Thermal Isomerization in Polycrystalline *exo*- and *endo*-5-Norbornene-2,3-dicarboxylic Anhydrides[1]

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Abstract: At temperatures below the melting points of the pure isomers, the thermal isomerization of neat, polycrystalline samples of *exo*- and *endo*-5-norbornene-2,3-dicarboxylic anhydrides proceeds in both the liquid and solid states. A kinetic treatment for these two-phase, "frozen-state" reactions gives values for the liquid- and solid-phase rate constants. Down to as low as 120° the higher melting *endo* isomer (mp 164°) reacts with the same rate constant in the solid as in the liquid state, and the rate constants are the same as obtained by extrapolation, from above the melting point, of liquid-phase rate constants. In contrast, at less than 10° below its melting point, the *exo* isomer (mp 143°) has a slower rate in the solid than in the liquid and reaction in the solid phase decreases relatively quickly with temperature. Conversions below the eutectic temperature (109°) confirm that solid-state reactions occur; at 97° crystalline *endo* anhydride isomerizes faster than *exo* isomer. *endo* anhydride is transformed at 94° (ΔH_{tran} = 23 cal/g, ΔS_{tran} = 10 eu) to a body-centered cubic structure (a_0 = 7.57 A) in which molecular rotation is relatively free. This "crystalline liquid" shows its considerable liquid properties by its narrow nmr spectrum at 115° (three peaks centered at τ 3.3, 6, and 8 with $W_{1/2}$ 15–30 cps), by its relatively diffuse X-ray powder pattern, by its low heat and entropy of fusion (ΔH_{fus} = 5 cal/g, ΔS_{fus} = 2 eu), and by its ability to react at the rate of a liquid. *exo* isomer shows no transformation until its melting point (ΔH_{fus} = 32 cal/g, ΔS_{fus} = 12 eu) and gives no high-resolution nmr spectrum. An independent evaluation, based on calorimetric data, of the liquid–solid relative rate constants is consistent with the observation of facile solid-state reaction with *endo* isomer and more difficult reaction in the solid state of *exo* isomer.

Recent studies of reactions in frozen solutions have presented a general kinetic method for analysis of chemical transformations in two-phase (liquid and solid) systems.[3] In practice, the method accounts for that part of the observed reaction which proceeds in small liquid regions in equilibrium with solid, so that any contributions by a reaction in a coexistent, relatively large, solid phase would become apparent. Several common reactions in frozen organic solvents and in water were completely explained by reaction only in liquid regions of the frozen system, and there was no necessity to consider further any solid-phase reaction or special catalytic effects. It would seem that a simple extention of this work would be to "frozen-state reactions" in high-melting solids; *i.e.*, to systems that are ordinarily solid at room temperature but react thermally below their melting points when a liquid phase may contribute to the over-all reaction.[4] Many so-called "solid-state" decompositions or isomerizations (where the inert frozen solvent of previous studies[3] is replaced by the crystalline reactant itself) might best be considered to be "frozen-state" reactions as viewed from still higher temperatures where the system would be completely melted.[5]

Although few cases have been studied in any detail, thermal decompositions of organic solids with accompanied formation of a liquid phase are fairly common. There is, moreover, a tendency to neglect the contribution of the liquid phase to total reaction and ascribe at least the initial reaction solely to a solid-phase decomposition.[6] Thus the slowly accelerating reaction progress typical of decompositions of solids (the S-shaped reaction *vs.* times curves) may sometimes arise not only from development of cracks, crevices, and other lattice imperfections, but also from the growth of a reactive liquid phase without any solid-phase reaction at all.[4,7] Indeed, it seems that if a true solid-state reaction were occurring randomly throughout the entire solid matrix at a rate competitive with that in an equilibrated liquid phase, the rate of reaction would be greatest when the greatest amount of solid were present, *i.e.*, at the initial stages of the decomposition. As S-shaped curves are almost exclusively observed[7] (however, see below), growth of either imperfections or of liquid regions is necessary for reaction progress; no controlled reaction involving the *total* solid phase seems to have been reported.

To investigate the possible extention of the kinetic treatment of two-phase systems to reactions in organic solids at high temperatures and to possibly separate out contributions from solid- and liquid-state reactions, we have investigated the thermal isomerization of polycrystalline *exo*- and *endo*-5-norbornene-2,3-dicarboxylic anhydrides. This interconversion, noted by Craig[8] to occur when the anhydrides were heated above their melting points, has been very

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(1) Reactions in Frozen Solutions. IX. Research sponsored by the U. S. Air Force Office of Scientific Research, Grant No. AFOSR 1102-66, and by the National Research Council of Canada.

(2) Alfred P. Sloan Foundation Fellow.

(3) *Cf.* T. E. Kiovsky and R. E. Pincock, *J. Am. Chem. Soc.*, **88**, 4704 (1966).

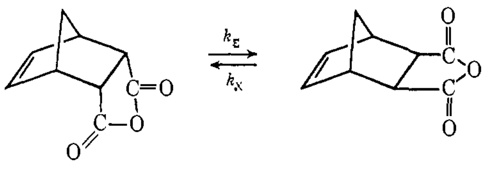
(4) R. E. Pincock and T. E. Kiovsky, *Chem. Commun.*, 864 (1966).

(5) The term "frozen" conveniently refers to the state of a two or more component system in the temperature range below the melting point but above the eutectic point, *i.e.*, in the range where solid and liquid are in equilibrium. On this basis frozen state is not synonymous with solid state as the former means *partly* solid while the latter means *completely* solid. *Cf.* R. E. Pincock and T. E. Kiovsky, *J. Chem. Educ.*, **43**, 358 (1966).

(6) The only explicit treatment of the growth of a liquid phase in decomposition of an organic solid is that of Hinshelwood who showed that the gradual decomposition of the explosive tetryl (N-2,4,6-tetranitro-N-methylaniline) arises from the development of a liquid phase: C. N. Hinshelwood, *J. Chem. Soc.*, **119**, 721 (1921).

(7) (a) C. E. H. Bawn, "Chemistry of the Solid State," W. E. Garner, Ed., Butterworth and Co. (Publishers) Ltd., London, 1955, p 254; (b) H. Morawetz, "Physics and Chemistry of the Organic Solid State," Vol. 1, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 287.

(8) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).



endo, mp 164° *exo*, mp 143°

thoroughly studied in dilute solutions at *ca.* 170–190°.[9–11] Under these conditions the reaction involves a unimolecular, retro-Diels–Alder reaction followed by recombination to finally yield an equilibrium mixture of *exo* and *endo* isomers.[9] As only minor side products are initially formed, and as the two crystalline isomers have sufficiently high melting points and widely different physical characteristics (see below), they provide an ideal pair of compounds for comparison of liquid- and solid-phase isomerization kinetics.

Kinetic Results

The isomerization of neat samples of *exo* and *endo* anhydrides was simply carried out by heating sealed vials containing *ca.* 0.03 g of compound for various times at constant temperature. After dissolving in chloroform-*d*, the mole fraction of *exo* isomer present in a sample was obtained by integration of the nmr absorption for *exo* at τ 6.95 relative to the olefinic hydrogens of the *exo–endo* mixture (at *ca.* τ 3.6). At a later stage in the study, a more convenient analysis based on vapor phase chromatography under conditions mild enough to prevent cracking or isomerization was developed.

Isomerization in the Melted System. Above their melting points the isomers reach an equilibrium composition of about 54% *exo*–46% *endo* beginning with either isomer.[12] Within the accuracy of the analysis, this equilibrium ratio seemed essentially independent of temperature from 140 to 190°. Yellowing of the samples occurred as equilibrium was approached, indicating as noted by Craig,[8] that other minor products are produced. With either isomer, plots of log (per cent$_\infty$ − per cent$_t$) against time gave identical observed rate constants, $k_{obsd} = k_X + k_E$, where k_X and k_E are first-order rate constants for reaction of *exo* and *endo* isomers, respectively (see Table I). As the equilibrium constant is near unity, the rate constants for interconversion of the anhydrides in the liquid phase are essentially identical ($k_X = k_E$). The constants obtained for the melt agree closely with those reported for isomerization of *endo* anhydride in decalin solution.[10]

Isomerization in the Frozen System. Surprisingly, the reaction of *endo* isomer below its melting point of 164° proceeded with no inhibition period of any sort. With great dissimilarity to the S-shaped curves of the usual solid decomposition, the reaction *began* at its highest rate and then slowed down like any ordinary first-order reaction. The reaction was accompanied by melting of the frozen system and, depending on the temperature, the liquid phase became visually apparent at different times. As shown in Figure 1, which illustrates the percentage of *exo* isomer produced at various times from polycrystalline *endo* samples, no break in the curves appear when the samples became completely melted (at the points marked by arrows in the figure), and no unusually great decrease in rate occurred when the samples were all initially solid (*e.g.*, 155°) or all melted (*e.g.*, 165°). The observed per cent conversions at various times were also independent (within experimental error of *ca.* ±2%) of the origin of the sample (crystallized in different habits from different solvents), of sample size or shape (finely ground or large crystals) and apparently independent of other

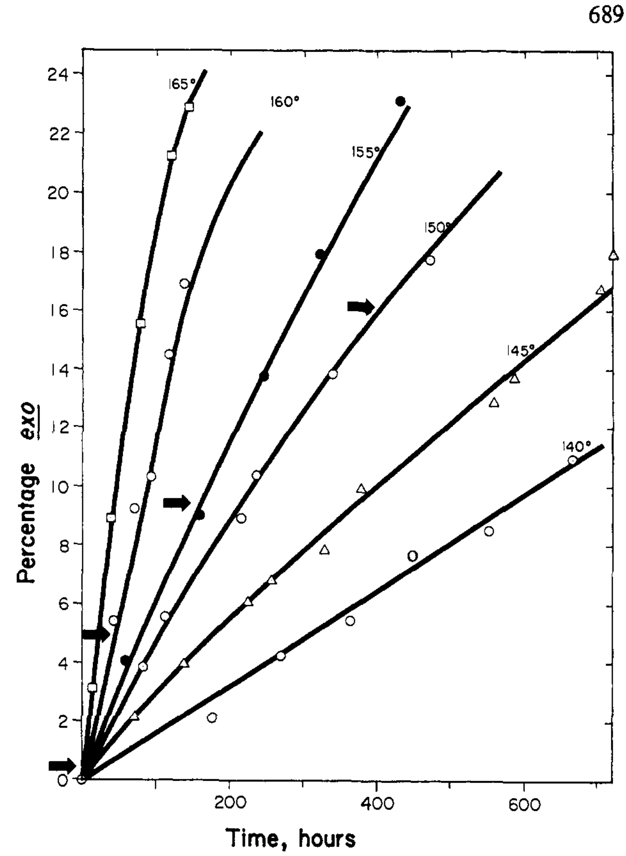


Figure 1. Isomerization of *endo* anhydride below its melting point (164°). The arrows indicate approximate points of complete melting.

Table I. Observed First-Order Rate Constants for Isomerization *exo* and *endo* Anhydrides in Melted and Frozen States

Temp, °C	Isomer	$k_{obsd} \times 10^6$, sec^{-1}	Temp, °C	Isomer	$k_{obsd} \times 10^6$, sec^{-1}
186	X	619	141	E	6.28
185	E	602	140	X	5.64
176	X	226	140	E	5.48
175	E	180	138	E	3.52
165	E	73.6	135	E	2.52
165	X	86.7	135	X	1.93[a]
160	X	47.2	130	E	1.67
160	E	44.2	130	E	1.46
155	E	21.6	130	X	0.90[a]
155	X	30.5	125	X	0.42[a]
150	E	14.9	120	E	0.62
145	X	9.2	120	X	0.15[a,b]
145	E	8.6			

[a] Calculated from *initial* slopes of log (46 − % *endo*) *vs.* time plots. [b] Calculated only from 6% reaction in 264 hr.

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(9) C. Ganter, V. Scheidegger, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 2771 (1965), and references therein.

(10) J. E. Baldwin and J. D. Roberts, *ibid.*, **85**, 115 (1963).

(11) J. A. Berson and W. A. Mueller, *ibid.*, **83**, 4940 (1961), and references therein.

(12) Craig[8] reports 56% *exo* at 190°.

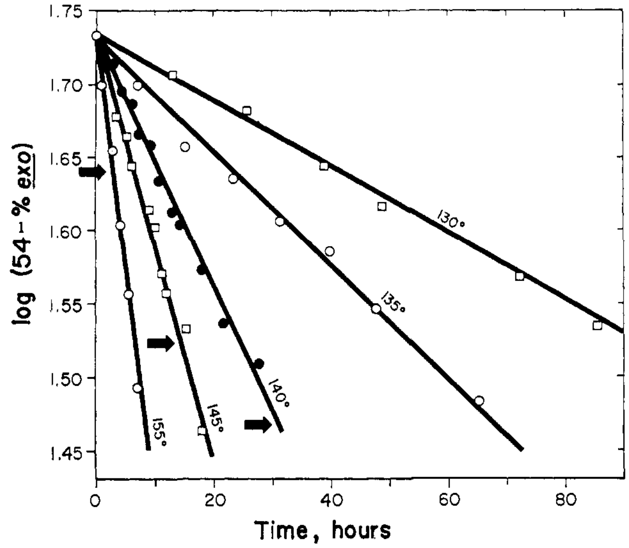

Figure 2. First-order kinetic plots for isomerization of *endo* anhydride below its melting point. Arrows denote approximate points of complete melting.

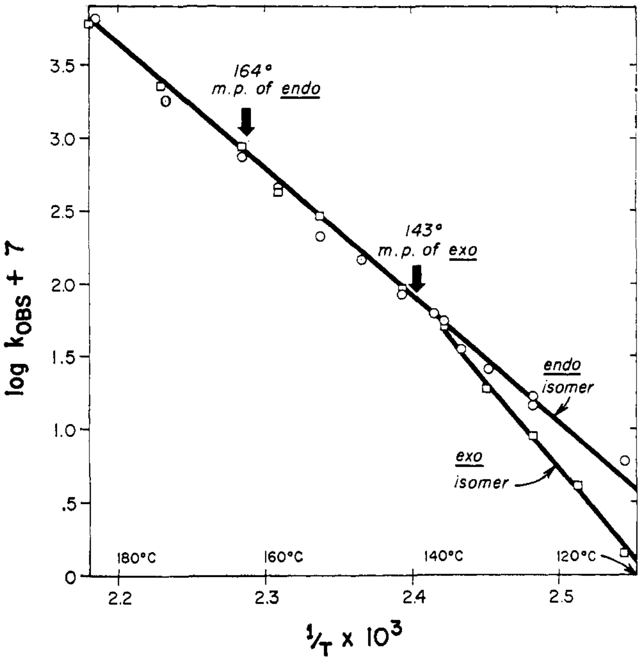

Figure 3. Relation of the log of the observed first-order rate constants to reciprocal temperatures for *exo* and *endo* anhydrides in melted and frozen states.

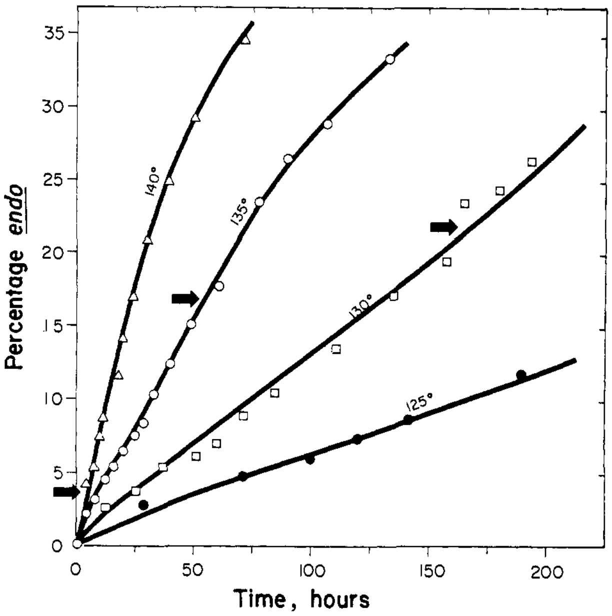

Figure 4. Isomerization of *exo* anhydride below its melting point (143°). Arrows denote approximate points of complete melting.

factors (*e.g.*, trace impurities) which often make kinetic results with inorganic solids difficult to reproduce.[13]

When data from frozen *endo* runs were treated by the same reversible first-order kinetic equation used in melted runs, the plots of log (54 − % *exo*) against time were good straight lines (see Figure 2), and the calculated rate constants decreased with temperature in an orderly manner. Kinetic runs were made to as low as 120° (44° below the melting point of pure *endo*), where the samples do not completely melt until the system contains nearly 50% *exo* isomer. An Arrhenius plot of log k_{obsd} against reciprocal temperature gave a linear relationship from 180°, through the melting point of 164°, down to 120° (see Figure 3). There is no doubt that the existence of varying amounts of solid and liquid phases throughout this temperature range and throughout the range of composition in a run at constant temperature have no measurable effect on the rate of isomerization; the reaction proceeds equally well in the liquid and solid states.

The isomerization of polycrystalline *exo* anhydride also proceeded at temperatures below the melting point (see Figure 4) and was not noticeably dependent on the source nor size of the crystals. Again inhibition times and S-shaped curves were not obtained. However, up to the time of complete melting, the per cent conversion–time relationships were straighter lines than with the *endo* isomer, and the isomerization was also slower than with the *endo* isomer. This is shown most distinctly in Figure 5, which illustrates that although melted *exo* and frozen *endo* have identical rates at 140°, the isomerization of frozen *endo* at 130° is faster than with frozen *exo* at that temperature. It should be remembered that the temperature of 130° is 34° below the melting point of pure *endo* but only 13° below that of pure *exo;* still the *endo* isomer reacts faster.

Although the over-all observed rate of reaction of *endo* is faster than that of *exo*, the two isomers do have the common feature of concurrent reactions in both the liquid and solid phases of the frozen systems. A solid-state *exo* reaction is indicated by the fact that the observed rate of conversion of *exo* is much greater, and the shape of the conversion against time curves is much different,[4] than can be accounted for by reaction only in a growing liquid phase.

When the reaction of frozen *exo* isomer was treated as a reversible first-order reaction (as with the *endo* isomer above), the observed initial rate constants decreased relatively quickly with temperature. Figure 3 shows the departure of these *exo* rate constants from the Arrhenius line of the *endo* isomer. It is apparent, even without a rigorous kinetic separation of the contributions of liquid- and solid-phase reactions, that some

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(13) *Cf.* D. A. Young, "Decompositions of Solids," Pergamon Press Ltd., Oxford, 1966, Chapter 1.

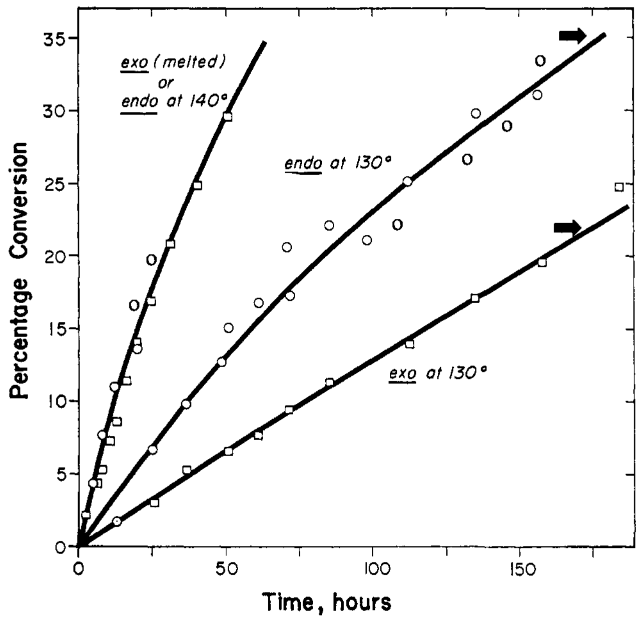

Figure 5. Comparisons of per cent conversion against time for *exo* and *endo* anhydrides at 130 and 140°.

reaction of *exo* isomer occurs in the solid phase but that the rate is less than in the coexisting liquid phase.

Isomerization in the Solid State. Below the eutectic point of 109°,[8] the *exo–endo* system is necessarily solid at any composition. That isomerization can nevertheless occur was shown by storing sealed vials of the isomers at 97° for long periods of time. At this temperature clear crystals of *endo* anhydride turned somewhat opaque, due to isomerization, in a few weeks, and the *exo* isomer was found to be present to the extent of 5, 10, 22% after 31, 78, and 180 days, respectively. However, the *exo* compound remains clear at 97° and the *endo* isomer is produced relatively slowly (a sample stored 190 days increased from *ca.* 8 to 16% *endo*). Below 109° the isomerization is a true solid-state reaction and *endo* reacts faster than *exo*. However, with both compounds the slow rate of reaction prevents a convenient kinetic study of the isomerization.

Thermochemical and Structural Results

The well-known *endo* anhydride has always been noted to melt in a normal manner at *ca.* 163–165°. Under polarized light, however, an unmistakable transformation becomes apparent at 93–94° when the crystals become optically isotropic without otherwise fusing or changing shape. The high-temperature form may easily be supercooled below 93°, and at times to room temperature,[14] before the return of color due to optical birefringence indicates a return to the original crystal structure.[15] *exo* anhydride, on the other hand, remains anisotropic, as is usual with organic solids, until melting at 143°.

Pirsch[16] has shown by melting point depression experiments that *exo* isomer has a much greater heat of fusion than does *endo*, and correspondingly, that *endo* has the low entropy of fusion (*ca.* 2 eu) often found with spherically shaped molecules.[17] To further characterize the two pure isomers and to expand the known features of the phase diagram for mixtures of the two, thermochemical experiments were carried out by differential calorimetry. This quickly confirmed that a transition occurs in *endo* anhydride at 94° and showed that it is a relatively drastic change (ΔH_{tran} = 23 cal/g). There is a further change of only 5 cal/g when the *endo* isomer finally melts at 164°. *exo* anhydride does not undergo any thermal transitions from room temperature until it melts, with ordinary heat and entropy changes, at 143° (see Table II). Mixtures of the two isomers show thermal halts, similar to that of pure *endo* isomer at 94°, but, over a wide range of composition, the transition temperature is lowered to 75°. These results are combined with the liquidus curve reported by Craig to give the phase diagram of Figure 6. The structural similarity of the two isomers and the form of the thermochemical data suggest the existence of solid solutions indicated by α_E and α_X on the diagram.[18]

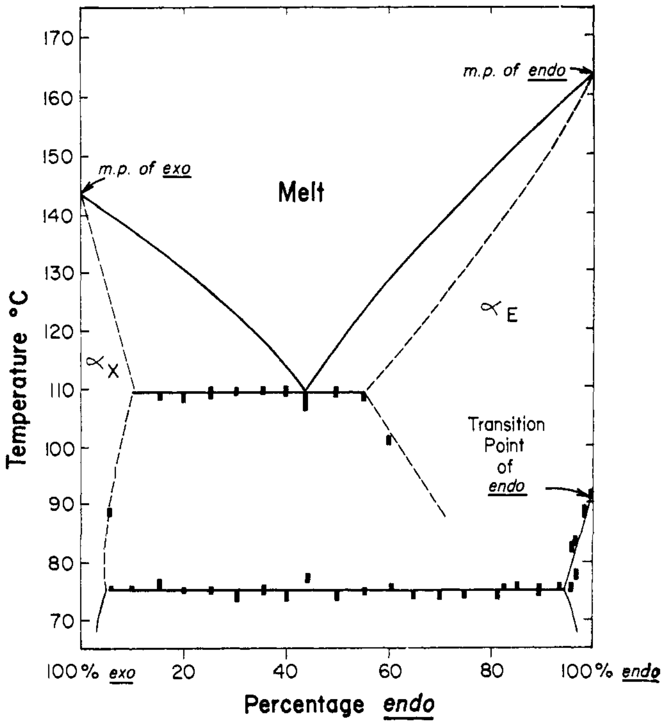

Figure 6. Phase diagram for *exo*- and *endo*-5-norbornene-2,3-dicarboxylic anhydrides. Dashes indicate observed thermal halts on heating mixtures of the anhydrides. Liquidus curves taken from ref 8.

Table II. Heats and Entropies of Phase Transformations for *exo* and *endo* Anhydrides

Compd	Temp, °C	ΔH, cal/g	ΔS, eu
endo	94	22.9 ± 0.5	10.0 ± 1
	164	5.4 ± 0.5	2.0 ± 0.2
exo	143	31.7 ± 1	12.5 ± 0.4

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(14) A translucent ("glassy") appearance was early noted in samples which had been melted, or largely melted, and then returned to room temperature. On standing they would sometimes change, essentially instantaneously and often with emission of weak sonic "cracks," to a mass of white, opaque solid.

(15) *Cf.* C. Bunn, "Crystals: Their Role in Nature and in Science," Academic Press Inc., New York, N. Y., 1964, Chapters 9 and 10.

(16) J. Pirsch, *Monatsh.*, **86**, 216 (1955).

(17) A. R. Ubbelohde, "Melting and Crystal Structure," Clarendon Press, Oxford, 1965, p 98.

(18) Reference 17, pp 35, 108.

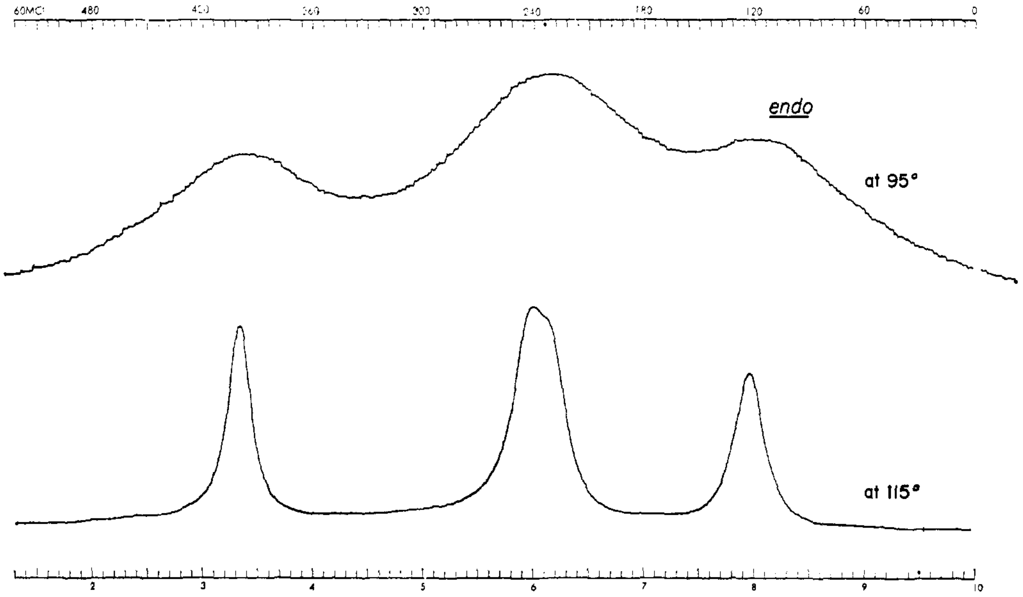

Figure 7. Proton magnetic resonance spectra from solid *endo* anhydride (mp 164°) at 95 and 115° as obtained with a high-resolution 60-Mcps spectrometer. See ref 31–33. *exo* isomer (mp 143°) under the same conditions gave no nmr signal.

The crystal structures of the two anhydrides were also investigated by X-ray powder diffraction. The *exo* isomer at room temperature or at 110°, and the *endo* isomer at room temperature, each gave distinctive but intricate sets of many lines which were not indexed (or indexable). In contrast, the *endo* isomer at 110° gave only four lines. These fitted the first four reflections of a body-centered cubic cell of dimensions 7.57 A.[19] This transformation to an isotropic cubic structure, consistent with loss of optical birefringence,[15] together with the large ΔH and ΔS of transformation, shows that *endo* isomer (although crystalline) is well on its way to a liquid state above 94°.

Discussion

The thermal isomerization of polycrystalline *endo* anhydride presents an apparently unique example of a unimolecular reaction occurring throughout the entire solid state with facility equal to that of the liquid-state reaction. This unusual property of the *endo* compound remains at some 45° (probably more) below the melting point, while the reaction in solid *exo* is noticeably slower than in the liquid at less than 10° below its melting point. While at first this is quite surprising, the X-ray and calorimetric data collected for the two isomers provide a helpful basis for interpretation. Although both isomers are spherically shaped, only the *endo* isomer enters a "rotator phase" [21] below its melting point. At 93–94° its sharp loss of optical anisotropy, great increase in entropy, and transformation to a symmetric cubic structure all denote conversion to a "plastic crystal" [22] where molecular rotation occurs with relative ease.[20–24] Melting at 164° results in a further gain only in translational freedom ($\Delta S_{\rm fus} = 2$ eu $\simeq R$), while the *exo* isomer gains both rotational and translational freedom at its melting point ($\Delta S_{\rm fus} = 12$ eu).

Thus the *endo* compound, in the temperature range where it reacts like a liquid, has some rotational characteristics of a liquid but the restricted translational motion of a solid.[26–29] This similarity to a liquid is also shown by the high-resolution nmr spectrum of solid *endo* anhydride illustrated in Figure 7. At 115° the pure solid compound gives three broad peaks corresponding to olefinic, bridgehead and α-hydrogens, and bridge hydrogens, respectively.[31] These peaks at 115° each have widths at half-heights of *ca.* 20 cps (or 5 mgauss), a value which is far less than that in nonrotating solids and much closer to that of a nonviscous liquid.[32] Three broad humps are still visible at *ca.*

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[19] However, the presence of only four reflections, with a strong background blackening, shows that *endo* is not highly crystalline at 115°.[20]

[20] W. J. Dunning, *Phys. Chem. Solids*, **18**, 21 (1961).

[21] J. Timmermans, *ibid.*, **18**, 1 (1961).

[22] J. G. Aston, "Physics and Chemistry of the Organic Solid State," Vol. 1, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 543.

[23] C. P. Smyth, *Phys. Chem. Solids*, **18**, 40 (1961).

[24] Such mesomorphic forms of globular molecules, termed "plastic crystal" or "rotator phases," might also be characterized as "crystalline liquids" as their properties are complementary[21] to the rather better known "liquid crystals."[25]

[25] G. H. Brown and W. G. Shaw, *Chem. Rev.*, 1049 (1957); G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press Inc., London, 1962.

[26] However, this rotation is not "free" and for the following reason must be subject to steric hindrance.[20] In a body-centered cubic cell of $a_0 = 7.57$ A the closest distance between centers of molecules is $\sqrt{3}a_0/2$, corresponding to a diameter of 6.56 A. As Courtauld models indicate a spherical diameter of about 7.5 A would be required to sterically allow free rotation of *endo* isomer, rotation can occur only by cooperative actions of surrounding molecules.[27] Since the reverse Diels–Alder reaction has a positive volume of activation,[28] still further disruption (melting) of the solid seems required around a reacting molecules.

[27] M. Davies, *J. Chim. Phys.*, **63**, 67 (1966).

[28] C. Walling and H. J. Schugar, *J. Am. Chem. Soc.*, **85**, 607 (1963).

[29] *exo* isomer does not begin significant rotation until at or near its melting point. This difference in the isomers may arise from the slightly less spherical shape of *exo* and from the different relative positions of olefinic and anhydride dipoles in the molecule. However, this last possibility cannot be a factor in the saturated analog, *endo*-norbornane-2,3-dicarboxylic anhydride, which also undergoes transformation to a crystalline liquid at 95° before it melts at 167°. Positions of nonpolar groups seem most important; *exo*- and *endo*-2-methylnorbornane are another pair with phase properties analogous to those of *exo*- and *endo*-norbornene anhydrides.[30]

[30] E. A. Seregin, N. N. Groshko, V. P. Kolesov, N. A. Belikova, S. M. Skuratov, and A. F. Plate, *Dokl. Akad. Nauk SSSR*, **159**, 1381 (1964); *Chem. Abstr.*, **62**, 12513 (1965).

[31] A dilute solution of *endo* in $DCCl_3$ shows these hydrogens centered at τ 3.68, 6.40 and 6.45, and 8.20–8.45, respectively.

[32] *E.g.*, some typical organic solids, while not in rotator phases,

95° while the absorptions become quite narrow at 130°. This partial resolution of the intramolecular magnetic environments in a solid *endo* sample at over 50° below its melting point is striking evidence of liquid like properties.[33] Rotational motion, with even some translational contribution from a diffusion process, is required in this crystalline liquid to give such relatively narrow resonance lines.[22,32,35]

Even if *endo* anhydride has properties similar to a liquid, both *endo* and *exo* compounds are still crystalline compounds. The occurrence of reactions in the solids shows that the loss of translational and rotational freedom in the bulk of the solid samples does not greatly (with *exo*) nor noticeably (with *endo*) affect the rate of isomerization compared to a liquid phase. The presence of a liquid-like, crystalline phase (*endo*) allows the reaction to proceed essentially at an unperturbed rate, but reaction in a more ordered crystalline phase (*exo*) is not greatly depressed.

For more quantitative comparisons an analysis of the separate kinetic contributions of liquid and solid phases in the frozen system is necessary. This would be difficult to do in general for the complex phase relationships of the system illustrated in Figure 6. Above the eutectic point, where good experimental kinetic data are available, transformations as well as reactions in all phases (liquid and solid solution α_E or α_X of Figure 6) should be considered; *i.e.*

$$\mathrm{E_S} \underset{\text{solidify}}{\overset{\text{melt}}{\rightleftarrows}} \mathrm{E_L} \underset{k_{\mathrm{X,L}}}{\overset{k_{\mathrm{E,L}}}{\rightleftarrows}} \mathrm{X_L} \underset{\text{melt}}{\overset{\text{solidify}}{\rightleftarrows}} \mathrm{X_S} \underset{k_{\mathrm{E,S}}}{\overset{k_{\mathrm{X,S}}}{\rightleftarrows}} \mathrm{E_S}$$

where X and E indicate *exo* and *endo* compounds and subscripts S and L denote solid and liquid phases. However, with *endo* isomer, since it reacts equally well in solid and liquid phases, the above complex kinetic relationships can be easily simplified. In this case the first-order rate constants are related by $k_{\mathrm{E,S}} = k_{\mathrm{E,L}}$ and, in the solid solution α_E, $k_{\mathrm{X,S}} = k_{\mathrm{X,L}}$. Assuming, as usual, that the phases are always at equilibrium (*i.e.*, the melting and solidifying is rapid relative to the reaction itself), the rate of isomerization in frozen *endo* anhydride is given by $\mathrm{d}X_{\mathrm{total}}/\mathrm{d}t = k_{\mathrm{E,L}}E_{\mathrm{L}} - k_{\mathrm{X,L}}X_{\mathrm{L}} + k_{\mathrm{E,S}}E_{\mathrm{S}} - k_{\mathrm{X,S}}X_{\mathrm{S}} = k_{\mathrm{E,L}} - (k_{\mathrm{E,L}} + k_{\mathrm{X,L}})X_{\mathrm{total}}$. This integrates, with use of the equilibrium relationship $k_{\mathrm{X,L}}X_\infty = k_{\mathrm{E,L}}E_\infty$, to $\log(X_\infty - X_t) = -k_{\mathrm{obsd}}t + \log X_\infty$ (where $k_{\mathrm{obsd}} = k_{\mathrm{E,L}} + k_{\mathrm{X,L}}$) which is the first-order kinetic relationship actually observed for the frozen *endo* system (see Figure 2 and Table I).

With *exo* isomer the rate constants in solid and liquid are not identical. Fortunately, since this more compact, nonrotating solid cannot accommodate much *endo* before beginning to melt (see the phase diagram of Figure 6 where the solid solution α_X contains little *endo* isomer), another type of simplification of the general reaction scheme is possible. The contribution of the solid solution α_X to the total reaction may be modified and the system treated as pure solid *exo* in equilibrium with melt containing *exo* and *endo*, *i.e.*

$$\mathrm{X_S} \underset{\text{solidify}}{\overset{\text{melt}}{\rightleftarrows}} \mathrm{X_L} \underset{k_{\mathrm{E,L}}}{\overset{k_{\mathrm{X,L}}}{\rightleftarrows}} \mathrm{E_L} \overset{k_{\mathrm{X,S}}}{\longleftarrow} \mathrm{X_S}$$

The total rate of production of *endo* isomer from frozen *exo* is then $\mathrm{d}E_{\mathrm{total}}/\mathrm{d}t = k_{\mathrm{X,S}}X_{\mathrm{S}} + k_{\mathrm{X,L}}X_{\mathrm{L}} - k_{\mathrm{E,L}}E_{\mathrm{L}}$. Unlike the *endo* case, this observed rate of reaction depends on the relative amounts of solid and liquid phases present at any time, and some phase relationship must then be brought into the kinetic equation.

From phase equilibrium, the ratio $E_{\mathrm{L}}/X_{\mathrm{L}}$ is constant at constant temperature and, together with the mole fraction relationship $X_{\mathrm{S}} + X_{\mathrm{L}} + E_{\mathrm{L}} = 1$, the rate equation takes the form

$$\mathrm{d}E_{\mathrm{total}}/\mathrm{d}t = k_{\mathrm{X,S}} + KE_{\mathrm{total}}$$

where K is a constant depending only on the ratio $E_{\mathrm{L}}/X_{\mathrm{L}}$ and on the rate constants $k_{\mathrm{X,L}}$, $k_{\mathrm{E,L}}$ and $k_{\mathrm{X,S}}$ (and is therefore dependent only on temperature). Three examples of the application of this rate equation are as follows. If the rate constant for direct reaction of solid *exo* is zero ($k_{\mathrm{X,S}} = 0$) the integrated form of the kinetic expression generates the initial accelerating part of the S-shaped curve for growth of a reactive liquid phase. If the rate constant for reaction in the solid is equal to that in the liquid ($k_{\mathrm{X,S}} = k_{\mathrm{X,L}}$) the integrated expression generates a decelerating composition against time curve (similar to that found with *endo* kinetic runs, Figure 1). And if $k_{\mathrm{X,L}} > k_{\mathrm{X,S}} > 0$, intermediate curves are obtained. This latter possibility seems to be the case with *exo* isomer where a flat, essentially linear relation of per cent *endo vs.* time is found until complete melting occurs (see Figure 5). Under these conditions, the rate constants for solid-phase reaction are equal to the initial slopes of the composition against time plots, *i.e.*, $\mathrm{d}E_{\mathrm{total}}/\mathrm{d}t = k_{\mathrm{X,S}}$. By this means the rate constants for solid-phase reaction of *exo* isomer were obtained, and they are compared with liquid-phase rate constants in Table III. As mentioned in the results section, this table shows more quantitatively that the reaction in solid *exo* is somewhat slower than in the liquid phase, *i.e.*, $k_{\mathrm{X,L}} > k_{\mathrm{X,S}}$, and the ratio between $k_{\mathrm{X,L}}$ and $k_{\mathrm{X,S}}$ increases as the temperature is lowered.

Table III. First-Order Rate Constants for Solid-Phase ($k_{\mathrm{X.S}}$) and Liquid-Phase ($k_{\mathrm{X.L}}$) Isomerization of *exo* Anhydride at Various Temperatures

Temp, °C	$k_{\mathrm{X.L}} \times 10^7$, sec^{-1}	$k_{\mathrm{X.S}} \times 10^7$, sec^{-1}	$k_{\mathrm{X.L}}/k_{\mathrm{X.S}}$	$(k_{\mathrm{X.L}}/k_{\mathrm{X.S}})_{\mathrm{calcd}}$
140	27[a]	22[b]	1.2	1.05[c]
135	12.6	8.6	1.5	1.13
130	8.4	3.5	2.4	1.23
125	4.7	1.7	2.8	1.33
120	3.1	0.63[b]	4.9	1.45

[a] Equal to one-half of the observed first-order rate constant for reaction of *endo* ($k_{\mathrm{obsd}} = k_{\mathrm{X.L}} + k_{\mathrm{E.L}} = 2k_{\mathrm{X.L}}$). [b] Obtained from the initial slopes (slopes = $k_{\mathrm{X.S}}$) of plots of mole fraction *endo* against time up to the time of complete melting. [c] Calculated from the ΔH_{fus}–rate ratio relationship presented in the Discussion. [d] Very slow reaction at this temperature, calculated from 6% conversion in 264 hr.

It is interesting to consider the possibility of calculating the solid-phase rate constants by completely inde-

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have half-widths on the order of 30 kcps or about 7 gauss: E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950); *Phys. Chem. Solids*, **18**, 9 (1961); E. R. Andrew and P. S. Allen, *J. Chim. Phys.*, **63**, 85 (1966).

(33) *exo* isomer at 115° under the same conditions gives no observable nmr signal at all.[34] Only when heated until a liquid phase developed did a signal appear.

(34) A broad line nmr study of the *exo* and *endo* anhydrides has been carried out by T. Cyr, University of British Columbia.

(35) F. A. Rushworth, *Phys. Chem. Solids*, **18**, 77 (1961).

pendent means. A suggested[6,7a] relation between rate constants for reaction in a solid and in a liquid is ln $k_L/k_S = \Delta H_{fus}/RT$. However, a relationship based on free energy would seem more appropriate. Thus if it is assumed that the reaction in each phase proceeds through identical transition states ($G_S{}^* = G_L{}^*$) then ln $k_L/k_S = (G_L - G_S)/RT$ and the relative rate of reaction depend only on the free-energy difference between solid and liquid. At the melting point, $\Delta G = 0$, and the rate constant for reaction in the solid is the same as in the liquid state. The convergence near the *exo* melting point of the two curves in Figure 3 and the approach of $k_{X,L}/k_{X,S}$ to unity (see Table III) as the temperature approaches 143° seem to support this treatment.

For temperatures a few degrees below the melting point, where the differences in enthalpy and entropy of solid and of liquid have not changed much from the corresponding differences at the melting point,[36] the following equation gives an estimate of the expected rate differences.

$$\ln k_L/k_S = \Delta H_{fus}/RT - \Delta S_{fus}/R = \Delta H_{fus}(1/T - 1/T_m)/R$$

Using this equation with the heat of fusion of *exo* isomer, the calculated ratio of k_L/k_S is 1.13 at 135°. The 13% difference predicted on this basis is perhaps sufficiently large to expect to observe. At least there is no doubt that the experimental curve for *exo* isomer departs from the *endo* line (*i.e.*, the liquid line) near this temperature. The experimental ratio k_L/k_S of 1.5 at 135° is considerably larger than the 1.13 calculated, and, not surprising considering the assumptions, the experimental ratio of liquid to solid rate constants increases faster than the calculated ratios (see Table III).

A similar calculation for *endo* isomer, using $\Delta H_{fus} =$ 5.4 cal/g and a temperature 7° below its melting point, gave $k_L/k_S = 1.02$, and even 30° below T_m the calculated ratio was only 1.09. This small calculated difference indicates why, in contrast to *exo* anhydride, no experimentally observed difference was observed for the *endo* anhydride throughout the range of temperatures used. On an energetic (as well as structural) basis, solid *endo* isomer above 94° is insufficiently different from liquid *endo* to give rise to different rate constants for liquid- and solid-state reactions.

It seems reasonable, therefore, that isomerization of solid *exo* and *endo* anhydrides occurs by the same mechanism as in the liquid state, with free-energy differences in the initial states largely accounting for the observed rate differences. The main additional factor is that, simultaneous with reaction, melting occurs around an isomerizing molecule and the energy required to cause this disruption is partly compensated for by an increase in entropy. At the melting point these factors cancel out, and the rate constants for both phases are equal as shown in the above equation.

Solid *endo* anhydride above 94° has liquid characteristics and, at least above 120°, reaction proceeds at the same rate as in a true liquid phase. Solid *exo* at the melting point is able to react at a rate equivalent to that of liquid *exo*, but at lower temperatures the greater energy required to disrupt the more cohesive crystal structure is not compensated by a sufficient increase in entropy. As shown in Table III, the solid-phase reaction rate constant then decreases with temperature faster than the liquid-phase rate constant.

Observations of this type for frozen-state reactions might be quite rare. Possibly they will be found only for unimolecular, nonpolar reactions (*e.g.*, the reverse Diels–Alder reaction) which are not greatly sensitive to environmental factors (such as solvent effects) even under more common reaction conditions. Further studies of reactions in polycrystalline organic solids, with attempts to kinetically separate the liquid- from the solid-phase contributions, will be required to indicate more general features of such biphase reactions.

Experimental Section

Materials. Commercially available *endo*-5-norbornene-2,3-dicarboxylic anhydride was crystallized from petroleum ether–benzene or from CCl_4. Several different batches of material were used, and melting ranges varied by 1 or 2° from 164°. Vpc analyses of these *endo* samples generally showed no *exo* isomer present (*ca.* 0.5% should have been observable). The *exo* isomer was prepared by thermal conversion of *endo* at *ca.* 190° followed by recrystallization from benzene several times.[8] After five crystallizations *ca.* 5% *endo* isomer was still present. Sublimation at 100° (4 mm) gave *exo* with *ca.* 1% *endo* present, mp 141.5–144°. To prepare the purest sample of *exo* anhydride, a 90% pure batch was hydrolyzed in boiling water and the resulting diacid crystallized six times from water followed by three times from acetonitrile. This acid was dried, pulverized, suspended in dry benzene (10 g in 300 ml), and refluxed in a Soxhlet apparatus containing $CaSO_4$ as a drying agent. After about 12 hr all the acid had reacted and dissolved. The cool solution was further dried with $MgSO_4$ and partly evaporated to crystallize the *exo* anhydride, mp 142–143.5°. Other methods of dehydration resulted in production of some few per cent (by vpc analysis) *endo* anhydride.

Kinetic Procedure. For each run crystalline samples (usually 0.01–0.05 g) were sealed under air in up to 40 (usually 10–15) 1-ml vials. *endo* samples early in the study were sometimes premelted by quick heating to just above the melting point; later samples of other runs were long needles (from petroleum ether (bp 30–60°)–benzene), flakes (from CCl_4), or powder, and no observable differences in kinetic results were obtained. Samples were placed in constant temperature (±0.1°) baths for various lengths of time. As each sample was an individual point, not necessarily connected with the analysis of others, some of the runs reported (*e.g.*, see Figure 5) are the composite results of analyses carried out at different times on samples of different origin by a different worker.

Analysis by Nmr Spectra. After collecting all the samples of a run they were dissolved in chloroform-*d*. A small quantity of insoluble (polymeric?) material was present, but the nmr spectra showed no maleic anhydride. The nmr integral heights of the α-hydrogen absorption of *exo* anhydride at τ 6.95 and the combined *exo–endo* olefinic absorptions at *ca.* τ 3.6 were obtained using a Varian A-60 spectrometer. The ratio of the integrals gave the per cent *exo* in the sample. The internal consistency of the method for each individual sample resulted in a good measure of percentage, small amounts (1–2%) of *exo* in *endo* were noticeable if not accurately measurable, but *endo* in *exo* could not be adequately obtained since the bridgehead hydrogens (τ 6.5) of the two isomers interfered with the *endo* α-hydrogens at τ 6.4.

Analysis by Vpc. The kinetic samples, dissolved in acetone, were analyzed with a Varian Aerograph 90P3 gas chromatograph using a 6 ft × 0.25 in. column containing 20% SF-96 on Diatoport-S (80–100 mesh) at 135°. With a low injector temperature (175°), thermal cracking of the isomers (indicated by a maleic anhydride peak) was negligible; calibration with known mixtures showed that any minor isomerization did not interfere. At a flow rate of *ca.* 40 ml/min the retention times were 30–40 min; *endo* followed *exo* in sufficiently separate peaks. One peak area over the sum of the two gave the per cent isomer with an estimated variation of ±2%.

Phase Diagram. Calorimetric data were obtained using a Perkin-Elmer differential scanning calorimeter DSC-1B, with heats of fusion calibrated with a standard indium sample. Sublimation of *endo* near its melting point makes the measured heat of fusion less reliable. Endothermic transitions (at 75 and 109°) were noted as

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[36] *Cf.* B. Hannay, "Solid-State Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1967, p 8.

marked on Figure 6, the relative magnitude of these decreased to zero with approach from 40 to 100% *exo*, but were observable in samples with 5% *endo*. Pure *exo* showed no transformations from room temperature to melting at 143°. Samples with over 60% *endo* showed transitions at 75–94° (pure *endo*) but no transition at 109°. Thermal halts at 75–77° (mixtures) and 94–96° (pure *endo*) were also observable with an Aminco "Accumelt" thermocouple embedded in prefused samples.

X-Ray Diffraction Studies. A General Electric powder camera, A4969, was used with Cu Kα irradiation. Temperature control was by directing a stream of hot air over the 0.3-mm capillary containing the pulverized sample. The temperature at 110° varied by $\pm 5°$ around the critical volume of the sample, as estimated with a thermocouple. *endo* isomer at 110° gave one strong reflection $\theta = 8.28°$, and three much weaker ones, $\theta = 11.74$, 14.44, and 16.78°. These correspond to a body-centered cubic structure of cell dimensions $a_0 = 7.57 \pm 0.05$ A. (Other body-centered cubic structures were compared: camphene at room temperature also gave only four lines, $a_0 = 7.95$ A (lit.[37] *ca.* 8.00 A), and hexamethylenetetramine gave $a_0 = 7.03$ A (lit.[38] 7.02 A). The saturated compound, *endo*-norbornane-2,3-dicarboxylic anhydride, gave only four lines at 110° and a slightly larger unit cell, $a_0 = 7.63$ A, than the *endo*-norbornene anhydride.) On cooling to room temperature a complex, many-line diffraction pattern appeared which was not always identical with the equally complex, but distinct, pattern for initial *endo* isomer as obtained by crystallization from CCl$_4$ or benzene-petroleum ether. Apparently two forms of nonrotating *endo* isomer may exist at low temperatures; in one case recrystallization by cooling with Dry Ice occurred in a 0.3-mm capillary containing an *endo* sample which had been heated to 110°. The X-ray pattern then corresponded to a "spotty" *endo* pattern with spacings the same as obtained from an unheated sample. *exo* anhydride gave the same unique, many-line pattern at 110° as at room temperature.

Solid-State Nmr Spectra. High-resolution nmr spectra were obtained on neat, polycrystalline samples of *endo* anhydride utilizing a Japan Electron Optics Laboratories C-60H spectrometer. Samples were first melted and solidified into ordinary sample tubes. The spectrum at 115° was three broad humps with peaks at *ca.* τ 3.3, 6, and 8, standardized against external TMS. These correspond to olefinic, bridgehead and α-hydrogens, and to bridge hydrogens, respectively. A mixture of 50–50% *exo–endo* was completely melted (see Figure 6) at 115° and served as a standard of comparison. This liquid mixture gave the sharp lines (*e.g.*, the $W_{1/2}$ for the α-hydrogen signal of *exo* isomer was *ca.* 2 cps) and also gave the spin–spin splittings which are obtained from a dilute solution of the compounds in chloroform-*d*. The amplitude of the three broad signals from pure solid *endo* was about the same as from the completely liquid *exo–endo* mixture. *exo* anhydride gave no signal at this temperature.

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(37) C. Finback, *Arch. Math. Naturvidenskab*, **B42**, 71 (1938); *Chem. Abstr.*, **34**, 12 (1940).

(38) R. G. Dickinson and A. L. Raymond, *J. Am. Chem. Soc.*, **45**, 22 (1923).

Base-Catalyzed Isomerization of Bicyclic Olefins[1]

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Abstract: The rates of base-catalyzed isomerization of three bicyclic olefins in which the double bond is exocyclic have been studied. Using the system potassium *t*-butoxide–dimethyl sulfoxide, the rate constants, activation enthalpies, and entropies for the isomerization of 2-methylenebicyclo[2.2.1]heptane, 2-methylenebicyclo[2.2.2]octane, and β-pinene were obtained. The observed relative rates (statistically corrected) at 55° are β-pinene, 43; 2-methylenebicyclo[2.2.2]octane, 3.9; 2-methylenebicyclo[2.2.1]heptane, 2.6; and methylenecyclohexane, 1.0. In addition, the rates of the base-catalyzed endocyclic to exocyclic olefin isomerization have been calculated for the cyclic and bicyclic olefins. From the relative rates of the exocyclic compounds the relative importance of angle strain contributions is assessed to be minor. By contrast, angle strain factors are important in the endocyclic isomerization. The principal factors governing the rate of isomerization of the exocyclic olefins are the torsional effects.

Structural influences on the physical and chemical properties of cyclic and bicyclic compounds have been investigated in considerable detail during the last 20 years.[4] The fixed and known geometries of these readily available systems provide the framework for attempts to derive predictive relationships governing their behavior. As a result, considerable information about the factors influencing the rate-determining step(s) of a variety of reactions has been derived from studies of the rate variation with change in ring size.[5]

For some time we have been interested in the base-catalyzed isomerization of olefins. Previously, the effect of ring size on the rate of isomerization of monocyclic compounds was investigated.[6] In the present study, the base-catalyzed isomerizations of several bicyclic olefins are determined, and these are compared with the monocyclic compounds to provide insights into the factors governing reactivity.

Mechanistic studies of the base-catalyzed olefin isomerization have provided some detail on the nature

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(4) For a review with leading references see Ya. I. Goldfarb and L. I. Belenkii, *Russ. Chem. Rev.*, **29**, [4], 214 (1960).

(5) For an excellent discussion with leading references, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; several recent examples include H. C. Brown and R. L. Klimisch, *J. Am. Chem. Soc.*, **88**, 1430 (1966), and M. Byrn and M. Calvin, *ibid.*, **88**, 1916 (1966).

(6) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).