior activation. More usually the real cryogenic reagents are free radicals or excited species from photolyses of discharges or whatever. The solventless reaction at -145° was facilitated by the close melting points of diazomethane (-145°) and ketene (-151°). The heat of reaction, which is much in excess of the activation energy for ring decomposition, causes the immediate loss of the ketone when the same reaction is conducted in the gas phase,⁵ but the low temperature liquid phase reaction retards decomposition, polymerization, and the further reaction of the ketone with another diazomethane to produce cyclobutanone; this larger ketone is nonetheless always a coproduct.

Expectedly, low temperature reactivity decreased with decreasing ring strain.

The large peaks at *m/e* 28, 27, and 26 from cyclopropanone (see Table I) are in agreement with earlier data⁴ and as would be expected from the reported decomposition of the ketone into CO and C₂H₄ upon its formation in the gas phase.⁵ Its IP of 9.1 eV is much lower than that of its open-chain isomer, acrolein at 10.1 eV.⁹ This general characteristic of ring isomers is understood in terms of the increased ground-state energy of the ring and the decreased energy of the ion because of the ability of the electronegative ring to accommodate the positive charge. The ketene fragment, A(42), at 9.9 eV is close to the ionization potential of ketene itself at 9.6 eV, and the ethylene fragment, A(28), at 10.2 eV is actually lower than the ionization potential of ethylene at 10.6 eV. This is reasonable in a strained ring compound with weak bonds which can form new and more stable bonds upon its fragmentation. The reactivity of cyclopropanone upon warming may result from a ring opened dipolar ion which MO calculations have predicted to be about 1 eV more stable than the closed-ring isomer,¹⁰ or it may rearrange in some other way upon warming. The lower energy configuration among the four possible tautomers



is not completely obvious but, should an equilibrium exist among them, the mass spectrum and particularly the ionization potential would change with temperature, to reflect their changing relative concentration. Our fast flow heated inlet, except for the "furnace" operating at room temperature, is a common technique for observing short-lived free radicals produced by pyrolyses, but here merely translated

for operation at much lower temperatures with these much more labile molecules. Measurements on cyclopropanone at -90° and at room temperature revealed no significant differences, and we conclude that no such rearrangements or tautomeric shifts occur. Although the present samples contained about 10% cyclobutanone, its presence did not interfere with the AP measurements on cyclopropanone since the AP of each ion was higher when produced from the heavier ketone.

The mass spectrum, the appearance temperature, I(70), and A(42) for our product m/e 70 at -90° and at room temperature agreed with similar data on an authentic sample of cyclobutanone (see Table I), and thus the four-membered ketone is formed at -145° by the insertion of a CH_2 group into the cyclopropanone ring by diazomethane.

The mass spectrum and critical potentials of cyclopropane and cyclopropene agreed well with previous data where available (see Table I). The abundant ring ions arise from the electronegative character of the ring and from the fact that the planar cyclopropenyl cation at m/e 39 is the simplest possible aromatic system ($4N + 2$ rule) resulting in electron delocalization stabilization of the ion.

The IP of cyclopropene of 9.7 eV is somewhat less than previous values (compare IP of propyne and allene at 10.54 eV¹¹ and 10.16 eV, respectively¹²), but the scatter in our data was not temperature correlatable, and we have found no evidence for rearrangement to a trimethylene structure or other isomerization that would influence the reactivity of cyclopropene. Cyclopropene reacts with itself in dilute solution at -25° to form a still very labile dimer.¹³ The strain energy is about 54 kcal/mol, and the energy of isomerization to propyne is 22 kcal/mol. Although it is one of the most reactive known olefins, cyclopropene was much more stable and easier to handle than would be expected from the literature, and we certainly observed no explosive tendency.¹³ Soaking experiments like those discussed with cyclopropanone revealed no volatile decomposition products and

noticeable polymerization only at room temperature with some olefin remaining even after a week at room temperature. A dimer of undetermined structure was observed from this room temperature experiment, though it was presumably the "bow-tie" structure observed earlier.¹³ The white, waxy polymer smeared upon contact, exhibited no gaseous evolution on heating to 300° , and was soluble in benzene but insoluble in acetone, methanol, and water at room temperature.

Detailed appearance potential studies of these two very interesting ketones and the corresponding cyclic hydrocarbons, including measurements of excess energy in the ion fragmentation processes, have been completed, and the resulting development of the molecular energetics of these molecules will appear elsewhere.

References and Notes

- (1) (a) Research supported by the National Aeronautics and Space Administration through Grant NGL-11-002-005; (b) abstracted in part from a Ph.D. thesis in chemical engineering by R. J. Holt, Georgia Institute of Technology, Atlanta, September 1969.
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- (8) Compare similar reactions in matrices at 20 K reported by W. B. DeMore, H. O. Prichard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).
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A Synthesis of (\pm)-Cembrene, a Fourteen-Membered Ring Diterpene^{1,2}

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Abstract: A convergent synthesis of cembrene (**1**), which employed a nickel carbonyl catalyzed coupling of a terminal allylic bromide as the key step, is described.

Cembrene [1-isopropyl-4,8,12-trimethylcyclotetradeca-2,4,7,11-tetraene (**1**)] is a crystalline, diterpene hydrocarbon first isolated from the Japanese black pine (*P. thunbergii*)⁵ and subsequently from many species of pine,⁶ in addition to several varieties of trees.⁷ The 14-membered ring of cembrene was the first such structural unit encountered in nature⁸ and represents an example of the simple biogenetic-like ring closure postulated to lead to many known compounds⁹ (in this instance, compounds derived from geranylgeraniol).

Since the elucidation of the cembrene structure,⁸ a rapidly expanding group of diterpenes which contain a 14-membered

ring has emerged.¹⁰ This group includes: the isomeric hydrocarbons isocembrene and neocembrene;^{10b,11} several triene alcohols, the cembrols;^{10b} the duvatriene diols and related compounds from tobacco smoke and tobacco products;^{10a} incensol and isoincensol oxide from frankincense resin;^{10c} and a group of highly oxygenated analogs from soft corals.^{10d} Two of these compounds are of particular interest. Neocembrene,¹¹ the perfect biogenetic ring closed product of geranylgeraniol, has been found in the spruce and hinoki trees, commiphora mukul gum resin (Guggulu oil used in folk medicine) and, somewhat surprisingly, it was found to be the trail substance of the Australian termite. Further-