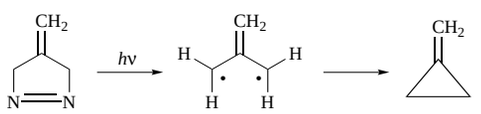
Fluxional cyclopropanones. Approaching measurable equilibrium concentrations of acyclic oxyallyls

Theodore Strang Sorensen * and F. Sun

The Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

The preparation of five new *cis*-2,3-di-R-cyclopropanones is described where R = *tert*-amyl, thexyl, 2-(2,3,3-trimethylbutyl), 1-adamantyl and 1-(7,7-dimethylnorbornyl). As structure proof for these labile compounds, the [3 + 4] furan adducts were characterized, and the *cis* cyclopropanones were also converted into the much more stable *trans* isomers for further characterization. Except for the 1-adamantyl case, all of these *cis* cyclopropanones exhibit dynamic NMR line-broadening at low temperature due to the reversible conversion into an unseen oxylallyl valence-bond isomer, the first time such behavior has been observed for any cyclopropanone. In the most facile example, that due to the R = 2-(2,3,3-trimethylbutyl) substituent, $\Delta G^{\ddagger}$ was found to be only 9.8 kcal mol^{-1}. This barrier was solvent sensitive and data for this solvent dependence are given. These low $\Delta G^{\ddagger}$ barriers also suggest that the oxyallyl equilibrium concentrations are approaching detectable levels.

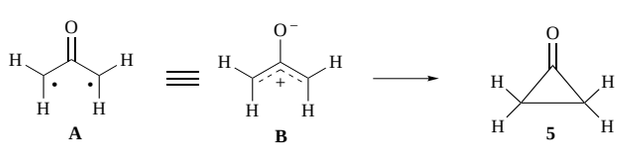
Since the inception of Hückel MO theory, trimethylenemethane **1** has been recognized as an especially interesting and important species, including the prediction that **1** should have a triplet ground state. In a single author communication,[1] widely noted at the time, Dowd described the preparation of 4-methylene-Δ^1-pyrazoline **2**, whose matrix photolysis at 77 K gave an EPR



2 **1** **4**

signal which could be analyzed as a triplet structure, with zero-field parameters appropriate for **1**. Recently the infrared spectrum of **1** (and of various deuteriated isotopomers) has been reported[2] by Maier *et al.*

In his communication, Dowd notes the close resemblance of **1** to its oxygen analog **3**, now known as oxyallyl, and to the



A **B** **5**

3

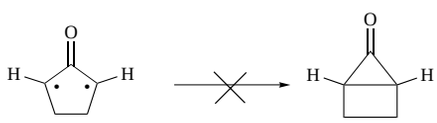
possibility that **3** might also be directly observable, to quote, 'That is, it was felt that if one could find a means of producing and detecting trimethylenemethane, then the problem of testing the cyclopropanone diradical hypothesis might be somewhat simplified.' However, more than 30 years later, the direct observation of **3** has still not been reported.

The activation energy for the loss of the EPR signal for **1** (with formation of **4**) has been measured by Dowd and Chow[3] as 7 kcal mol^{-1}. This value does not agree very well with gas-phase experimental[4] and theoretical estimates of the singlet–triplet energy difference in **1** (or to the lowest energy crossing of the singlet–triplet surfaces),[5] but it seems reasonable to assume that this sizeable 7 kcal mol^{-1} frozen-matrix barrier is due in some manner to the fact that **1** exists in a triplet ground state.

In contrast, the most recent MO calculations[6] of the lowest singlet and triplet states of **3** show that these are very similar in energy. Both singlet and triplet states are best written as **3A** since the C=O bond is a normal carbonyl (many earlier descriptions of **3** appear to have overemphasized the supposed zwitterionic character, as in the **3B** formulation). The barrier to ring closure of singlet **3** to cyclopropanone **5** has been calculated as a miniscule 0.33 kcal mol^{-1}.[6b] Thus the possible frozen matrix detection of **3**, compared with **1**, suffers from the problem that an experimentally convenient EPR signal may or may not be seen (and could depend on how it was generated), and that singlet **3** would have to be produced from some precursor molecule under extreme cryogenic conditions in order to prevent ring closure.

Gas-phase mass spectrometric (or related) techniques are another approach to 'observing' metastable intermediates and a recent paper by McLafferty and co-workers is illustrative.[7]

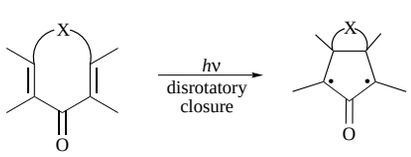
Turning to derivatives of **3**, one finds that substituted oxyallyls are nearly as elusive as the parent. One can solve the problem of the expected extremely low barrier to cyclization of oxyallyls to cyclopropanones by using a cyclopentane ring system, because in this case the singlet cyclopentane oxyallyl **6**



6 **7**

is calculated[8] to be thermodynamically more stable than the bicyclo[2.1.0]pentan-5-one partner **7** (reversing the calculated 21–27 kcal mol^{-1} free energy difference between the parent cyclopropanone **5** and the parent singlet oxyallyl **3**.[6b] From calculations,[6] alkyl substitution of an oxyallyl seems to favor the singlet state, so that one can probably assume that these oxyallyls, when generated from singlet precursors such as cyclopropanones, *etc.*, will have a singlet ground state.

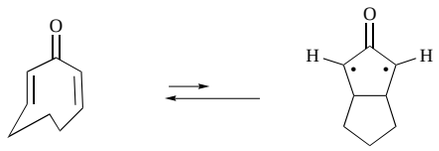
In fact, the stability of **6** *vs.* **7** has long been known from photolysis experiments on various cross-conjugated cyclic dienones and γ-pyrones, where evidence for the oxyallyl photoproduct can be deduced from various trapping experiments, including intramolecular versions.[9] Photolysis of dienone-



X = $(CH_2)_n$, O, *etc.*

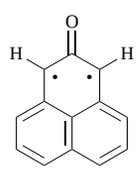
containing matrices at 77 K has in several instances produced blue colors and these have been attributed to an oxyallyl.[10] However, a full discussion of this extensive research area is beyond the scope of this overview; for a review see reference 11.

Recently the *cis–trans* cyclooctadienone **8** has been characterized,[12] and shown to react with trapping agents to give products derived from the bicyclic oxyallyl **9**. The postulated equilibrium of **8** and **9** (an allowed conrotatory closure) seems plausible.



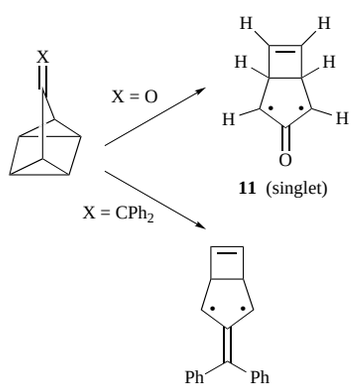
8 **9**

An unsuccessful attempt to prepare the (resonance-delocalized?) cyclohexyl oxyallyl **10** has been reported.[13]



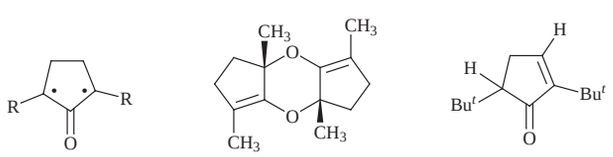
10

Miyashi, Akiyama and co-workers have reported[14] the photogeneration of oxyallyl **11** at 77 K in a frozen matrix, and in a parallel experiment, the trimethylenemethane **12**, with only



the latter showing an EPR signal. In addition, trapped products of both **11** and **12** could be isolated.

Notwithstanding the considerable progress which has been made in the chemical and physical characterization of these cyclic oxyallyls, the UV, IR and solid-state NMR characterization of oxyallyl **6** seems to us a very worthy and reasonably realistic goal, the crucial and unsolved problem being to find a suitable precursor molecule for the matrix generation. We have recently generated the putative oxyallyls **13a** and **13b** in solution



13a, R = CH_3
b, R = *tert*-butyl

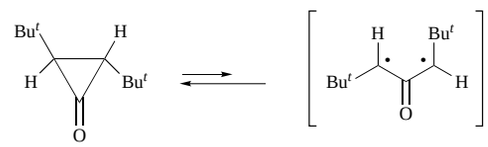
14 **15**

at temperatures as low as 153 K, intending to carry out NMR characterization. However, **13a** immediately forms a dimer **14**,[15] and **13b** rearranges to the ketone **15**.[16] Unfortunately, our synthesis of **13a** or **13b** does not appear to be applicable to a 77 K matrix isolation experiment.

Finally, it should be mentioned that there is a large (and continuing) literature on synthetic applications of both acyclic and cyclic oxyallyls in organic chemistry (mainly 3 + 4 or 3 + 2 cycloaddition reactions), including *O*-complexed oxyallyls, oxyallyl cations, heteroatom-substituted oxyallyls. There are a number of reviews of this area.[17]

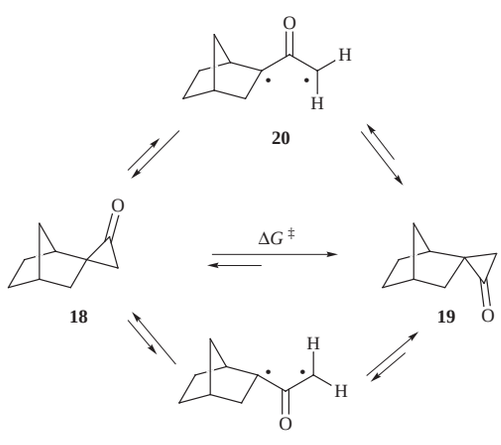
The present paper describes experiments which could eventually lead to the preparation of a stable *acyclic* oxyallyl. As mentioned, recent theoretical calculations[6b] give the gas-phase singlet oxyallyl **3**–cyclopropanone **5** energy difference (ΔG^{298}) as 21 kcal mol^{-1} (CASSCF), but with a considerably larger value (*ca.* 28 kcal mol^{-1}) found using the CASPT2N method (inclusion of MP2 correlation). Very recent calculations[18] using large basis sets in the optimization and involving G2 (MP2′) energies give values of 31–32 kcal mol^{-1}, which are in the range of the CASPT2N value. Although oxyallyl is a transition-state in the optimization procedure, there are indications that a very shallow minimum is present at the G2 level.

There are two experimental estimates of a solution oxyallyl–cyclopropanone energy difference, both involving substituted derivatives of **3**–**5**. Greene and co-workers[19] have found $\Delta G_f^{\ddagger}$ values of 27–29 kcal mol^{-1} for the racemization of (+)-*trans*-2,3-di-*tert*-butylcyclopropanone **16**, using various solvents.



16 **17**

This reaction is assumed to take place *via* the achiral oxyallyl **17**. Assuming that $\Delta G_r^{\ddagger}$ is very small (calculated to be 0.33 kcal mol^{-1} in oxyallyl itself), one can approximate $\Delta G_f^{\ddagger}$ with $\Delta\Delta G_{16-17}$. This 27–29 kcal mol^{-1} experimental $\Delta\Delta G$ estimate agrees reasonably well with the gas-phase 28 kcal mol^{-1} value calculated for the parent system if one takes into account the sizeable steric strain in **17** due to the *anti* (to oxygen) *tert*-butyl group and the off-setting increased oxyallyl stability brought about by the two alkyl substituents[6,8a] (inductive or hyperconjugative stabilization). Recently, Cordes and Berson[20] have reported the interconversion barrier for the tricyclic cyclopropanones **18** and **19**, a process which involves the

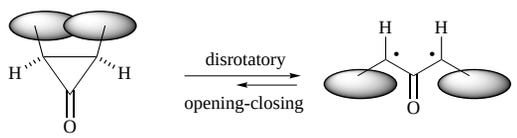


20 **18** **19** **21**

oxyallyls **20** and **21**, and found a much smaller $\Delta G^{\ddagger}$ barrier of 16–19 kcal mol^{-1} (again a solvent dependence was noted). Cordes and Berson have rationalized this *ca.* 10 kcal mol^{-1} decrease relative to **16**–**17** in terms of a destabilizing angle strain at the spiro center in **18**–**19**, and the non-bonded interactions which make oxyallyl **17** strained relative to **16** (see previous discussion). In this connection we have observed[21]

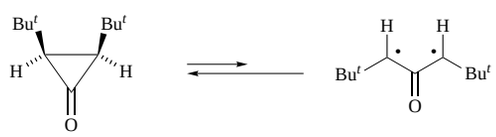
that cyclopropanones with single or double spiro fused cyclopentane rings, *i.e.*, similar to but less strained than the five-membered ring in norbornane, are also destabilized relative to their oxyallyls, compared with their acyclic counterparts.

In this paper we describe an approach designed to further reduce the oxyallyl–cyclopropanone energy difference, with the ultimate intent of directly detecting equilibrium concentrations of the oxyallyl partner. This approach is most easily shown in a pictorial way.



22 **23**

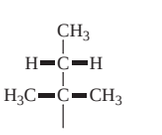
Sterically large *cis* substituents in a cyclopropanone **22** will naturally destabilize this structure whereas the oxyallyl can nicely accommodate these groups in the respective *syn*,*syn* positions of **23**. In addition these bulky groups could have the ancillary benefit of shielding the reactive oxygen center in **23**, one of the termini for allowed [3 + 3] oxyallyl–oxyallyl dimerization reactions.[15] In a recent publication[22] we have described the preparation of a cyclopropanone fitting the **22** requirement, *cis*-2,3-di-*tert*-butylcyclopropanone **24**. Using the previously mentioned



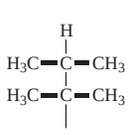
24 **25**

data of Greene,[19] together with high level MO energy calculations of the *cis* and *trans* cyclopropanones **16** and **24** and lower level estimates of the steric strain in the respective oxyallyls **17** and **25**, we estimated that the **24**–**25** free energy difference would be only 10.5–12 kcal mol^{-1}. This indirectly determined $\Delta\Delta G$–$\Delta G^{\ddagger}$ barrier would be well within the range of NMR line-broadening experiments, but the high symmetry of a *tert*-butyl group precludes such experiments using **24**. Less symmetrical groups such as *tert*-amyl have diastereotopic entities (quaternary methyls and the CH_2s of ethyl) in the cyclopropanone, and these become chemically equivalent in a planar oxyallyl, making NMR line-broadening experiments potentially feasible. The ^{1}H and ^{13}C NMR differentiation of diastereotopic groups is relatively unpredictable in these examples, however sharp single peaks such as quaternary methyls are likely to be advantageous in avoiding overlaps.

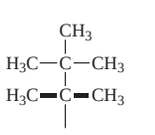
In this project the following substituents were tested (diastereotopic groups are shown in bold). Except for 1-adamantyl there are also diastereotopic carbons in the ^{13}C NMR spectra. In order to keep the spectra simple, both substituents were kept the same in the *cis*-2,3-disubstituted cyclopropanones.



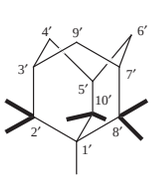
tert-amyl



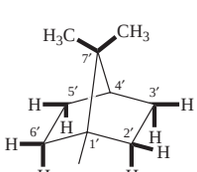
thexyl



2,3,3-trimethyl-2-butyl



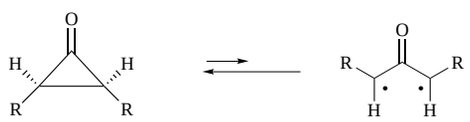
1-adamantyl



7,7-dimethyl-1-norbornyl

Although not expected to be a large factor, there are hopefully some steric differences among these five groups, *viz*. the 1-adamantyl and norbornyl groups have three β carbons 'tied back' and this may somewhat reduce steric repulsions in the corresponding cyclopropanones.[23] We also hoped that the 2-(2,3,3-trimethylbutyl) group might be somewhat bulkier than *tert*-butyl.

This paper describes the preparation of *cis*-2,3-di-R-cyclopropanones **26**, and then we examine these compounds to see if one can detect NMR line-broadening due to rapid equilibration with the corresponding oxyallyls **27**.



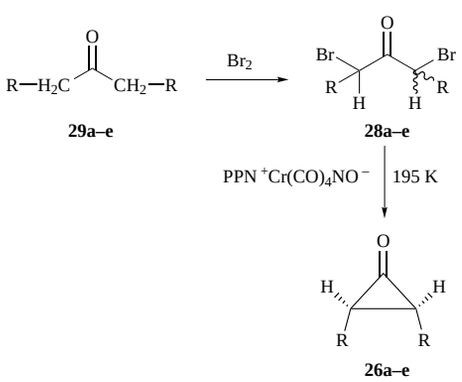
26a, R = *tert*-amyl
b, R = thexyl
c, R = 2,3,3-trimethyl-2-butyl
d, R = adamantyl
e, R = 7,7-dimethyl-1-norbornyl

27a, b, c, d, e

Results and discussion

Synthetic aspects

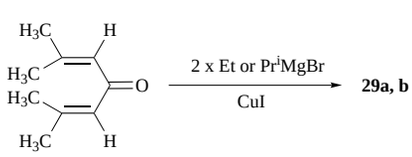
The cyclopropanones **26a**–**e** were prepared from α,α′-dibromo ketones **28a**–**e** using the same procedure [employing the



29a–e **28a–e** **26a–e**

organometallic anion $Cr(CO)_4NO^-$] previously described[22] for the synthesis of **24**, omitting the final sublimation step because of the increased molecular weights of the present systems and a general lessening of crystallinity. The α,α′-dibromo ketones **28a**–**e** were produced by direct bromination. A mixture of diastereomers was generally produced, but since both diastereomers can be used for the cyclopropanone synthesis, diastereomeric mixtures were mostly employed (in the **28c** case, the separated diastereomers were individually tested).

Ketones **29a**,**b** were prepared from phorone using sequential



CuI-catalyzed 1,4-Grignard additions. With Bu^{t}MgBr, only the first stage addition could be accomplished, but this adduct was a convenient source of the ester **30c**. Ketones **29c**–**e** were prepared by a Claisen condensation route from the esters **30c**–**e**.

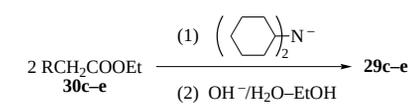
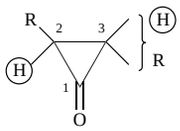


Table 1 ^{1}H Chemical shift[a] of the H2–H3 hydrogen peak in **16**, **24**, **26a–e** and **31a–e**

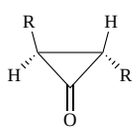


R	*cis*	*trans*
Bu^t	3.04	1.67
Am^t	3.03	1.63
Thexyl	3.08[b]	*c*
2-(2,3,3-Trimethylbutyl)	3.65	1.82
1-Ad	2.88	*d*
1-(7,7-Dimethylnorbornyl)	2.93[b]	1.64[b]

[a] Unless otherwise noted, in $CDCl_3$ at ambient temperature. [b] CD_2Cl_2 at 203 K. [c] Not measured. [d] Obscured by larger peaks.

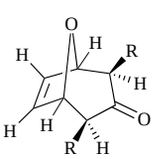
Characterization

In each case, the cyclopropanones **26a–e** were initially examined *in situ* by low temperature ^{1}H and ^{13}C NMR spectroscopy, as previously described for other cyclopropanones.[21,22,24] However, **26a–e** are stable enough for a work-up procedure which generates the cyclopropanones essentially free from reaction by-products and solvents. The compounds exist at low temperature as oils or low-melting solids and they must be stored at 195 K to prevent decomposition. The main NMR feature which can be used as a structure proof for *cis*-di-R-cyclopropanones is the H2–H3 NMR peak. This peak position is quite low field compared with that found in methyl-substituted cyclopropanones, and compared with the same hydrogens in the corresponding *trans*-di-R-cyclopropanones **31a–e** (Table 1). These *trans* isomers can be formed by an alternative work-up procedure of the initially formed *cis* analogs, and involves letting the solution warm to room temperature.



31a–e

As further structure proof, furan adducts of **26b–e**, structures **32b–e**, were prepared at or below room temperature and these stable compounds were characterized. The corresponding *trans* cyclopropanones **31b–e** do not undergo this cycloaddition reaction.



32b–e

NMR line-broadening studies at 400 MHz

The initial *in situ* NMR studies in CD_2Cl_2 solvent were generally begun at a precooled temperature of *ca.* 183 K, and then the sample was progressively warmed in about 10 °C steps. Low temperature line-broadening was easily seen in the **26a–c** cases. In **26a**, the diastereotopic CH_3 groups are well separated in the 'frozen-out' spectrum, but the diastereotopic CH_2 hydrogen quartets are substantially overlapped. In **26b**, one of the diastereotopic $\geqslant$C–CH_3 signals and one of the diastereotopic $^H\geqslant$C–CH_3 peaks were resolved but their corresponding 'partners' were overlapped. However, a line-broadening analysis was possible using the resolved $\geqslant$C–CH_3 peak because after coalescence, the 'averaged' $\geqslant$C–CH_3 peak is not obscured. Cyclopropanone **26c** is potentially the simplest of all the cyclopropanones, having only two diastereotopic $\geqslant$C–CH_3 groups. Fortunately both of these, and the 'averaged' signal, are all well-resolved (see Fig. 1, 213 K for 'frozen-out', 260 K for 'averaged'). Interestingly, at very low temperatures the *tert*-butyl group in the crowded R functionality begins to broaden in a dynamic process unrelated to the cyclopropanone–oxyallyl equilibrium (see Fig. 1, 203 K and lower, and later discussion).

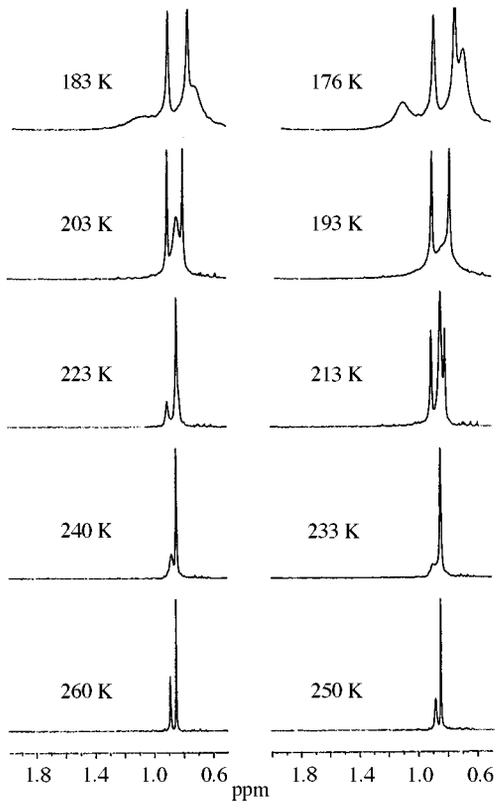


Fig. 1 Reversible ^{1}H NMR line-broadening observed for cyclopropanone **26c** in [$^2H_6$]toluene solvent. The 213 K temperature shows a 'frozen-out' spectrum of **26c** with separate signals for the diastereotopic CH_3 groups. By 260 K these have become a sharp single peak. Starting at 231 K and lower, the *tert*-butyl group peak broadens and decoalesces in a process unrelated to the cyclopropanone–oxyallyl interconversion.

The 1-adamantyl system **26d** proved to be a disappointment. The *in situ* low temperature spectra in CD_2Cl_2 at 223 K had three ^{1}H peaks for the 1-adamantyl part, area 6:12:12. The broad, area six, peak was clearly the methine hydrogens, but the featureless twelve hydrogen peaks at 1.63 and 1.59 were not immediately assignable. Using isolated **26d** in $CDCl_3$ solvent at ambient temperature, a poorly resolved doublet (2.2 Hz) at δ 1.72 (12 H) and an apparent doublet of doublets at *ca.* 1.68 (12 H) could be correlated (2D HETCOR) with ^{13}C peaks at 41.9 and 36.1, respectively. The former is more closely assignable (related structures) to C2′, 8′, 10′, *i.e.*, the carbons with the diastereotopic methylenes. This assignment was also in accord with decoupling results, *i.e.*, irradiating the CH protons (H3′, 5′, 7′) decoupled the 1.72 peak and converted 1.68 into two resolved peaks which can be assigned to the non-diastereotopic methylene protons at C4′, 6′, 9′. The presence of the reasonably sharp δ 1.72 ^{1}H peak at room temperature for the diastereotopic protons is consistent with rapid averaging at this temperature, but this interpretation is tenuous because cooling the solution stepwise to 203 K only slowly broadens the peak, *i.e.*, the diastereotopic hydrogens may well be accidentally equivalent and therefore unusable for our purposes. As further evidence for this, the gradual broadening observed for the δ 1.72 peak is similar to that undergone by the cyclopropanone CH singlet, which is not involved in an exchange process. Other solvents ($CDCFCl_2$, toluene) also failed to show evidence for NMR line-broadening.

Table 2 $\Delta G^{\ddagger}$ barriers for ^{1}H NMR line-broadening in cyclopropanones **26a**–**c**,**e** in CD_2Cl_2

Cyclopropanone	$\Delta G^{\ddagger}$/kcal mol^{-1} [a]
26a	12.2 [b]
26b	11.6
26c	10.8 [c]
26e	12.5

[a] Determined from the coalescence temperature T_c. [b] Also measured in $CDCl_3$, $\Delta G^{\ddagger} = 11.4$. [c] See Table 3 for other solvent systems.

Table 3 Solvent dependence of NMR line-broadening for **26c**

Solvent	T_c/K	Δ/Hz	k/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
CD_2Cl_2	223	58	129	10.8
$CDCl_3$	203	49	109	9.8
$CDFCl_2$	203	72	160	9.7
[$^2H_8$]Toluene	233	36	80	11.5
[$^2H_6$]Acetone	230	62	73	11.4

With fast rotation about the C2(3)–C1′ bond in **26d**, there are no diastereotopic ^{13}C carbons. Given this fact and the negative ^{1}H NMR results we have no experimental way to reach any conclusion about the cyclopropanone–oxyallyl barrier in the **26d** case.

The dimethylnorbornyl system **26e** also proved problematic. In the ^{1}H NMR spectrum at 223 K (*in situ* conditions), the diastereotopic methyl groups showed up as nearly overlapped peaks ($\Delta = 0.02$ ppm) and in the ^{13}C spectrum, a single $^{13}CH_3$ peak was seen (accidental equivalence). The remaining norbornyl ring ^{1}H peaks form a complex spectrum unsuitable for line-broadening analysis. However, the norbornyl C2′–C6′ and C3′–C5′ carbons are all seen as four separate and only slightly broadened peaks, showing that equilibration *via* the oxyallyl is slow under these temperature conditions.

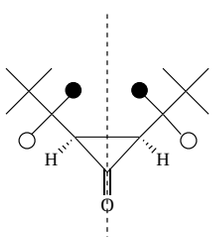
By 243 K, a single ^{1}H methyl signal is observed ($T_c \approx 238$ K). A comparison of the respective $\Delta G^{\ddagger}$ values for the line-broadening process in cyclopropanones **26a**–**c**,**e** is shown in Table 2.

Solvent effects

Both the Greene and Cordes–Berson studies found fairly large solvent effects on the measured cyclopropanone $\rightleftharpoons$ [oxyallyl] rates. In our work cyclopropanone **26c**, as the simplest system to analyze, was also studied in a number of different solvents. The results are presented in Table 3, and indeed there are noticeable differences in the rates (discussed later).

Discussion

The cyclopropanone **26c** will be used for discussion purposes. This particular R group is very likely the most sterically congested, but conversely is the simplest group to analyze in terms of symmetry.

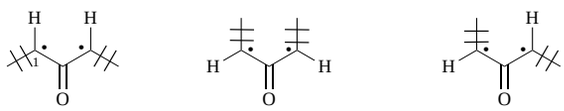


26c C_s-averaged symmetry

The NMR spectra of **26c** indicate a C_s symmetry plane, as shown above, *i.e.*, both R groups as a unit are equivalent on the NMR timescale. The methyl groups marked ○ and ● are diastereotopic within each R group, but because of the averaged C_s molecular symmetry these show up collectively as two 6 H peaks. Even at the lowest temperature (176 K) only two peaks are seen, showing that this symmetry plane (or averaged symmetry plane) is still present (Fig. 1). This result is also confirmed from the behavior of the ring methine hydrogens, which remain as a relatively sharp singlet (2 H) peak at all temperatures.

In [$^2H_8$]toluene solvent, but less so in the other solvents, the *tert*-butyl peak broadens starting about 213 K, and by 183 K has decoalesced into two broad peaks in a 6:12 ratio (see Fig. 1). This result also shows that the C_s symmetry remains and that restricted rotation about the *tert*-butyl group itself renders one CH_3 of the *tert*-butyl distinctly different from the other two CH_3 groups.

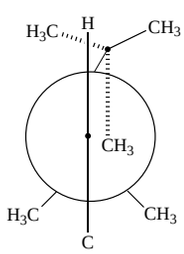
Cyclopropanones undergo *disrotatory* ring opening when forming the oxyallyl valence bond tautomer. There are two possible disrotatory modes for **26c**, one yielding oxyallyl **27c**, the



27c **33** **34**

other **33**. Since **33** is expected to be highly strained there is effectively only one possible disrotatory opening. In contrast, the *trans* isomer of **26c**, cyclopropanone **31c**, which exists in enantiomeric forms, has degenerate ring opening modes to give oxyallyl **34**.

In oxyallyl **27c**, the most stable conformation for the R group results directly in C_{2v} symmetry for this species (or something very close to this), as shown in the following Newman projection [sighting along the C1(C3)–R bond].



In this C_{2v} conformation the formerly diastereotopic CH_3 groups are now chemically equivalent. A planar C_{2v} oxyallyl **27c** can return to cyclopropanone **26c** by degenerate disrotatory closure modes, one of which results in exchange of any arbitrarily labeled diastereotopic methyl group, producing the line-broadening sequences shown in Fig. 1.

The conformational behavior of oxyallyl **27c** relates directly to how one quantitatively interprets the $\Delta G^{\ddagger}$ value derived from the experimental line-broadening data, as illustrated in the Fig. 2 drawings. Our interest of course is to determine the $\Delta\Delta G$ (and associated equilibrium constant) for the cyclopropanone **26c** $\rightleftharpoons$ [oxyallyl **27c**] system. The assumption of a C_{2v} oxyallyl is embodied in the Fig. 2(*a*) sketch, where the experimental $\Delta G^{\ddagger}$ differs from $\Delta\Delta G$ only by the barrier $\Delta G_r^{\ddagger}$, and as given in the Introduction the latter has been computed to be <1 kcal mol^{-1} in the parent system **3**–**5**. If the oxyallyl **27c** were not C_{2v} symmetric and required further bond rotations in the R group to symmetrize the system [sketch (*b*)], then one could be measuring a barrier considerably higher than the cyclopropanone–oxyallyl $\Delta\Delta G$ value. However, as already argued, we believe that **27c** would be symmetric (or very close to this in energy terms).

The assumption that $\Delta G_r^{\ddagger}$ will be small [Fig. 2(*a*)] even with these very large R groups is also of concern if one wishes to equate $\Delta G_f^{\ddagger} \approx \Delta\Delta G$. However, based on MO calculations[22] of the related *cis*-2,3-di-*tert*-butylcyclopropanone **24**, the ground-

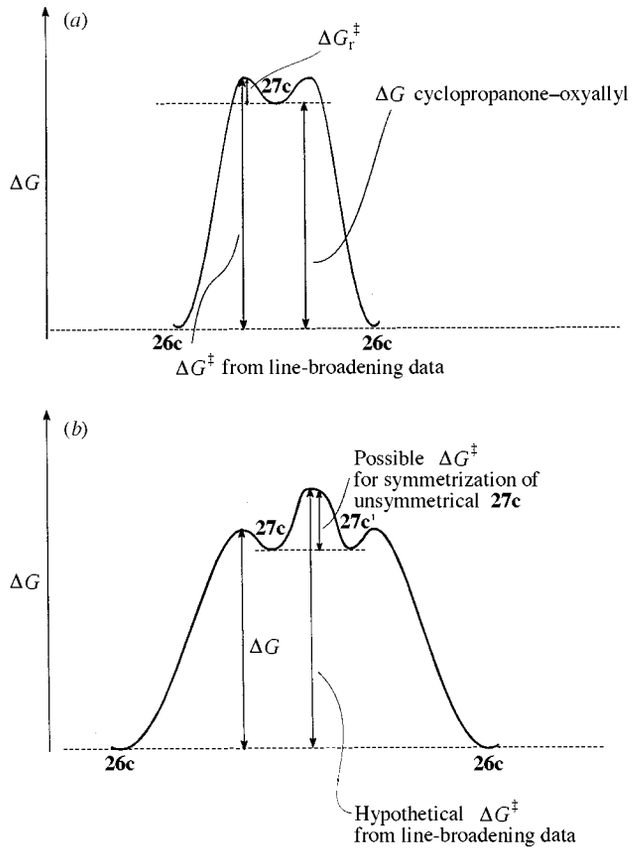
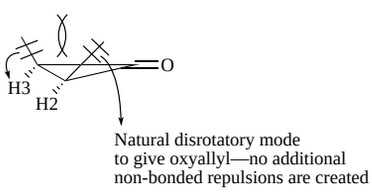


Fig. 2 Illustration of two possible interpretations of the NMR line-broadening shown in Fig. 1: (*a*) C_{2v} symmetric oxyallyl intermediate **27c** is directly formed from **26c**; (*b*) an unsymmetrical oxyallyl **27c** is formed, and the symmetrization of this involves another transition-state barrier. As discussed in the text, the situation (*a*) is our favored interpretation.



state structure of **26c** is expected to be already distorted in the direction of the oxyallyl, as shown above.

The H2–H3 hydrogens in the ^{1}H NMR spectrum of **26c** appear at the unusually low field position of δ 3.65 in $CDCl_3$, a δ value shifted towards that expected for hydrogens on sp^2-hybridized carbons, *i.e.*, **26c** appears to take on some oxyallyl 'character'. Such a merging of structural pairs having a low $\Delta G_r^{\ddagger}$ barrier is not unexpected. In fact, given the very low barrier calculated for $\Delta G_r^{\ddagger}$ in the parent system using the CASSCF procedure,[6b] and unpublished observations[18] that many high level theoretical methods consistently find singlet oxyallyl **3** to be a transition-state, one wonders whether there really is a true equilibrium situation between **26c** and **27c**, *i.e.*, the picture of **27c** being a transition-state would not differ much from the (*a*) picture in Fig. 2. Furthermore, even if **27c** were a transition-state the strategy embodied in our present work would not be materially changed since further increases in the bulk of the R groups in **26** would simply induce more and more oxyallyl 'character' in the single 'species' involved.

Oxyallyl–cyclopropanone transition-state barriers

Our study is now the third experimental measurement of a cyclopropanone–oxyallyl transition-state barrier, previous $\Delta G^{\ddagger}$ values of 27–29 and 16–19 kcal mol^{-1} are now reduced to 9.8 kcal mol^{-1} for our **26c** system in $CDCl_3$ solvent. As speculated in the Introduction, such a low barrier should be measurable by NMR line-broadening techniques and this has now been accomplished for the first time. Of the R groups used in our study, the **26c** system has a marginally lower $\Delta G^{\ddagger}$ value than for **26b** and **26a**, with the 1-norbornyl system **26e** the highest value (see Table 2), consistent with work on crowded alkenes where 'tied-back' substituents create smaller steric repulsions.[23]

As mentioned earlier, the *cis*-2,3-di-*tert*-butylcyclopropanone **24**–oxyallyl **25** free energy difference (assuming the latter to be a true intermediate) has been estimated[22] at 10.5–12 kcal mol^{-1} using a combination of experimental and calculated data. Using **26a** as a model for **24**, the direct $\Delta G^{\ddagger}$ measurement now gives 11.4–12.2 kcal mol^{-1} (Table 2). This excellent agreement offers one good assurances that the basic assumptions ($\Delta G_r^{\ddagger} \approx 0$) and computational estimates used to derive the original number were valid.

Cyclopropanone **26c** is reasonably stable in solution at 25 °C (no dimerization reactions have been observed). Assuming again a **26c**–**27c** equilibrium, a 9.8 kcal mol^{-1} value for $\Delta\Delta G$ in $CDCl_3$ solvent at 25 °C can be converted into an estimated K(**27c**/**26c**) of 6×10^{-8}, or about 60 nM oxyallyl for a 1 M cyclopropanone concentration. In practice solutions of **26c** would have to be ultra pure in order to hope to detect nM magnitude concentrations of **27c** (UV–VIS spectroscopy?) and this remains a problem.

Solvent effects on $\Delta G^{\ddagger}$ for 26c

These data are presented in Table 3, and the most striking observation is that $CDCl_3$ and $CDFCl_2$ solvents have the lowest $\Delta G^{\ddagger}$ values, with [$^2H_8$]toluene the largest. Our results show a smaller solvent dependence than that observed in the Greene[19] and Cordes–Berson[20] work, but the comparison is incomplete since these authors did not employ either $CDCl_3$ or $CDFCl_2$ solvent. It seems possible that the ⩾C–D dipole in $CDCl_3$ or $CDFCl_2$ interacts favorably with the oxygen atom of **26c** and that this interaction is even better in the oxyallyl 'partner' **27c**.

Summary

The preparation of five new *cis*-2,3-dialkylcyclopropanones is described. The alkyl groups include *tert*-amyl, thexyl, 2-(2,3,3-trimethylbutyl), 1-adamantyl and 1-(7,7-dimethylnorbornyl). Four of these cyclopropanones show low temperature dynamic NMR line-broadening due to the reversible conversion to an unseen oxyallyl 'partner'. In the best case, the $\Delta G^{\ddagger}$ calculated for this process from the NMR analysis was only 9.8 kcal mol^{-1}, much lower than in either of the two previous acyclic oxyallyl–cyclopropanone examples, and suggesting that actual nanomolar concentrations of the oxyallyl could be present in 1 M concentrations of the cyclopropanone.

Experimental

GC–MS data were obtained on a Hewlett-Packard Model 5890 gas chromatograph equipped with a 5971 mass selective detector. A 12 m × 0.2 mm id OV-101 column was used. High resolution MS data were obtained on a Kratos MS-80. NMR spectra were measured on Bruker ACE-200, AMX-300 or AM-400 instruments, J in Hz, d = doublet, t = triplet, q = quartet. The probe temperatures were calibrated using a standard methanol sample. Infrared spectra were determined on a Mattson Model 4030 interferometer. Dibromo ketone **28d** was prepared as described.[25]

4,6-Dibromo-3,3,7,7-tetramethylnonan-5-one 28a

A diethyl ether solution of ethylmagnesium bromide was prepared and the ether then replaced with THF (distillation of ether). On a 0.06 mol scale, 100 mg of CuI were added and the

mixture cooled to 0 °C. Phorone (2.84 g, 0.020 mmol) was then added with stirring. On work-up, 3.12 g of crude oil mono-adduct product were obtained (*ca.* 75% pure by ^{1}H NMR). 2,6,6-Trimethyloct-2-en-4-one δ_H 6.04 (m, 1 H), 2.25 (2 H), 2.10 (3 H), 1.86 (3 H), 1.33 (q, 7.5, 2 H), 0.94 (6 H), 0.83 (t, 7.5, 3 H). The same procedure was repeated using this crude product to give 3.21 g of an oil which was *ca.* 75% pure by ^{1}H NMR. 3,3,7,7-Tetramethylnonan-5-one **29a**: δ_H 2.27 (4 H), 1.35 (q, 7, 4 H), 0.97 (12 H), 0.85 (t, 7, 6 H); δ_C 211.2 (CO), 54.8 (CH_2), 34.6 (CH_2), 33.8 (C_q), 26.8 (CH_3), 8.4 (CH_3) (Found: 198.1978. Calc. for $C_{13}H_{26}O$: 198.198 365). This crude ketone (2.0 g, *ca.* 7.5 mmol of **29a**) was dissolved in 25 ml CCl_4 and 1.15 ml of Br_2 was added dropwise and the mixture sealed and kept at ambient temperature for 4 h. Work-up produced 4.17 g of an oily liquid which was chromatographed (hexane) and then distilled at 105–110 °C/0.03 mmHg, keeping a 1 g middle cut for further use. This material consists of a *ca.* 14:1 mixture of diastereomers (long retention: short retention isomers on GLC analysis).

δ_H(major) 4.47 (2 H), 1.4–1.62 (m, 4 H), 1.14 (3 H), 1.11 (3 H), 0.89 (t, 7, 6 H). The minor diastereomer has a distinctive ^{1}H peak at δ 4.58. δ_C 198.4 (CO), 62.3 (CH), 38.2 (C_q), 32.8 (CH_2), 24.0 (CH_3), 22.9 (CH_3), 8.2 (CH_3). In the GC–MS, a very weak M^+ peak at *m/z* 356 was observed (Found: 356.017 43. Calc. for $C_{13}H_{24}O^{79}Br^{81}Br$: 356.0145).

4,6-Dibromo-2,3,3,7,7,8-hexamethylnonan-5-one 28b

The reaction of phorone with isopropylmagnesium bromide–CuI was carried out using the same procedure as for the **29a** preparation (1.0 mmol phorone, 3 mmol Pr^{i}MgBr, 10 ml THF, 100 mg CuI) to give a near quantitative yield of the intermediate liquid ketone. 2,6,6,7-Tetramethyloct-2-en-4-one: δ_H 2.31 (2 H), 2.13 (3 H), 1.88 (3 H), 1.62 (septet, 7, 1 H), 0.96 (6 H), 0.87 (d, 7, 6 H); δ_C 202.0 (CO), 153.8 (C_q), 126.1 (CH), 52.9 (CH_2), 36.6 (CH), 27.6 (CH_3), 24.45 (CH_3), 20.53 (CH_3), 17.5 (CH_3). A second treatment of this intermediate (3.3 mmol, 10 mmol Pr^{i}MgBr, 60 ml THF, 150 mg CuI) gave a 99% crude yield of liquid 2,3,3,7,7,8-hexamethylnonan-5-one **29b**, a sample of which could be isolated pure by flash chromatography (1:1 hexane–CH_2Cl_2). δ_H 2.29 (4 H), 1.67 (septet, 7, 2 H), 0.94 (12 H), 0.83 (d, 7, 12 H); δ_C 211.9 (CO), 53.5 (CH_2), 36.2 (CH), 24.2 (CH_3), 17.4 (CH_3). A quaternary carbon is probably overlapped with δ 36.2; *m/z* 127, 85, 84 (100%) (Found: 127.1123. Calc. for $C_{15}H_{30}O - C_7H_{15}$: 127.1103). Ketone **29b** (0.74 g, 3.3 mmol) in 15 ml CCl_4 was directly brominated at 20 °C as described for the **28a** preparation to give 1.3 g of crude dibromo ketone. From the ^{1}H NMR spectrum, this product is a *ca.* 8:1 mixture of diastereomers, the major isomer having the higher field ≻CHBr signal (δ 4.70 *vs.* 4.82). The major diastereomer (liquid) was easily purified by flash chromatography (1:1 hexane–CH_2Cl_2). δ_H 4.70 (2 H), 1.90 (septet, 7, 2 H), 1.13 (6 H), 1.00 (6 H), 0.90 (d, 7, 12 H); δ_C 198.4 (CO), 61.9 (CH), 40.4 (C_q), 34.0 (CH_3), 21.3 (CH_3), 18.3 (CH_3), 17.4 (CH_3).

4-Methoxycarbonyl-2,2,3,3,7,7,8,8-octamethylnonan-5-one

Attempts to doubly add Bu^{t}MgCl to phorone failed in the second stage, and even the first stage yield was poor (20–30%). We therefore used the Claisen condensation route to the desired ketone, but the known[26] 3,3,4,4-tetramethylpentanoic acid starting material was more conveniently prepared from the phorone mono adduct already in hand rather than by the literature route. 2,6,6,7,7-Pentamethyloct-2-en-4-one [liquid, bp *ca.* 55 °C/0.025 mmHg; δ_H 6.10 (6, 1 H), 2.35 (2 H), 2.13 (3 H), 1.89 (3 H), 0.97 (6 H), 0.89 (9 H)] was oxidized with aqueous $KMnO_4$ to give a *ca.* 1:1 mixture of the desired acid and the substituted pyruvic acid. This mixture was treated with 30% H_2O_2 overnight at 20 °C to give the acid, mp 63–65 °C, lit.,[26] 66–67 °C. The liquid methyl ester was prepared using TMS-Cl and CH_3OH, δ_H 3.65 (OCH_3), 2.26 (2 H); 0.97 (6 H), 0.87 (9 H); δ_C 174.0 (CO), 51.1 (CH_2), 41.9 (CH_3), 36.0 (C_q), 38.0 (C_q), 25.4 (CH_3), 21.9 (CH_3). This ester (2.18 g, 12.7 mmol) was converted into the title product using a previously described Claisen condensation procedure;[25] 2.18 g of crude yellow oil was produced, δ_H 3.87 (1 H), 3.66 (3 H), 2.45–2.63 (AB, 18, 2 H), 1.20 (3 H), 1.02 (3 H), 1.01 (3 H), 1.00 (3 H), 0.90 (9 H), 0.88 (9 H). A single peak is seen on GC analysis.

2,2,3,3,7,7,8,8-Octamethylnonan-5-one 29c

The above crude keto ester was hydrolyzed in refluxing ethanol (50 ml)–10% NaOH (10 ml) solution (3 days), and after work-up, 1.4 g (87%) of the title liquid ketone was obtained. δ_H 2.38 (4 H), 0.99 (12 H), 0.88 (18 H); δ_C 213.7 (CO), 51.1 (CH_2), 36.6 (C_q), 36.2 (C_q), 25.3 (CH_3), 21.5 (CH_3) (Found: 239.2372. Calc. for $C_{17}H_{34}O - CH_3$, 239.237 49).

4,6-Dibromo-2,2,3,3,7,7,8,8-octamethylnonan-5-one 28c

Bromination of **29c** was carried out as described for **29a** and a *ca.* 10:1 mixture of diastereomers was obtained. In this case, the major diastereomer had the low field ≻CHBr peak and the shorter GC retention time. A pure sample of the major isomer could be obtained by flash chromatography (hexane), this isomer eluting first, mp 50–52 °C, δ_H(major isomer) 4.93 (2 H), 1.28 (6 H), 1.24 (6 H), 1.04 (18 H); δ_C 189.1 (CO), 61.4 (CH), 41.0 (C_q), 37.8 (C_q), 26.8 (CH_3), 21.6 (CH_3), 20.6 (CH_3) (Found: 277.0967. Calc. for $C_{17}H_{32}O^{79}Br^{81}Br - C_4H_8{}^{79}Br$: 277.099 19); δ_H(minor isomer) 4.84 (2 H), 1.26 (6 H), 1.10 (6 H), 1.04 (18 H). This isomer was not obtained in a totally pure state.

1,3-Di(7,7-dimethylbicyclo[2.2.1]heptan-1-yl)propan-2-one 29e

7,7-Dimethyl-1-vinylbicyclo[2.2.1]heptan-2-one[27] (1.0 g, 6.1 mmol) was reacted under standard Wolff–Kishner reduction conditions (1.5 ml 98% hydrazine, 1.5 g KOH, 25 ml triethyleneglycol) to give 0.70 g (77%) of 7,7-dimethyl-1-vinylbicyclo[2.2.1]heptane, as an oil. This compound has been previously prepared by an alternative route.[28] δ_H 5.88 (dd, 17.5, 11, 1 H), 5.06 (dd, 11, 2, 1 H), 4.98 (dd, 17.5, 2, 1 H), 1.75–1.85 (m), 1.72 (1 H), 1.2–1.4 (m), 0.87 (6 H); δ_C 140.6 (CH), 113.9 (CH_2), 51.8 (C_q), 48.7 (C_q), 48.2 (CH), 33.8 (CH_2), 28.4 (CH_2), 19.3 (CH_3); single peak on GC analysis; *m/z* 150 (M^+), 107 (80%), 93 (75), 79 (100). This alkene (0.53 g, 3.5 mmol) was hydroborated with four equivalents of BH_3·THF in 15 ml of THF at 20 °C. After an hour, 2 ml of 3 M NaOH and 2 ml of 30% H_2O_2 were added and the mixture kept at 35 °C for 4 h. After isolation, the crude alcohol(s) were directly oxidized to the carboxylic acid (Jones' reagent), 0.28 g (44%), white solid, mp 60–62 °C, previously described in the patent literature.[29] 7,7-Dimethylbicyclo[2.2.1]heptan-1-ylethanoic acid: δ_H 2.28 (2 H), 1.72–1.85 (m, 2 H), 1.6–1.72 (m, 3 H), 1.5–1.6 (m, 2 H), 1.18–1.3 (m, 2 H), 0.90 (6 H); δ_C 179.8 (CO), 47.9 (C_q), 46.6 (C_q), 45.3 (CH), 36.8 (CH_2), 33.6 (CH_2), 28.2 (CH_2), 19.1 (CH_3). The above acid was esterified (2.5 ml ethanol, 5 mg toluene-*p*-sulfonic acid, 30 ml benzene, azeotropic distillation) to give 0.30 g (94%) of the liquid ethyl ester. δ_H 4.11 (q, 7, 2 H), 2.22 (2 H), 1.7–1.85 (m, 2 H), 1.6–1.7 (m, 3 H), 1.4–1.5 (m, 2 H), 1.26 (t, 7, 3 H), 1.15–1.23 (m, 2 H), 0.87 (6 H); δ_C 173.3 (CO), 59.9 (CH_2), 47.8 (C_q), 46.6 (C_q), 45.3 (CH), 37.0 (CH_2), 33.7 (CH_2), 28.2 (CH_2), 19.1 (CH_3), 14.3 (CH_3). The Claisen condensation of this ester (0.30 g, 1.4 mmol) was carried out as described for the **29c** preparation, with the crude keto ester directly hydrolyzed to the title ketone, an oil, 0.13 g (62%). δ_H 2.33 (4 H), 1.47–1.85 (m, 14 H), 1.1–1.3 (m, 4 H), 0.87 (12 H); δ_C 212 (CO), 48.1 (CH_2), 46.9 (C_q), 46.1 (C_q), 44.8 (CH), 33.4 (CH_2), 28.3 (CH_2), 19.2 (CH_3); *m/z* 302 (M^+), 165 (80%), 137 (70), 122 (30), 95 (50), 81 (100) (Found: 302.2610. Calc. for $C_{21}H_{34}O$: 302.260 97).

1,3-Dibromo-1,3-di(7,7-dimethylbicyclo[2.2.1]heptan-1-yl)-propan-2-one 28e

Bromination of **29e** was carried out as described for the **29a** preparation. Two diastereomers were produced in a *ca.* 2:1 ratio (high field ^{1}H NMR isomer: low field, or long retention:

short retention GC peaks). The ^{1}H NMR spectrum of the mixture showed peaks at δ 4.92 and 4.73 (CHBr); complex multiplet from 2.2 to 1.5 and 1.32–1.18, and two sets of diastereotopic CH_3 groups at 1.11 and 0.98 (major), 1.08 and 1.00 (minor); δ_C 196.4 (CO), 190.06 (CO), 55.7 (CH), 54.8 (CH), 50.3 (C_q), 49.8 (C_q), 49.7 (C_q), 49.5 (C_q), 47.4 (CH), 46.9 (CH), 34.0 (CH_2), 32.7 (CH_2), 31.8 (CH_2), 30.0 (CH_2), 28.1 (CH_2), 28.0 (CH_2), 27.7 (CH_2), 27.4 (CH_2), 22.3 (CH_3), 21.5 (CH_3), 19.7 (CH_3), 19.5 (CH_3). The major diastereomer was isolated by crystallization, mp 123–124 °C (Found, 460.080 14. Calc. for $C_{21}H_{32}O^{79}Br^{81}Br$: 460.0806).

Cyclopropanone preparation

These were all produced by the same procedure; the preparation of **26c** which follows is illustrative. Since the *cis* cyclopropanones are unstable above 0 °C in the condensed state, no attempt was made to physically characterize these compounds, although some are solids at −78 °C. Based on *in situ* NMR studies, the reaction is essentially quantitative, although there is probably some small loss of material in the work-up.

Dibromo ketone **28c**, major diastereomer (0.180 g, 0.44 mmol) in 1 ml of dry methylene chloride was added dropwise by syringe to a stirred solution of $PPN^+Cr(CO)_4NO^-$ [30] (0.350 g, 0.48 mmol) in 1 ml of dry methylene chloride. The latter solution was contained in a small Schlenk tube protected with a septum, was prepared under an N_2 atmosphere and was pre-cooled to −78 °C. After 20 min, 15 ml of dry, but not deoxygenated, pentane were slowly added by syringe, keeping the resulting mixture at −78 °C. Stirring was continued for 10 min and then the mixture let stand for 30 min to precipitate the suspended solids. The supernatant solution was transferred by syringe to a clean Schlenk tube also equipped with a septum. The solvents were evaporated at *ca.* −40 to −50 °C under vacuum (*ca.* 0.01 mmHg) to leave a viscous residue. This was redissolved in 5 ml of pentane at *ca.* −50 °C, the solution let stand for 30 min and then filtered by quickly drawing the cold solution into a syringe, replacing the needle with one fitted with a Spartan 3 filter, and then reintroducing the filtered solution into a clean Schlenk tube. The solvent was evaporated as above to leave the residual cyclopropanone which was stored at −78 °C.

***cis*-2,3-Di-(2,3,3-trimethyl-2-butyl)cyclopropanone 26c.** δ_H($CDCl_3$, −80 °C) 3.67 (s, 2 H), 1.03 (br s, 6 H), 0.91 (br s, 24 H); δ_C(CD_2Cl_2, −80 °C) 206.7 (CO), 48.1 (CH), 38.3 (C_q), 36.4 (C_q), 25.0 (br, CH_3), 24.0 (CH_3), 19.3 (CH_3); ν_{max}/cm^{-1} 1791 (C=O).

To prepare the *trans* isomer, the initial pentane solution was allowed to warm to room temperature and kept *ca.* 10–20 min, filtered as above, and then the solvents were evaporated. The reaction byproduct, $Cr(CO)_4NOBr$, is thermally and oxidatively unstable at room temperature, and the breakdown products from this appear to catalyze the *cis* ⟶ *trans* interconversion. A purely thermal conversion at a somewhat higher temperature also occurs.

***trans*-2,3-Di-(2,3,3-trimethyl-2-butyl)cyclopropanone 31c.** This cyclopropanone was crystalline, mp 52–54 °C (softening at 48 °C), after sublimation (45 °C/0.01 mmHg). δ_H($CDCl_3$) 1.81 (s, 2 H), 1.02 (s, 6 H), 0.95 (s, 18 H), 0.69 (s, 6 H); δ_C 217.6 (CO), 39.1 (C_q), 36.2 (C_q), 29.5 (CH), 25.9 (CH_3), 22.6 (CH_3), 19.5 (CH_3).

***cis*-2,3-Di-*tert*-amylcyclopropanone 26a.** δ_H($CDCl_3$, −70 °C): 3.07 (s, 2 H), 1.36 and 1.35 (overlapping quartets, 4 H), 1.02 (s, 6 H), 0.96 (s, 6 H), 0.90 (t, 7.6, 6 H); δ_C 212.5 (CO), 45.5 (CH), 36.6 (CH_2), 34.0 (C_q), 27.3 (CH_3), 25.4 (CH_3), 8.8 (CH_3); ν_{max}/cm^{-1} 1789.6 and 1808.9 (C=O).

***trans*-2,3-Di-*tert*-amylcyclopropanone 31a.** δ_H($CDCl_3$) 1.63 (s, 2 H), 1.41 (q, 7.3, 4 H), 0.94 (s, 6 H), 0.89 (t, 7.3, 6 H), 0.84 (s, 6 H); δ_C 219.1 (CO), 35.1 (CH_2), 33.6 (C_q), 31.8 (CH), 28.0 (CH_3), 24.2 (CH_3), 8.6 (CH_3); ν_{max}/cm^{-1} 1814.7 (C=O).

***cis*-2,3-Di-(2,3-dimethyl-2-butyl)cyclopropanone 25b.** δ_H(CD_2Cl_2, −80 °C) 3.08 (s, 2 H); 1.45 (septet, 7, 2 H), 0.97 (6 H), 0.86 (d, 7, 6 H), *ca.* 0.78 (d, 6 H), 0.77 (s, 6 H); δ_C(CD_2Cl_2) 210.4 (CO), 45.1 (CH), 38.2 (CH), 36.2 (C_q), 26.0 (CH_3), 20.4 (CH_3), 17.4 (CH_3), 16.8 (CH_3).

***cis*-2,3-Di(tricyclo[3.3.1.1^{3,7}]decan-1-yl)cyclopropanone 26d.** δ_H($CDCl_3$) 2.815 (s, 2 H), 1.935 (br s, 6 H), 1.67 and 1.66 (both s, 12 H total), 1.62 (br s, 12 H); δ_C(CD_2Cl_2, −50 °C): 205.0 (CO), 47.8 (CH), 41.5 (CH_2), 35.7 (CH_2), 32.9 (C_q), 27.9 (CH); ν_{max}/cm^{-1} 1791.5, with a higher frequency shoulder (C=O).

***cis*-2,3-Di(7,7-dimethylbicyclo[2.2.1]heptan-1-yl)cyclopropanone 26e.** δ_H(CD_2Cl_2, −50 °C) 2.91 (s, 2 H), 1.9–1.0 (complex), 0.82 and 0.84 (both s, 12 H); δ_C(CD_2Cl_2, −60 °C) 212.3 (CO), 49.9 (C_q), 45.8 (C_q), 43.4 (CH), 34.3 (CH_2), 32.1 (CH), 29.1 (CH_2), 28.0 (CH_2), 27.6 (CH_2), 18.5 (CH_3).

***trans*-2,3-Di(7,7-dimethylbicyclo[2.2.1]heptan-1-yl)cyclopropanone 31e.** δ_H($CDCl_3$) 1.65 (s, 2 H), 1.85–1.55 (m, 8 H), 1.45–1.25 (m, 4 H), 1.25–1.1 (m, 6 H) 0.92 (s, 6 H), 0.88 (s, 6 H); δ_C 219.0 (CO), 48.3 (C_q), 48.2 (C_q), 45.3 (CH), 33.5 (CH_2), 32.2 (CH_2), 28.2 (CH_2), 28.1 (CH_2), 24.6 (CH), 19.4 (CH_3), 19.3 (CH_3).

Furan adducts

The furan cycloaddition reactions were carried out using a few milligrams of the *cis* cyclopropanone and a large excess of furan, at (or below) 20 °C. Removal of solvent and excess furan gave the crude adduct, which, where necessary, was purified by preparative TLC. The adducts were characterized by NMR, GC and high-resolution mass spectrometry. No physical characterizations were made because of the small scale involved. Based on *in situ* NMR studies, the reactions are essentially quantitative, and only one isomer was produced in each case, assigned the *endo* configuration shown in the structure **32**.

Adduct 32b. δ_H 6.28 (2 H), 5.05 (d, 3.5, 2 H), 2.905 (d, 3.5, 2 H), 2.01 (septet, 6.8, 2 H) 0.95 (6 H), 0.87 (d, 6.8, 6 H), 0.87 (6 H), 0.81 (d, 6.9, 6 H); δ_C 206.6 (CO), 133.2 (CH), 80.9 (CH), 64.3 (CH), 36.0 (C_q), 33.7 (CH), 21.4 (CH_3), 21.1 (CH_3), 17.1 (CH_3), 17.0 (CH_3) [Found: 249.1855. Calc. for M^+ ($C_{19}H_{32}O_2$) − C_3H_7: 249.1853].

Adduct 32c. δ_H 6.27 (2 H), 5.20 (d, 3.5, 2 H), 3.03 (d, 3.5, 2 H), 1.03 (6 H), 0.94 (6 H), 0.89 (18 H); δ_C 205.7 (CO), 132.8 (CH), 82.8 (CH), 64.4 (CH), 38.9 (C_q), 37.4 (C_q), 26.9 (CH_3), 23.0 (CH_3), 22.4 (CH_3) [Found: 263.2011. Calc. for M^+ ($C_{21}H_{36}O_2$) − C_4H_9: 263.2010].

Adduct 32d. δ_H 6.27 (2 H), 5.09 (d, 3.5, 2 H), 2.42 (d, 3.5, 2 H), 1.97 (br, 6 H), 1.76 (12 H), 1.72 (12 H); δ_C 206.2 (CO), 132.8 (CH), 79.8 (CH), 67.5 (CH), 40.6 (CH_2), 37.1 (CH_2), 34.0 (C_q), 28.7 (CH) [Found: 392.2715. Calc. for M^+ ($C_{27}H_{36}O_2$): 392.2689].

Adduct 32e. δ_H 6.25 (2 H), 5.12 (d, 3.0, 2 H), 2.95 (d, 3.0, 2 H), 1.82–1.10 (complex 18 H), 1.04 (s, 6 H), 1.02 (s, 6 H); δ_H 205.1 (CO), 132.8 (CH), 81.6 (CH), 61.7 (CH), 48.6 (C_q), 47.6 (C_q), 47.2 (CH), 34.2 (CH_2), 31.7 (CH_2), 28.3 (CH_2), 27.9 (CH_2), 21.8 (CH_3), 20.7 (CH_3) [Found: 368.2715. Calc. for M^+ ($C_{25}H_{36}O_2$): 368.2681].

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for generous financial support.

References

1 P. Dowd, *J. Am. Chem. Soc.*, 1966, **88**, 2587.
2 (*a*) G. Maier, H. P. Reisenauer, K. Lanz, R. Tross, D. Jürgen, B. A. Hess, Jr. and L. J. Schaad, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 74; (*b*) G. Maier, D. Jürgen, R. Tross, H. P. Reisenauer, B. A. Hess, Jr. and L. J. Schaad, *J. Chem. Phys.*, 1994, **189**, 367.
3 (*a*) P. Dowd and M. J. Chow, *J. Am. Chem. Soc.*, 1977, **99**, 6438; (*b*) P. Dowd and M. J. Chow, *Tetrahedron*, 1982, **38**, 799.
4 P. G. Wenthold, J. Hu, R. R. Squires and W. C. Lineberger, *J. Am. Chem. Soc.*, 1996, **118**, 475.

5 C. J. Cramer and B. A. Smith, *J. Phys. Chem.*, 1996, **100**, 9664 and references contained therein.
6 (*a*) M. B. Coolidge, K. Y. Yamashita, K. Morokuma and W. T. Borden, *J. Am. Chem. Soc.*, 1990, **112**, 1751; (*b*) D. Lim, D. A. Hrovat, W. T. Borden and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1994, **116**, 3494.
7 F. Turecek, D. E. Drinkwater and F. W. McLafferty, *J. Am. Chem. Soc.*, 1991, **113**, 5950.
8 (*a*) A. S. Ichimura, P. M. Lahti and A. R. Matlin, *J. Am. Chem. Soc.*, 1990, **112**, 2868; (*b*) D. A. Hrovat, A. Rauk, T. S. Sorensen, H. K. Powell and W. T. Borden, *J. Am. Chem. Soc.*, 1996, **118**, 4159.
9 (*a*) A. G. Schultz, M. Macielag and M. Plummer, *J. Org. Chem.*, 1988, **53**, 391; (*b*) F. G. West, C. Hartke-Karger, D. J. Koch, C. E. Kuehn and A. M. Arif, *J. Org. Chem.*, 1993, **58**, 6795.
10 (*a*) M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, 1968, **90**, 1547; (*b*) M. H. Fisch, *J. Chem. Soc.*, *Chem. Commun.*, 1969, 1472.
11 K. Schaffner and M. M. Demuth in *Rearrangements in Ground and Excited States*, ed. P. de Mayo, Academic Press, New York, 1980, vol. 3, pp. 281–319.
12 A. R. Matlin and K. Jin, *Tetrahedron Lett*, , 1989, **30**, 637.
13 A. S. Kende, R. Greenhouse and J. A. Hill, *Tetrahedron Lett.*, 1979, 2867.
14 T. Hirano, T. Kumaggi, T. Miyashi, K. Akiyama and Y. Ikegami, *J. Org. Chem.*, 1991, **56**, 1907.
15 A. P. Masters, M. Parvez, T. S. Sorensen and F. Sun, *J. Am. Chem. Soc.*, 1994, **116**, 2804.
16 T. S. Sorensen and F. Sun, unpublished results.
17 (*a*) J. Mann, *Tetrahedron*, 1986, **42**, 4611; (*b*) H. M. R. Hoffmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1984, **23**, 1; (*c*) H. M. R. Hoffmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1973, **12**, 819; (*d*) R. Noyori, *Acc. Chem. Res.*, 1979, **12**, 61; (*e*) R. Noyori and Y. Hayakawa, *Org. React.* (NY), 1983, **29**, 163.
18 A. Rauk, personal communication.
19 J. F. Pazos, J. G. Pacifici, G. O. Pierson, D. B. Sclove and F. D. Greene, *J. Org. Chem.*, 1990, **39**, 1990.
20 (*a*) M. H. J. Cordes and J. A. Berson, *J. Am. Chem. Soc.*, 1996, **118**, 6241; (*b*) M. H. J. Cordes and J. A. Berson, *J. Am. Chem. Soc.*, 1992, **114**, 11 010.
21 C. Black, P. Lario, A. P. Masters and F. Sun, *Can. J. Chem.*, 1993, **71**, 1910.
22 (*a*) T. S. Sorensen and F. Sun, *J. Am. Chem. Soc.*, 1995, **117**, 5592; (*b*) T. S. Sorensen and F. Sun, *Can. J. Chem.*, 1997, **75**, 1030.
23 T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, *J. Chem. Soc.*, *Perkin Trans. 1*, 1975, 539.
24 T. S. Sorensen and F. Sun, *Can. J. Chem.*, 1996, **74**, 79.
25 H. Stetter and G. Becker, *Liebigs Ann. Chem.*, 1976, 1992.
26 F. C. Whitmore, R. E. Marker and L. Plambeck, Jr., *J. Am. Chem. Soc.*, 1941, **63**, 1626.
27 N. Fischer and G. Opitz, *Org. Synth. Coll.*, vol. 5, p. 877.
28 P. Veeravagu, R. T. Arnold and E. W. Eigenmann, *J. Am. Chem. Soc.*, 1964, **86**, 3072.
29 *Chem. Abstr.*, **87**, P102022x; **94**, P120978m.
30 D. R. Mantell and W. L. Gladfelter, *J. Organomet. Chem.*, 1988, **347**, 333.

Paper 7/06265F
Received 27*th August* 1997
Accepted 26*th November* 1997