64–65° (14.5 mm) (lit.[13b] 60° (11 mm)); λ (hexane) 465 mμ (ε 9.0), 238 mμ (ε 2.25 × 10^3) (lit.[13b] 465 mμ (ε 8.9), 238 mμ (ε 2.14 × 10^3)).

Commercial Materials. Diphenylpicrylhydrazyl (DPPH) was purchased from Aldrich Chemical Co. and recrystallized prior to its use. **Chlorobenzene** (MCB) was treated with sulfuric acid, and aqueous sodium bicarbonate, washed, dried, and distilled, bp 129.8–129.9°. **Cumene** (MCB) was treated with sulfuric acid and aqueous sodium bicarbonate, washed, dried, and distilled under an atmosphere of nitrogen, bp 145.5–147.0°. It was stored and opened only under atmospheres of argon or nitrogen. **Toluene** (Mallinckrodt Reagent Grade) was acid-washed, dried, and distilled, bp 107.1–107.5°. ***tert*-Butylbenzene** (MCB Reagent Grade) was used without further purification. Analysis by glpc indicated the presence of only a trace of high-boiling impurities.

Kinetic Studies. Solutions 1.5 × 10^{-2} *M* in RR′ were prepared in the various solvents. Those containing scavengers were prepared to be *ca.* 3 × 10^{-2} *M* in DBNO or DPPH. Solvents were purged with argon for 30 min, and solutions were prepared and stored in a glove bag under a positive pressure of argon. Solutions were purged with argon subsequent to their preparation and used shortly thereafter. All manipulations were carried out under an inert atmosphere. Individual kinetic samples in capped Teflon ampoules were decomposed under high pressure following standard procedures.[3] Atmospheric pressure samples were decomposed in degassed glass ampoules. Samples for each run were analyzed for intensity of the infrared absorption band at 2020 cm^{-1} using either a PE 621 or PE 21 infrared spectrometer. Control experiments indicated that both instruments gave comparable kinetic results within experimental error.

Product Studies. Solutions containing RR′ (*ca.* 1.5 × 10^{-2} *M*) and an internal standard were prepared in the various solvents as described above. These were completely decomposed and analyzed by glpc using a temperature programmed F & M Model 700 thermal conductivity gas chromatograph equipped with a matched pair of 6 ft × 1/8 in. 10% UC-W98 columns. Product identities were deduced from retention times (*vide infra*), and yields were determined from peak areas measured using a Disc integrator. Under conditions used in these studies authentic samples gave the following retention times: RR (27.0 min), RH (13.4 min), bicumyl (28.5 min), and bibenzyl (22.6 min).[14] A peak detected at 14.6 min in all reaction mixtures was assumed to be R(–H). In cumene, a product presumed to be RS was observed at 29.0 min; in toluene, peaks at *ca.* 25 min are also presumed to be RS. Accurate area ratio–concentration ratio data were determined for RR and RH. A value for R(–H) was assumed to be the same as for RH; values for SS and RS were assumed to be the same as those for RR.[15]

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[14] Bicumyl and bibenzyl were available from earlier studies.[3]

[15] Complete experimental details can be found in the Ph.D. dissertation of M. J. Amrich, University of California, Riverside, Calif., 1971.

Boiling Points and Structure of Chloro- and Methyl-Substituted Ethylene Carbonates. Steric Hindrance to Dipolar Interaction

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Abstract: Data which show the degree to which five-membered cyclic compounds boil higher than their acyclic analogs are presented. This effect is due mainly to the increase in dipole moment of the cyclic compounds as compared to the acyclic analogs. Substitution of chlorine and methyl groups in ethylene carbonate causes a decrease in boiling point. Part of this decrease is due to steric hindrance to dipolar interaction. By empirical calculations based on qualitative assumptions, the steric effects of methyl groups and chloro groups on the boiling point of ethylene carbonate are shown to be about the same.

The main objectives of this article are to point out the unusually high boiling points of certain oxygen five-membered heterocyclic compounds, as compared to those of the corresponding acyclic analogs, and to show how polar and steric factors affect the boiling points of substitution products of ethylene carbonate, a representative five-membered heterocycle.

The interest in this area arose from the fact that both chloroethylene carbonate (**2**), bp 212°, and *rac*-dichloroethylene carbonate (**3**), bp 178°, boil[2] appreciably lower than ethylene carbonate (**1**), bp 248°.[3] These results were surprising because normally the replacement of a hydrogen on carbon by chlorine leads to an appreciable increase in boiling point.[4]

Before discussing the lowering of the boiling point of **1** by substitution of chlorines, it is of interest to know why **1** has such a high boiling point and to compare the boiling points of a number of five-atom cyclic compounds with those of the corresponding acyclic analogs (see Table I).

The boiling point of a liquid has been defined by eq 1,[5] where T = boiling point in degrees absolute,

$$T = \Delta H_{\text{vap}}/\Delta S_{\text{vap}} \qquad (1)$$

ΔH_{vap} = heat of vaporization in kcal/mol at the boiling point, and ΔS_{vap} = entropy of vaporization in kcal/(mol deg) at the boiling point.

ΔH_{vap} represents the intermolecular forces which must be overcome before vaporization can occur. These forces arise from van der Waals attractions (dispersion forces), dipole–dipole interaction, and hydrogen bonding. In this discussion hydrogen bonding is ignored because hydrogen bonding is not thought to be appreciably involved in the compounds under

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[1] The data presented in this paper were taken from the M.S. thesis of R. A. M., Ohio State University, 1964.

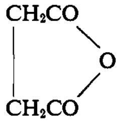
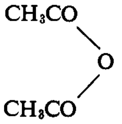
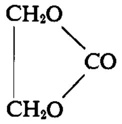
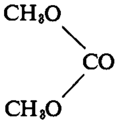
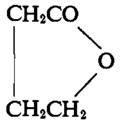
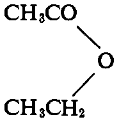
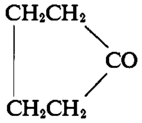
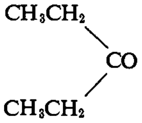
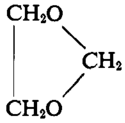
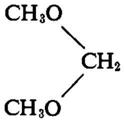
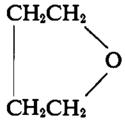
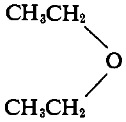
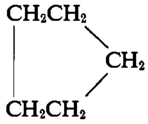
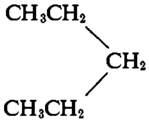
[2] All boiling points cited in this article are in °C at atmospheric pressure, 750 ± 10 mm, and are taken from the "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967–1968, unless otherwise noted.

[3] M. S. Newman and R. Addor, *J. Amer. Chem. Soc.*, 77, 3789 (1955).

[4] For example, ethyl acetate boils at 77°, whereas ethyl chloroacetate boils at 144°, α-chloroethyl acetate at 121.5°, and β-chloroethyl acetate at 145°.

[5] W. J. Moore, "Physical Chemistry," Prentice-Hall, 3rd ed, Englewood Cliffs, N. J., 1962, p 80.

Table I. Data for Five-Membered Ring Compounds and Acyclic Analogs

		Bp,[a] °C	μ^b	μ^2	ΔH_{vap}	$\Delta S_{vap} \times 10^3$		Bp,[a] °C (bp corr[c])	μ^b	ΔH_{vap}	ΔS_{vap}	Bp diff,[d] °C
4		261	4.2	17.6	13.9	26.1		138 (136)	3.0	7.88	21.7	125
1		248	4.87	23.7	12.2	23.4		90 (86)	1.07			162
5		206	4.03	16.2				77 (73)	1.85			133
6		131	2.9	8.4				103 (99)	2.8			32
7		78	1.47	2.16				45.5 (41)	0.67			37
8		65	1.7	2.89	7.60	22.4		35 (31)	1.3	6.37	20.7	34
9		49	0		6.50	20.2		36 (32)	0	6.16	19.6	17

[a] See ref 2. [b] Taken from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963. [c] The boiling points in parentheses were obtained by plotting boiling point *vs.* molecular weight for the acyclic homologous series and extrapolating to the molecular weight of the cyclic analog. [d] The boiling point difference is that between the corrected boiling point for the acyclic compound and the cyclic analog.

consideration. ΔS_{vap} is a function of the relative degrees of order in the liquid and vapor states at the boiling point; the greater the decrease in order on vaporization the lower the boiling point. As can be seen in Table I the cyclic compounds boil higher than the acyclic analogs in every case. Cyclization results in an increase in both ΔH_{vap} and ΔS_{vap}, but the increase in ΔH_{vap} is relatively large compared to the increase in ΔS_{vap}. Actually, since the boiling point is inversely proportional to ΔS_{vap} the increase in ΔS_{vap} on cyclization causes the boiling points of the cyclic compounds to be lower than they would be if there were no change in ΔS_{vap}. Hence the higher boiling points of the cyclic compounds are due entirely to increases in ΔH_{vap}.

In order to understand why ΔH_{vap} is larger for ethylene carbonate than for dimethyl carbonate, the geometry of the molecules must be considered. Ethylene carbonate is essentially a planar molecule;[6,7] hence the molecules can orient themselves in the liquid state so that the dipole–dipole interactions are large. In dimethyl carbonate which need not be coplanar because of free rotation of the two methoxy groups, the important dipole–dipole interactions of the carbonate moieties are decreased because of steric effects, and the dipole–dipole interactions themselves are lessened because of the variable geometric patterns which the molecule can assume.[8,9] If the above picture is approximately correct, the lower boiling points of **2** and **3** are the resultant of two factors: the polar effect of chlorine atoms and their size. The polar effect lies mainly in the effect of the chlorine atoms on the dipole moment. To explain the steric effect, we propose that a phenomenon termed *steric hindrance of dipolar interaction* be invoked. This concept means that the introduction of a group in a molecule which will produce a steric effect to hinder the association of such molecules will lower the boiling point.[10] This effect should be greater in cyclic compounds (only five-membered

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(6) C. L. Angell, *Trans. Faraday Soc.*, **52**, 1178 (1956).

(7) C. J. Brown, *Acta Crystallogr.*, **7**, 92 (1954).

(8) R. Kempa and W. H. Lee, *J. Chem. Soc.*, 1936 (1958). The dipole moments for chloroethylene carbonate and *rac*-dichloroethylene carbonate are 3.99 and 3.44 × 10^{-18} esu, respectively.

(9) G. F. Longster and E. E. Walker, *Trans. Faraday Soc.*, **49**, 228 (1953).

(10) This effect is different from the decrease in van der Waals forces in going from pentane, bp 36°, to neopentane, bp 9.5°.

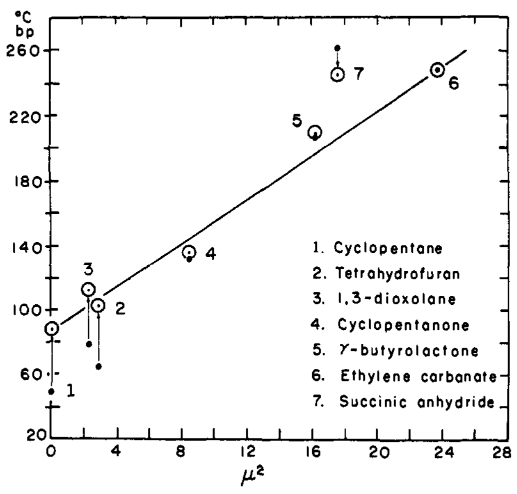

Figure 1. Plot of boiling points and corrected boiling points of five-membered ring compounds *vs.* the square of the dipole moment, μ^2.

cyclics are discussed here) and should be greater the larger the dipole moment of the cyclic compound.[11]

A discussion of the boiling points of the compounds in Table I in terms of the above concepts is of interest. The increase of 17° in the boiling point in going from pentane to cyclopentane is due solely to the greater van der Waals forces, as cyclopentane and pentane have no dipole moment. The other compounds fall into two classes. Cyclopentanone, 1,3-dioxolane, and tetrahydrofuran, with dipole moments of less than 3, boil about 34° higher than the acyclic analogs. Thus, the increase in boiling points in these cases is due both to van der Waals forces and to dipole interaction. Succinic anhydride, ethylene carbonate, and γ-butyrolactone, with dipole moments greater than 4, boil over 100° higher than their acyclic analogs. In these cases the increase in boiling points may be attributed mainly to the increase in dipole interaction. Since none of the cyclic compounds in Table I carries a methyl or chloro substituent, steric factors are not involved.

In connection with the effect of dipole moment on boiling point, Noller[12] suggested that the boiling point increase is proportional to the square of the dipole moment. Accordingly, we have plotted the boiling points of a number of unsubstituted cyclic compounds against the squares of the dipole moments in Figure 1. The agreement with Noller's suggestion[12] is fair. Since comparison should really be made with compounds of equal molecular weight,[13] we calculated corrected boiling points for each compound by plotting the boiling points of each of the cyclic compounds on a graph of the boiling points of normal alkanes *vs.* molecular weight. Curves were then drawn parallel to the curve of the *n*-alkanes through each point representing a cyclic compound. The points at which these curves intersect the ordinate at 88 were taken as the boiling points the compounds in question would have if they had a molecular weight of 88, that of ethylene carbonate.

If a straight line is now drawn between the corrected boiling points for cyclopentane and ethylene carbonate, most of the corrected boiling points lie close to this line (see Figure 1). Only succinic anhydride lies appreciably off the line. It is higher boiling than expected. No reason can be given for this other than to suggest that (a) the "correction" for van der Waals forces is for some reason not valid in this case, (b) the experimentally determined dipole moment is too low, or (c) some attractive force other than van der Waals and dipolar interaction forces is involved. The latter possibility suggests weak intermolecular hydrogen bonding.

To sum up, ethylene carbonate boils much higher than dimethyl carbonate mainly because of the large difference in dipole moments (4.9 *vs.* 1.1).[14]

We next turn to an explanation of the lower boiling points of chloroethylene carbonate and dichloroethylene carbonate. Two factors might contribute to the observed facts: a polar factor and a steric factor. The polar factor would be felt in the effect on the dipole moments and the steric factor would be related to the effect of the bulky chlorine atom on the interaction of the liquid molecules. The idea occurred that the size of the chlorine would prevent the cyclic molecules from approaching closely enough so that the dipole–dipole interaction could be as effective as in the case of the planar[6] ethylene carbonate. Accordingly we reasoned that if a nonpolar group of roughly the same size as a chlorine atom were introduced in its place, we could estimate how much of the lowering of the boiling point of ethylene carbonate was due to the polar effect (chlorine substitution) and how much was due to the steric effect. For a suitable nonpolar group we chose the methyl group because it is approximately the same size as a chlorine.[15]

The boiling points of ethylene carbonate and all of the possible methyl-substituted compounds (except trimethylethylene carbonate) are listed in Table II. In addition the *pseudo boiling points* are listed. The pseudo boiling point represents the boiling point calculated for a methyl-substituted cyclic carbonate if there were no steric effects. The pseudo boiling points were calculated by adding two increments to the boiling point of ethylene carbonate: the *cyclopentane factor* and the *moment factor*. The cyclopentane factor was calculated by subtracting the boiling point of cyclopentane from that of the methylated cyclopentane corresponding to

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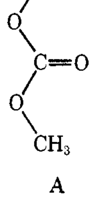
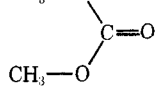
[11] Furthermore, the steric factors act to lower the boiling point despite the increased van der Waals forces occasioned by the increase in molecular dispersion forces due to substitution of the group involved for a hydrogen atom.

[12] C. Noller, "Chemistry of Organic Compounds," 2nd ed, W. B. Saunders, Philadelphia, Pa., 1957, pp 251–252.

[13] Actually, comparison would be better if equal molecular volumes were used. However, changes in molecular volumes in the compounds discussed here are roughly proportional to changes in molecular weight.

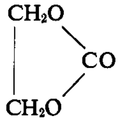
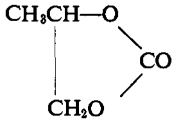
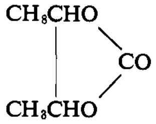
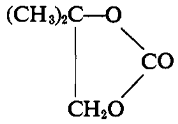
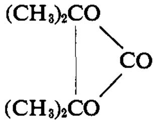
[14] Calculations of the dipole moments for the extreme conformations A and B lead to the values of 1.04 μ for A and 3.33 μ for B: G. Thomson, *J. Chem. Soc.*, 1118 (1939).


A


B

[15] The van der Waals radius of chlorine is given at 1.80 Å and that of a methyl group 2.0: L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1945, p 189.

Table II. Boiling Points[a] of Methylated Cyclic Carbonates

Compound	Cyclopentane factor[b]	Moment factor	Pseudo bp	Actual bp[c]	Decrease due to steric factor total	Per methyl group
	0	0	248	248	0	0
	23	5	276	242	34	34
						
cis (*meso*)	51	10	309	249	60	30
trans (*rac*)	43	10	301	237	64	32
	38	10	296	224	72	36
	76[d]	20	344	251	93	23

[a] All numbers refer to °C. [b] Estimated by subtracting the boiling point of cyclopentane from that of the corresponding methylated cyclopentane. [c] Boiling points are (estimated) at 760 mm and are rounded off to the nearest degree. [d] Estimated by averaging the increases per methyl group over cyclopentane (49°) in methylcyclopentane (71°), *meso*-, *rac*-, and *gem*-dimethylcyclopentanes (100, 92, and 88°), and tetramethylcyclopentane (114°). The average is 19° per methyl group. These boiling points were taken from "Beilstein."

the methylated carbonate. The moment factor was estimated at a 5° increase in boiling point for each methyl group involved. This figure was arrived at by using the slope of the line in Figure 1 and assuming that each methyl group adds 0.07 to the dipole moment of the cyclic carbonates.[16]

The decrease in boiling point attributed to steric hindrance to dipolar interaction is obtained by subtracting the actual boiling point from the pseudo boiling point.

Examination of Table II reveals that substitution of one methyl group on ethylene carbonate causes a 34° decrease in the boiling point due to steric factors and that substitution of two methyls causes a greater decrease. The *gem*-dimethyl arrangement is more effective than the trans and the latter more effective than the cis in causing a decrease of boiling point. These results can be rationalized by invoking steric factors although one would not necessarily have predicted that the *gem*-dimethyl effect would be greater than the trans arrangement. The decrease in the tetramethyl case is the largest but, if one considers that four methyl groups are involved, each methyl group is somewhat less effective than in the dimethyl compounds. Since the drop in the trans case is pertinent to the discussion concerning the steric effects in *rac*-dichloroethylene carbonate, the value of 32° for the decrease due to the steric factor per methyl group should be kept in mind.

With values available for the reduction of the boiling point of ethylene carbonate attributable to the steric factor of methyl groups, we now discuss the lowering of the boiling point of ethylene carbonate by chlorine atoms. The use of the boiling points of chlorinated cyclopentanes to estimate pseudo boiling points as the use of methylated cyclopentanes in the case of the methylated compounds cannot be justified because of the differing dipole moments of the chlorinated cyclopentanes.

In order to estimate the pseudo boiling points of chloroethylene carbonate (**2**) and *rac*-dichloroethylene carbonate (**3**) in the absence of steric factors, we must estimate the boiling point increases over ethylene carbonate (**1**) due to increase of molecular weight[13] and the boiling point decreases below **1** due to the lower dipole moments (3.99 for **2** and 3.44 for **3**).[8] To estimate the boiling point increases we plotted the boiling points obtained by adding the cyclopentane factor (Table II) for propylene carbonate (23°) and for *rac*-dimethylethylene carbonate (43°) to the boiling point for **1** (248°) against the molecular weights. A third point was taken as the boiling point of ethylene carbonate. This curve was then extrapolated to give a boiling point increase of 50° for **2** (mol wt, 122.5) and 82° for **3** (mol wt, 157).[17] By using the plot of μ^2 against the boiling point (Figure 1), we estimated that

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(16) The μ's for 1 and propylene carbonate are 4.87 and 4.94, respectively,[8] and those for trimethylene carbonate and 1-methyltrimethylene carbonate are 5.21 and 5.28, respectively: B. A. Arbusov and J. G. Shavsha, *Dokl. Akad. Nauk SSSR*, **68**, 1045 (1949). The dipole moments for the other methylated cyclic carbonates are unknown, but we assume the 0.07 increase for each methyl group.

(17) In the absence of an estimate of values for molecular volume, we have used molecular weights for extrapolation.

2 (μ^2, 15.9) should boil 54° lower than **1**, and **3** (μ^2, 11.8) should boil 82° lower than **1** because of dipole moment differences. The predicted boiling points for **2** and **3** in the absence of steric factors are 244° (248° + 50° − 54°) and 248° (248° + 82° − 82°). Since the actual boiling points for **2** and **3** are 212 and 178°, the decrease due to steric factors is 32° for **2** (32° per Cl) and 70° for **3** (35° per Cl). Thus, we see that the steric effects of methyl groups and chlorines are about the same. The results are summarized in Table III.

Table III. Boiling Points[a] of Chlorinated Ethylene Carbonates

Compd	Mol wt[b] factor	Moment[c] factor	Pseudo[d] bp	Actual bp	Decrease due to steric factor	Per chloro group
1	0	0	248	248	0	0
2	50	54	244	212	32	32
3	82	82	248	178	70	35

[a] All numbers refer to °C. [b] See text for method of evaluation. [c] See text for evaluation. [d] Obtained by adding the molecular weight factor to, and subtracting the moment factor from, 248°, the bp of **1**.

Similar calculations of the steric factor per methyl group have been made for some of the methylated derivatives of the five-membered cyclic compounds listed in Table I.[1] Since no series is complete, no detailed discussion will be made. In general the steric factor due to methyl groups falls off as the dipole moment of the parent compound and as the number of methyl groups are increased.

In conclusion, it should be pointed out that changes in boiling point are not the only changes in physical properties subject to steric hindrance to dipolar interaction. This concept should be helpful in considering solvent properties and basicity in five-membered heterocyclic compounds in general. Furthermore, the unusually high boiling points of such heterocyclic compounds should be taken as evidence that other properties are expected to be unusual. Similar effects in heterocyclic compounds containing six and higher membered rings are to be expected but the steric factors will probably be smaller because of increased flexibility of the rings.

Experimental Section

meso- and *rac*-dimethylethylene carbonates were prepared by heating for 3–4 hr under nitrogen a mixture of 90 g of 2,3-butanediol and 148 g of dry diethyl carbonate to which 0.4 g of sodium had been added. The alcohol formed was collected by fractionation. After neutralizing the base with acetic acid, crude fractionation afforded a mixture of the desired carbonates in almost quantitative yield. By fractionation of 92 g at 20 mm through a 6 mm × 18 in. spinning band (Nester-Faust, Inc.) at a reflux ratio of 20/1, there was obtained 37 g of the racemic isomer, bp 123.8–124.0° (racemic isomer) and 22 g of the meso isomer, bp 133.7–134.0°. These fractions were estimated to be of 96–97% purity by glpc. In each case the impurity was the isomer.

Pinacol carbonate was prepared similarly, but the rate of ester interchange was much slower. After heating for 17 hr as above, only a 70% yield of 98% pinacol carbonate[18] was obtained. This was recrystallized four times from ethanol to yield pinacol carbonate, bp 247.8–248.0° (745 mm), mp 179.5–180.0° (>99% by glpc).

Propylene carbonate was generously donated by the Jefferson Chemical Co., Houston, Tex. It was twice redistilled under vacuum. The boiling point of *gem*-dimethylethylene carbonate is that reported.[19]

All boiling points were determined at about 745 mm in a distillation apparatus which was fitted with a short stem Anschutz calibrated thermometer. Corrections to 760 mm were then applied.

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(18) Compare S. Sarel, L. A. Pohoryles, and R. Ben-Shoshan, *J. Org. Chem.*, **24**, 1873 (1959).

(19) U. S. Patent 2,773,070 (1956).