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STERICALLY CROWDED ORGANIC MOLECULES: SYNTHESIS, STRUCTURE AND PROPERTIES

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Deformation of the normal geometries of organic molecules has been of continuing interest in the study of organic chemistry. Modification of the properties of compounds in this way has led to a deeper understanding of the fundamental principles that determine molecular structure, and the unusual properties of distorted structures have had many theoretical and practical applications.

There are two principal ways in which the geometries of organic structures have been changed from their more usual arrangements. The most widely studied of these is the construction of ring systems which force bond angle deformations, non-bonded repulsions between atoms, and eclipsing strains. The second method, which has not received the same degree of attention, is the use of bulky groups substituted on the molecules. In this case the non-bonded repulsions involving the large groups in turn induce bond-angle strain and other interactions in the molecule.

An excellent recent review (*A Survey of Strained Organic Molecules*[1a]) devotes most of its coverage to cyclic systems and only about 5% of the text deals with the effects of bulky substituents. The purpose of the present Report is to survey recent work in which bulky substituents have been applied to the study of structure and reactivity in organic chemistry, in the hope of thereby stimulating greater exploration of this valuable area. In particular the discussion will be concerned with recent developments in the study of the synthesis, physical properties, and reactivity (cationic, anionic and free radical) of crowded compounds substituted with bulky groups. Other reviews have touched on this area,[1] but have had other primary concerns. Strained cyclic compounds[2] will be mentioned only in the context of bulky substitution.

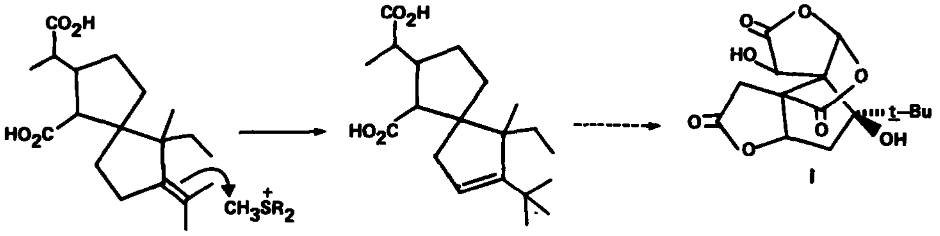
PREPARATION

Crowding in organic compounds can be induced by many different combinations of groups, but the *tert*-butyl substituent is the most desirable because its size and symmetry simplifies and clarifies the interactions. This group occurs only rarely in natural products although a recent example, bilobalide (**1**), from a venerable plant has been reported.[3a] The *tert*-butyl group in **1** was found to be derived from methylation of an isopropenyl group by methionine (eqn 1). A coumarin containing a *tert*-butyl ketone moiety has been isolated from the bark of a tree found in India.[3b] In this case the *tert*-butyl was proposed to be derived from cleavage of a cyclopropyl group (eqn 2).[3b]

Despite these reports, for practical purposes crowded substrates for study must be prepared in the laboratory.

Synthesis of crowded structures has been a demanding task, as the large groups often preclude the use of methods that are successful for less strained analogues, and the branched structures themselves are often prone to some complicated rearrangements.

One of the early sources of crowded structures was free radical coupling, which was the source of the dimer of triphenylmethyl (**2**, eqn 3), although the identity of this particular structure was not settled for many years.[4a] Recent calculations of the structure of the so-far unknown symmetrical hexaphenylethane indicate it is highly strained, with a central C–C bond length of 1.64 Å, and this strain would provide much of the impetus for the ease of formation of **2**.[4b] Radical-coupling and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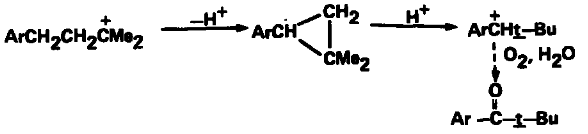
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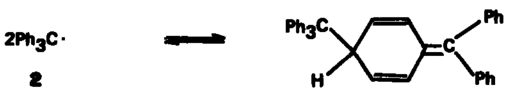
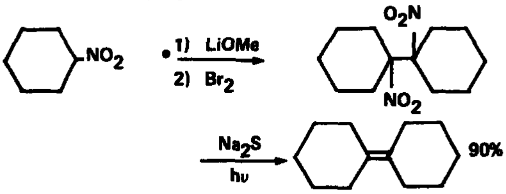

(3)

related reactions are still a powerful method for the preparation of crowded structures. 1,1,2,2-Tetra-*tert*-butylethane (**3**)[5a] was prepared by the route in eqn (4), a process that presumably involves radical-anion intermediates. A general synthesis of alkenes by a

$$t\text{-Bu}_2\text{CHCl} \xrightarrow{\text{Na}} \underset{\mathbf{3}}{t\text{-Bu}_2\text{CHCH-}t\text{-Bu}_2} \qquad (4)$$

radical-anion pathway has been developed by Kornblum[6] (e.g. eqn 5), and this route may potentially lead to crowded structures.



(5)

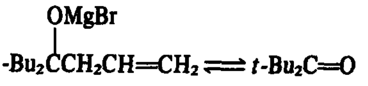
However, many crowded radicals, such as di- and tri-*tert*-butylmethyl (**4**, **5**),[7] and triisopropylmethyl (**6**),[7a] are resistant to dimerization and decay by other paths.

$$\underset{\mathbf{4}}{t\text{-Bu}_2\dot{\text{C}}\text{H}} \qquad \underset{\mathbf{5}}{t\text{-Bu}_3\dot{\text{C}}} \qquad \underset{\mathbf{6}}{i\text{-Pr}_3\dot{\text{C}}}$$

Grignard reactions have been valuable for the preparation of crowded molecules, but the initial preparation of *tert*-butyllithium[8] by an exceptional group of chemical investigations[8a,b] provided a more powerful tool for the facile preparation of structures such as tri-*tert*-butyl carbinol (**7**).[8c]

$$t\text{-Bu}_2\text{C=O} \xrightarrow[(2)\ \text{H}_2\text{O}]{(1)\ t\text{-BuLi}} \underset{\mathbf{7}}{t\text{-Bu}_3\text{COH}}. \quad (83\%)$$

In certain cases products of Grignard additions which are sterically crowded have been found to undergo reversals of the addition on heating, particularly when an allyl group could be expelled (eqn 6).[9]



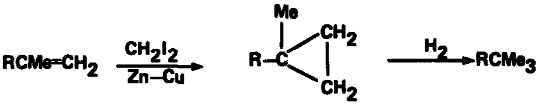
$$t\text{-Bu}_2\overset{\text{OMgBr}}{\text{C}}\text{CH}_2\text{CH=CH}_2 \rightleftharpoons t\text{-Bu}_2\text{C=O}$$
$$+\text{BrMgCH}_2\text{CH=CH}_2. \quad (6)$$

Organolithiums remain the most widely used reagents for attaching bulky groups to organic structures, although organoboranes (eqn 7)[10] and organocopper reagents (eqn 8)[11a,b] can be used for the facile preparation of some complex structures. Coupling of Grignard reagents with acyl chlorides is still a widely used route for *tert*-butyl ketones,[11c] and a recent variation using manganese has been reported (eqn 9).[11d]

Hydrogenolysis of methylcyclopropyl groups has been utilized as an alternative route for the incorporation of *tert*-butyl groups (eqn 10).[12]

$$t\text{-BuMgBr} \xrightarrow{\text{MnI}_2} \xrightarrow{\text{RCOCl}} t\text{-Bu}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R} \quad (60\%) \qquad (9)^{11d}$$

R = *n*-heptyl



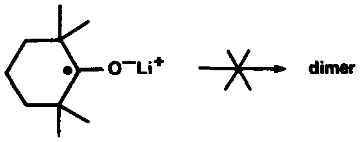
(10)[12]

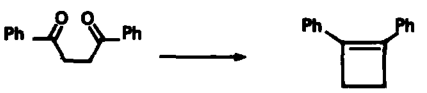
A very useful route to crowded structures involves the reductive dimerization of 2 ketones in a process formally equivalent to a pinacol reduction, and then deoxygenation to an alkene. The McMurry procedure,[13] using a reduced titanium reagent, has been applied to the preparation of tetra-isopropyl (**8**),[14a,b] tetrabenzyl (**9**)[14c] and tetraneopentylethylene (**10**),[14d] but so far attempted syntheses of tetra-*tert*-butylethylene (**11**)[14e] and a number of other crowded alkenes by this procedure have failed.[14e] Ketyls such as **12**, which could lead to molecules with the carbon skeleton of **11**, can be formed as stable entities in solution, but with no tendency to dimerize.[14f] Cycloalkenes have also been prepared by the McMurry procedure (eqn 11).[13e,f]

$$\text{R}_2\text{C=O} \xrightarrow[\text{TiCl}_3 \text{ or K-TiCl}_3]{\text{LiAlH}_4} \text{R}_2\text{C=CR}_2$$

R = *i*-Pr (**8**) 7–10%
R = PhCH₂ (**9**)
R = Np(Np = *t*-BuCH₂) (**10**)
R = *t*-Bu (**11**) 0% isolated

12





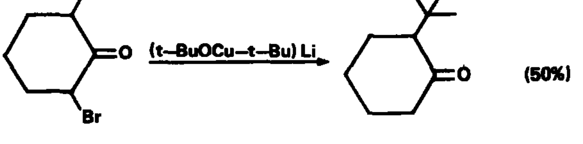
(11)[13f]

Another application of this procedure involved the preparation of two inherently dissymetric alkenes **12** and **13**, which could be resolved in optically active form (eqn 12).[14g]

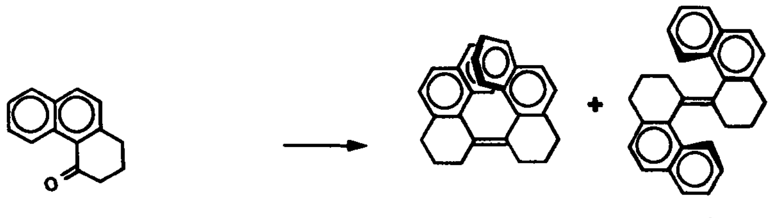
Another successful route to crowded alkene structures has been a double extrusion method. The reactions of thioketones[15] and selenoketones[16] have led to a number of extremely crowded tetrasubstituted alkenes, as illustrated in eqns (13) and (14). However, the attempted preparation of **11** by this method failed (eqn 15).[16]

The results in eqn (15) also indicate that the potentially

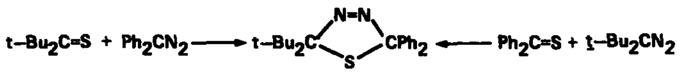
$$c\text{-Hx}_2\text{B-}t\text{-Bu} + \text{Cl}_2\text{CHOMe} \xrightarrow[(2)\ \text{H}_2\text{O}_2,\ \text{OH}^-]{(1)\ \text{LiOCEt}_3} c\text{-Hx}_2(t\text{-Bu})\text{COH} \quad (90\%) \qquad (7)^{10}$$



(8)[11a]


(12) (13)

(12)



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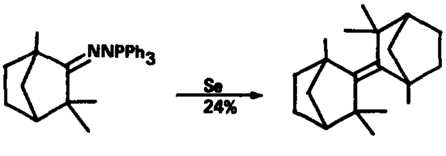
(13)[15a]

$14 \xrightarrow[2)\ Ph_3P]{1)\ \Delta} t\text{–}Bu_2C{=}CPh_2$ 15 (68%)



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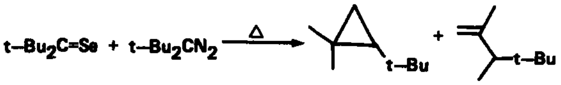
(14)[16]



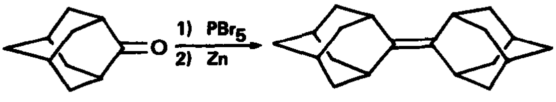
(15)[16]

simple carbene dimerization route to hindered alkenes is not practical for compounds with adjacent bonds vulnerable to insertion reactions to form cyclopropanes. The reduction in non-bonding strain resulting from cyclopropane formation enhances this route, whereas dimerization is sterically unfavorable. However this method was used successfully to produce tetra(2,4,6-trimethylphenyl)ethylene (eqn 16).[17a] Dimesitylacetylene and 2,4,6,2',4',6'-hexa-*tert*-butylacetylene were also prepared by dehydrohalogenation and acetylene coupling routes, respectively.[17b]

$$Mes_2CN_2 \xrightarrow{h\nu} Mes_2C: \longrightarrow Mes_2C{=}CMes_2 \quad (16)$$

Mes = 2,4,6-trimethylphenyl

Cyclic analogs of tetraisopropylethylene such as adamantylideneadamantane (17)[18a] and 7,7'-norbornylidenenorbornane[18b] are readily available by the reaction of geminal dibromides and metals.



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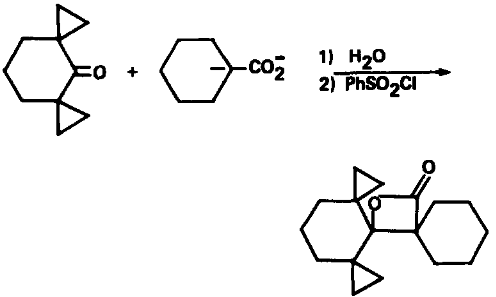
Another reaction which has been used to prepare crowded cycloalkylidenecycloalkanes utilizes a coupling of acid dianions with ketones (e.g. eqn 17).[19a]



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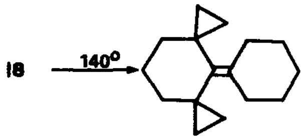
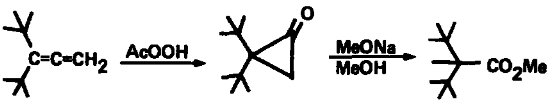
(17)



Oxidation of crowded ketenes produces some intermediates such as 1,1-di-*tert*-butylcyclopropanone (19, eqn 18)[20a] which have an attractive functionality for preparation of other crowded products. A large number of other small rings substituted with *tert*-butyl groups such as 20 and 21 are known,[20c–d] particularly heterocycles; the large angles between the bulky groups in such compounds favor cyclization.



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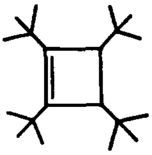
+ $t\text{–}Bu_2CH_2CH_2CO_2Me$ (18)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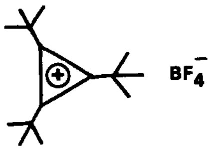

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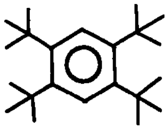
There are many as yet uncharacterized crowded structures with potentially informative properties that should be available by application of known synthetic methodologies. The continuing progress in synthetic chemistry also causes the author to be optimistic that other synthetic techniques will be developed so that structures presently seemingly inaccessible will soon be available for study.

MOLECULAR STRUCTURES

Molecular structures have been determined for only a relatively small number of the crowded compounds that have been prepared. The first of these were X-ray structures of 1,2,4,5-tetra-*tert*-butylbenzene (22) and analogous heterocycles.[21,22] The ring carbons and the attached quarternary carbons were essentially coplanar in 22 but the *tert*-butyl-ring angle was opened to 130° and the bond lengths between the ring and the *tert*-butyl groups increased to 1.57 Å. It has been inferred that 1,2-di-*tert*-butylbenzene (23) and *cis*-1,2-di-*tert*-butyl-ethylene (24) will also be planar[22] and simple calculations based on this premise agree that the internal angles in 23 and 24 will be opened to 136°.[22] Molecular mechanics calculations for 24 are in accord with this conclusion,[23] so an experimental determination of the geometry of 24 would provide. a useful test of the accuracy of this method. Bond angles at sp^2 carbons in a cyclo-octene derivative of 138.7° have been recently reported.[23d]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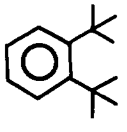
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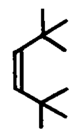
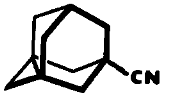

24

X-ray structures have been determined for di-*tert*-butylcarbinyl oxalate (25)[24a] and tri-*tert*-butylcarbinyl *p*-nitrobenzoate (26),[24b] and electron diffraction studies are available of the corresponding hydrocarbons di-*tert*-butylmethane (27)[24c] and tri-*tert*-butylmethane (28).[24d] Some of the salient comparative dimensions of these molecules are given in Table 1. Among the interesting features which appear in these structures are the long C–C bond lengths (the 1.64 Å distance in 26 matches the longest C–C bond reported in an acyclic compound).[25d] For a comparison a C–C bond length of 1.643 Å has been reported for the bridge bond in 29.[24e] The expanded C–C–C angles at the central carbons in 25–28 apparently result from back strain, and a close contact between the carbonyl oxygen and one of the tert-butyl hydrogens in 26 of 2.1 Å apparently causes one of its C–C–O angles to be larger than the others. Other structures which have been experimentally determined include trimesitylmethane,[24f] 1,1,3,3-tetra-*tert*-butylacetone (30),[25a] 15,[25b] 16[25c] and 1,3,6,8-tetra-*tert*-butylnaphthalene (31).[25e] The dihedral angle between the plane of the two olefinic carbons in 15 corresponds to a twist of the double bond of 24°, whereas the corresponding twist in 16 is only 12°. The C–C double bond lengths in both 15 and 16 are



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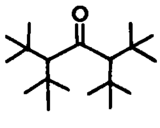

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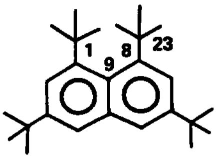

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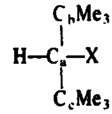
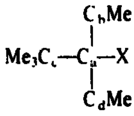
Table 1. Comparative molecular dimensions of di-*tert*-butylcarbinyl and tri-*tert*-butylcarbinyl derivatives


$$\mathrm{H{-}\overset{\displaystyle C_bMe_3}{\underset{\displaystyle C_cMe_3}{C_a}}{-}X}$$

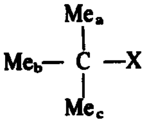
X = t-$Bu_2CHO_4C_2$ (25)
X = H (27)


$$\mathrm{Me_3C_c{-}\overset{\displaystyle C_bMe_3}{\underset{\displaystyle C_dMe_3}{C_a}}{-}X}$$

X = OPNB (26)
X = H (28)

Bond angle	25	27	26		28
$X–C_a–C_b$	105.8[a]	112.1[a]	$X–C_a–C_b$	102.6	101.6[a]
$C_b–C_a–C_c$	124.0[a]	128.0[a]	$X–C_a–C_c$	98.7	
			$X–C_a–C_d$	112.5	
			$C_b–C_a–C_c$	113.8	116.0[a]
			$C_b–C_a–C_d$	115.4	
			$C_c–C_a–C_d$	112.1	

Bond distances: (Å)
25: $C_a–C_b$: 1.54; $C_a–C_c$: 1.54
26: $C_a–C_b$: 1.64; $C_a–C_c$: 1.61; $C_a–C_d$: 1.61
27: $C_a–C_b$, $C_a–C_c$: 1.545[a]
28: $C_a–C_b$, $C_a–C_c$, $C_a–C_d$: 1.611[a]

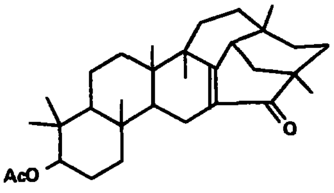

$$\mathrm{Me_b{-}\overset{\displaystyle Me_a}{\underset{\displaystyle Me_c}{C}}{-}X}$$

	Bond Angle	Bond distance (Å)
X = H[b]	C–Me 111.0[a]	C–Me 1.534[a]
X = RCO_2[c]	$C–Me_a$ 113.5 $C–Me_b$ 111.4 $C–Me_c$ 109.9 111.6[a]	C–Me 1.52[a]

[a] Av. value. [b] Ref. 22c. [c] Av. of values reported by T. Matsuzaki, *Acta Cryst*. **B30**, 1029 (1974); E. Benedetti, M. R. Ciajolo and A. Maisto, *Ibid*. **B30**, 1783 (1974); M. Cesari, L. D'Ilario, E. giglio and G. Perego, *Ibid*. **B31**, 49 (1975); S. Kashino, T. Ashida and M. Kakudo, *Ibid*. **B30**, 2074 (1974).

almost normal. The angle between the geminal *tert*-butyls in **30** is 118° and the C-*t*-Bu bond distances average 1.60 Å. In **31** much distortion is evident, with angles 1-9-8 and 9-8-23 of 129.9 and 125.8°, respectively.

As examples of the degree of geometrical distortion observed in alophatic systems **32**[26a] and **33**[26b] may be noted. Dihedral angles between the groups on the C–C double bond of **32** are 21° and 31°. In **33** the central C–C bond length is normal (1.54 Å) but this was proposed[26b] to result from a tendency to stretch the bond 0.04 Å due to non-bonded repulsion and a hybridization-induced shortening of the bond by 0.04 Å. A series of X-ray structures of substituted ethanes of the type **34** have recently been measured, and for the case where $R_1 = c$-Hx, $R_2 = t$-Bu, and $R_3 = H$, the central C–C bond attains a length of 1.61 Å.[27]



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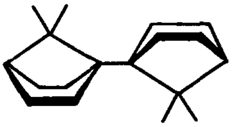

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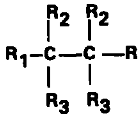


$R_1-\overset{R_2}{\underset{R_3}{C}}-\overset{R_2}{\underset{R_3}{C}}-R_1$

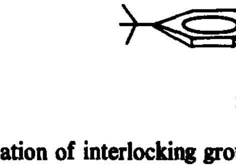
34

In an interesting case of conformational analysis by means of X-ray crystallography, one of the two isolated isomers of *o*-tolyldi-*tert*-butylcarbinol was shown to exist in the conformation **35**, with the C–OH bond deviating from the plane of the aryl ring by 11.6°.[28]

SPECTRAL PROPERTIES

Spectral properties of crowded structures often show distinct differences from those of less hindered materials. Vibrational spectra of saturated compounds such as tri-*tert*-butylmethane (**28**)[24d] and hexaethylethane (**34**, R=Et)[27b] reveal high C–H stretching frequencies (3000–3040 cm^{-1}) whereas the C=C stretching frequencies of crowded alkenes can be quite low (cf. 1583 cm^{-1} for tri-*tert*-butylethylene).[29a] It is surprising that the value found for the ^{13}C–H coupling constant for the methine hydrogen in **28** is what is considered "normal" for a saturated acyclic hydrocarbon (values of 126 Hz[29b] and 124 Hz[29c] have been determined from the partially decoupled ^{13}C and the ^{1}H spectra, respectively). Simple arguments based on an interrelation of bond angle, hybridization, and ^{13}C–H coupling constants predict[24d] values as low as 75 Hz for **28**, but it is clear that a more sophisticated theory of the connection between these is required. The effects of bulky substituents on the NMR,[29] UV,[30] and photoelectron[31] spectra of alkenes substituted with bulky groups have also been reported. There has been some confusion in the interpretation of these data. Thus incorrect ^{13}C chemical shifts (later corrected)[29e] were reported[32b] for *Z*-1,2-di-*tert*-butylethylene (**24**) and proposed to support a pyramidal geometry at the carbons in this molecule.[32a] It may also be noted that published[31a,b] photoelectron spectra for **24** and its *E*-isomer are not in agreement as to which compound has the higher ionization potential. Furthermore, the data are interpreted as indicating planar geometries for both compounds in one case,[31a] and a non-planar arrangement for the *cis*-isomer by a second group.[31b] The latter investigators[31b] studied a large series of compounds and observed noticeably low values for the ionization potentials of **24** and tri-*tert*-butylethylene and a lesser diminution for 1,1-di-*tert*-butylethylene. Since the latter group studied a larger series of compounds the trends in their experimental data may be more reliable. One of the authors of the former investigation has suggested[31d] that their reported values[31a] represent the vertical ionization potentials, that is, the value to ionize the alkene without geometrical reorganization. The measurements of the latter group[31b] are claimed[31d] to represent adiabatic ionization potentials which include relaxation of the ion to a different geometry. In any event it appears to this author that assignment of molecular geometries based on ionization potentials is not on firm grounds, emphasizing the need for an experimental structure determination for **24** (such a project is now underway using electron diffraction).[33] The photoelectron spectra of **8** and **17** have also been interpreted in terms of planar π-bonds.[31c]

Dynamic NMR studies of crowded molecules have revealed some interesting examples of steric hindrance to rotation about C–C single bonds. Some recent examples include 1,1,2,2-tetra-*tert*-butylethane (**3**),[5a] *o*-tolyldi-*tert*-butylcarbinol (**35**) (in which rotational isomers were isolable up to 100°C),[28,34a] 2,3,4,4-tetramethyl-3-*tert*-butyl-1-butene (**36**),[34b,c] 2,4,6-tri-butylphenyl ketones (**37**),[34d] **8**,[14a,b] **10**,[14d] and many others.[34e] The coupled rotation of interlocking groups such as the isopropyls in **8** has been designated as a "gear"[35a] or "cogwheel"[35b] effect. Although superficially cyclopropyl is a structural analog of isopropyl it has been found that the cyclopropyl analog of **8**, namely **38** shows no sign of restricted rotation down to −30°.[35c] Similarly although hexaisopropylbenzene **39** appears to have a locked geometry,[35d] the cyclopropyl analog **40** is much more conformationally mobile.[35e] Evidently the effective size of cyclopropyl is considerably reduced over isopropyl. Further



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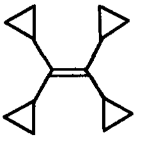

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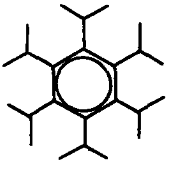

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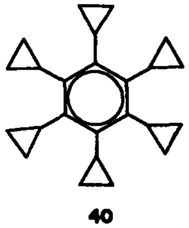


40

evidence for this is found in the fact that hexacyclopropylethane is known,[35f] whereas triisopropylmethyl radical (6) shows no tendency to dimerize.[7a]

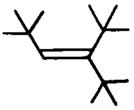
$$c\text{-}Pr_3C\cdot \longrightarrow c\text{-}Pr_3CC\text{-}c\text{-}Pr_3$$
$$i\text{-}Pr_3C\cdot \nrightarrow i\text{-}Pr_3CC\text{-}i\text{-}Pr_3$$

THEORETICAL CALCULATIONS

Theoretical calculations of the structures and properties of crowded molecules by the methods of quantum mechanics have so far been limited because of the large numbers of atoms involved. However, the energies of various distorted geometries of simple molecules such as methane and ethylene can be calculated by this method.[36] Some other fairly simple molecules have also been examined in this way to elucidate non-bonded attractive forces in some ethylenes, propenes,[36] and other systems.[36e–i]

For the study of complex organic structures with bulky substituents the method of molecular mechanics has been profitably utilized. In this technique potential functions for various intramolecular interactions including bond bending and stretching, dipole effects, and non-bonding interactions are considered and the total energy from these sources is calculated as a function of various geometries of the system. This method has been reviewed[37a,b] and is being continually improved.[37c,d]

The strain energies of various crowded hydrocarbons which have been obtained by this method are *cis*-1,2-di-*tert*-butylethylene (24): 11.1 kcal/mol,[23b] 1,1-di-*tert*-butylethylene: 12.0 kcal/mol;[23b] tri-*tert*-butylethylene (41): 32 kcal/mol;[23b] tetraisopropylethylene (8) 18 kcal/mol;[23b] tetra-*tert*-butylethane (3): 60 kcal/mol;[38] and hexaethylethane (34, R=Et): 35 kcal/mol.[38] It was concluded that the strain energy of the unknown tetra-*tert*-butylethylene (11) could not be reasonably estimated from this procedure. The most recent calculation predicts the pi-bond in 11 will be twisted by 43.3°.[23a] Thus the calculated geometries of 3[5a] and 11 are rather similar.



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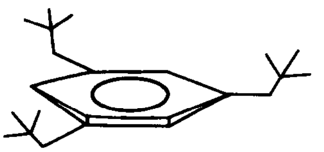
Calculation of rate differences due to changes in steric crowding between the ground state and transition state has been carried out by molecular mechanics methods for unimolecular reactions leading to both carbonium ions[39] and free radicals.[39a] In these treatments the ground state is approximated as the corresponding hydrocarbon with hydrogen substituted for the leaving group, and the transition state is represented by the fully formed intermediate, and the differences in strain energy of the two is compared. As has been pointed out[39] this approach suffers from the defect that interactions involving the leaving group in the ground and transition states have been ignored.[39d] The lack of suitable parameterization of the potential functions to accommodate hetero atoms is one cause of this problem, and until this difficulty is overcome the results of such treatments must be interpreted with caution. The recent availability of experimental molecular structures of esters of crowded structures[24a,b] should also serve as a critical test of the reliability of the calculations to predict structures. The fact that the experimental geometries of the esters, as collected in Table 1, are quite different from the geometry of the hydrocarbons shows that one of the assumptions of the molecular mechanics rate calculations, namely that hydrocarbons are good models for the corresponding esters, is incorrect.

Calculations of the molecular structures of di- and tri-*tert*-butylmethane[24c,d] and of tetra-*tert*-butylnaphthalene (31)[25e] have also been reported. Another interested application of this technique was to 1,3,5-trineopentylbenzene (42),[40] found to have as its most stable rotameter that with the three *tert*-butyl groups on the same side of the ring, a result attributed to an attractive van der Waals interaction between the groups.



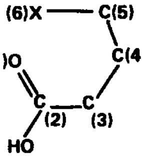
42

Correlations of steric hindrance to chemical reactivity include studies of the accessibility of different faces of molecules to incoming reagents ("congestion")[41a] and the interrelation of steric hindrance, rates of ester hydrolysis, and strain in hydrocarbons.[41b] The latter investigators[41b] found that by using a slight modification of the molecular mechanics methods used for hydrocarbons that the steric influences on the rates of acid-catalyzed ester hydrolyses could be correlated with the difference in steric strain between $RC(OH)_3$ and RCO_2H, taken as models of the transition state and ground state, respectively. These rates of ester hydrolysis were used to define the E_s steric parameters for different groups by Taft 20 years ago[42a] as $E_s = -\log k/k_0$ where k is the rate of hydrolysis for RCO_2Et and k_0 is the rate for CH_3CO_2Et. The correlation of these widely-used parameters with the molecular mechanics method lends greater validity to the use of the E_s parameters to evaluate the steric size of groups and insures their continued usage.[42a]

An empirical steric parameter, the ν value, has been calculated by Charton[43a] from van der Waals radii, and has been reported by him to be useful in the Taft equation, and for the calculation of such effects as steric barriers to biphenyl racemization.[43b] However, this approach has been criticized by Berger,[43c] who studied the NMR spectra of substituted *tert*-butylbenzenes. Another criticism of Charton's method was made by MacPhee and Dubois,[43d] and Charton has replied to their comments.[43e]

Discussion of the respective merits of the arguments presented in this controversy is beyond the scope of this report, but a few general comments are in order. Although schemes for the quantitative separation of polar and steric factors are quite useful in particular circumstances it must be borne in mind that these factors ultimately arise from the same source and are not divisible. Furthermore a single steric parameter can never suffice for one group, since the bulk of a group depends on its particular environment.[1d] Thus chlorine and bromine have the same effective size, which is smaller than that of methyl, as measured by their equatorial/axial preference on a cyclohexane ring, or *A* value, but the order for biphenyl racemization is Br > Cl > Me.[43b] Groups such as isopropyl may be expected to show variable behaviour depending upon whether or not the possibility of "gearing" or "cogwheeling" arises. Examples of non-linear response of the rates of various reactions with increasing substitution are discussed below.

A long established method for the estimation of steric factors is Newman's "rule of six", which was derived from rates of acid esterification; "in reactions involving addition to an unsaturated function, the greater number of atoms in the six position the greater will be the steric effect."[44a] The basis of this rule is the close approach possible for groups separated by five bonds in carboxylic acids derivatives, as shown in **41**. Extensions,[44b,c] and applications[45] of this rule continue to appear.



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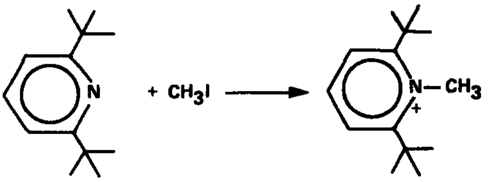
An apparent general trend has been noted that pressure effects on chemical reactivity are greatest in crowded systems.[46] The particular system which has been most studied is the Menschutkin reaction; for example with 2,6-di-*tert*-butylpyridine and methyl iodide (eqn 19).[46a] It was concluded that the greater effects of pressure were a demonstration of the Hammond postulate, in that the more crowded substrates had a later, and hence more compact, transition state and so were accelerated by increased pressure.[46a]



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STERIC CROWDING IN SOLVOLYSIS REACTIONS FORMING CARBONIUM IONS

During unimolecular conversion of an sp^3 hydridized ground state to an intermediate with sp^2 hybridization the system may undergo a net reduction in strain (eqn 20). This could arise from a decrease of the interaction between the substituents on carbon (*B*-strain)[47] which move apart as tbe bond angles increase during rehybridization and also a decrease in the interaction between the leaving group X and the rest of the molecule (*F*-strain).[47] Another factor which can be involved is the steric influence on solvation of the ground and transition states. Some of the reported examples,[34b,39c,48] of the rate effects observed in crowded substrates undergoing ionization to carbonium ions are shown (Table 2).

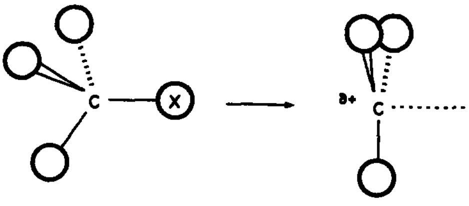
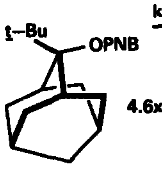
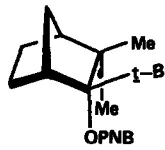
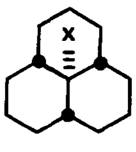


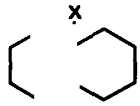
Table 2. Relative solvolysis rates of *p*-nitrobenzoate esters at 25°.

	34b k_{rel}		k_{rel}
t-BuOPNB	1.0	 **44**[39c]	4.6×10^5
t-Bu$_3$COPNB	1.4×10^4		
t-BuNp$_2$COPNB	6.8×10^4	 **45**[48a]	3.8×10^5
(Np = t-BuCH$_2$)			

The rate differences in Table 2 appear to arise exclusively from the effects of steric strain. However the separation of the observed rates into the components due to *B* and *F* strain, and to solvation, has not been accomplished. The importance of *F* strain has been illustrated by the fact that the *p*-nitrobenzoate ester **46** is 466 times more reactive than **48** whereas the corresponding rate ratio of the chlorides k47/k49 is only 0.077.[39d] This result indicates that specific interactions between the leaving group and the alkyl residue in **46** are relieved in attaining the transition state, whereas these interactions are much less significant with the corresponding chloride. A role for solvent effects was suggested based on the fact that the relative rates of reaction of crowded alcohols in acetic acid were much less than the relative rates of the corresponding *p*-nitrobenzoate esters.[49a] It was proposed[49a] that the low rates of the crowded alcohol dehydrations were due to steric hindrance to solvation of the developing cation, and that the more rapid rates of *p*-nitrobenzoates arose from *F* strain. However, an alternative explanation of the rate effects in the alcohol dehydrations is possible. The rates were proposed[49a] to involve rate-determining heterolysis of a protonated alcohol, and this appears reasonable. However, in acetic acid this heterolysis must be preceded by a pre-equilibrium protonation (eqn 21) whose magnitude would be diminished by crowding. The observed rate would be proportional to k_1K_{eq}, and in the absence of specific information as to the effects of crowding on both of these constants conclusions based on rates of dehydrations must be regarded as tentative. In a more recent paper[49b] a correlation was reported between dehydration rates and calculated strain energies



46 X = OPNB
47 X = Cl



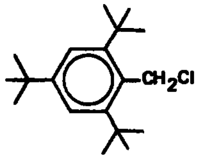
48 X = OPNB
49 X = Cl

$$\mathrm{ROH} + \mathrm{H}^+ \overset{K_{eq}}{\rightleftharpoons} \mathrm{ROH}_2^+ \xrightarrow[-\mathrm{H_2O}]{k_1} \mathrm{R}^+ \rightarrow \text{products} \qquad (21)$$

of hydrocarbons and planar carbonium ions. This study suffers both from the approximations in the molecular mechanics method already commented upon, and also the neglect of steric hindrance to solvation. The validity of this approach thus remains to be established.

In another approach to the problem, arylsulfonate leaving groups with different *o*-substituents (H, Me, *i*-Pr) were examined[49c] to see if any rate accelerations due to bulky *o*-groups could be detected. The result was that not only were no accelerations observed, but rather the most heavily substituted compounds had the lowest rates. This suggested that steric hindrance to solvation caused a rate retardation in the most subsitituted compounds, and that even larger *ortho*-substituents would be required to conclusively demonstrate the effect of *F* strain in these solvolyses. In the X-ray structure of tri-*tert*-butylcarbinyl *p*-nitro-benzoate (**26**)[24b] a very close contact with *tert*-butyl hydrogens of 2.2 Å for an *o*-hydrogen and 2.1 Å for the carbonyl oxygen, respectively, were observed, strongly implicating *F*-strain in the ground state of this molecule.

The solvolysis of **44** was found to be 1.11 times faster than the corresponding compound fully deuterated in the *tert*-butyl group.[50a] This result was ascribed to the lower effective size of deuterium relative to hydrogen, and a resulting lower steric acceleration of the deuterated compound. The solvolysis rate ratio k**50**/k**50**-d_{27} was found to be 0.87, but the greater reactivity of **50**-d_{27} was ascribed to greater inductive donation by deuterium relative to protium with no definite effect due to reduced steric bulk of the fully deuterated *tert*-butyl groups in **50**-d_{27}.[50b] The absence of a steric isotope deceleration in **50**-d_{27} probably arises from the rather low steric acceleration observed in **50**, which is only about seven times more reactive than 2,4,6-trimethylbenzyl chloride and 24 times more reactive than 2,4,6-triisopropylbenzyl chloride.



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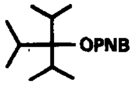
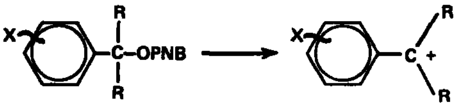
We have examined the solvolysis of triisopropylcarbinyl *p*-nitrobenzoate (**51**) fully deuterated in the methyl groups.[51]



51 and **51**-d_{18}

This compound shows a rate acceleration relative to *tert*-butyl *p*-nitrobenzoate of 206[48b], but the rates of **51** and **51**-d_{18} differed by less than 5%, showing no significant net isotope effect.

The solvolysis of a large number of aryl substituted benzyl *p*-nitrobenzoates (**52**) were studied by Tanida and Matsumura (eqn 22).[48c] In these compounds the rates were affected both by the relief of *B*-strain in the transition state but even more by the twisting of the phenyl ring out of conjugation by the bulky R groups. Thus when the rates for **52** are correlated by the Brown $\rho\sigma^+$ treatment for R=Me the value of ρ is -3.74, whereas for R = *t*-Bu, ρ is -1.30. The much lower magnitude of ρ for the case with bulkyl substituents indicates a much weaker interaction of the aryl ring with the developing positive charge due to twisting out of conjugation. The rate of phenyldi-*tert*-butylcarbinyl *p*-nitrobenzoate is actually less than that of phenyldimethylcarbinyl *p*-nitrobenzoate by a factor of 0.093. This difference also derives from steric hindrance to conjugation in the crowded transition state. The effect of solvation on reactivity in **52** (R = *t*-Bu) has also been examined and a linear correlation between solvent sensitivity (measured by *m*-values) and relative reactivities as a function of X was observed.[48d]



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R = Me, Np (neopentyl), or t–Bu

Reaction of tri-*tert*-butylmethane (**28**) in strong acid yielded methane and *tert*-butyl cation as the only observed products, presumably by protolysis of a C–C bond followed by bond cleavage (eqn 23).[52a]

$$\underset{\mathbf{28}}{t\text{-Bu}_3\text{CH}} \xrightarrow{\text{H}^+} \text{CH}_4 + \text{Me}_2\overset{+}{\text{C}}\text{CH-}t\text{-Bu}_2 \xrightarrow{-t\text{-Bu}^+} \text{Me}_2\text{C}{=}\text{CH-}t\text{-Bu} \qquad (23)$$

Cleavage of C–C bonds is a frequently observed reaction in crowded carbonium ions.[52b] In a elegant recent study the reversible addition of the *tert*-butyl cation to isobutene has been demonstrated (eqn 23a).[52c]

$$t\text{-Bu}^+ + \text{Me}_2\text{C}{=}\text{CH}_2 \rightleftharpoons t\text{-BuCH}_2\overset{+}{\text{C}}\text{Me}_2 \qquad (23a)$$

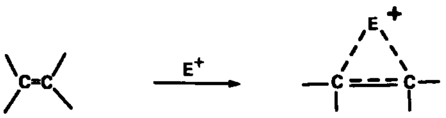
EFFECTS OF BULKY SUBSTITUENTS ON ADDITION REACTIONS OF ALKENES

The effects of *cis*/*trans* isomerism for a number of electrophilic additions to 1,2-distributed alkenes are shown in Table 3.

The addition of arylsulfenyl chloride has been interpreted as involving rate determining formation of a bridged intermediate in all cases (eqn 24)[53a,54] whereas hydration has been proposed as the prototype reaction involving a transition state resembling an open ion (eqn 25).[55] It was proposed that in formation of the bridged ion in arylsulfenyl halide additions to the 1,2-di-*tert*-butylethylenes that in the *E* isomer both sides of the molecule were blocked by *tert*-butyl groups so that access of the electrophile to the π-electrons was restricted, whereas in the *Z* isomer one side of the molecular was

Table 3. Rate ratios k*Z*/k*E* for electrophilic attack on alkenes RCH=CHR

	Electrophile				
R	ArSCl[53a]	H_3O^{+}[53b]	$Hg(OAc)_2$	Br_2	Cl_2
t-Bu (**24**)	1.6×10^5	3.8	> 100[53c]	52[53d]	0.37[53e]
i-Pr	9.7	0.50	—	0.42[53d]	—
Et	9.2	1.2	6.2[53f]	1.2[53g]	—
Me	3.1	2.1	3.4[53h]	1.6[53g]	1.3[53i]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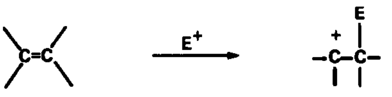
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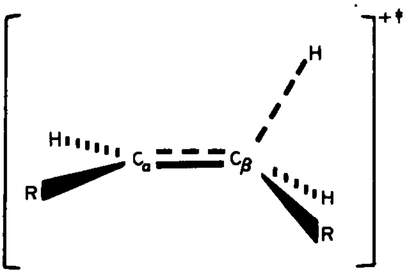
unhindered.[54a] The rates of the 1,1-di-*tert*-butyl isomer and tri-*tert*-butylethylene (**41**) were similar to that of the *E* isomer, in accord with this proposal.[54a] Steric factors were quite small in protonation, indicating very little hindrance to attack of a small electrophile on carbon. Oxymercuration and bromination of most 1,2-disubstituted alkenes, except those bearing strongly resonance electron donating substituents, have been proposed to involve bridged transition states.[56] These two reactions show large k*Z*/k*E* values for 1,2-di-*tert*-butylethylene, so if this correlation of reactivity with geometry is generally applicable it may be concluded that chlorination of these substrates more closely resembles an open than a bridged ion, contrary to the conclusion based on product stereochemistry.[53a] Bromination of tri-*tert*-butylethylene (**41**) was also very slow.[57c]

It has been suggested that solvation involving interactions of the solvent and the π-bond in *E*-**24** is negligible,[58] but both *Z*- and *E*-**24** are about as reactive as less crowded analogs in hydration. This may reflect equal inhibition of solvation in both the ground and transition states.

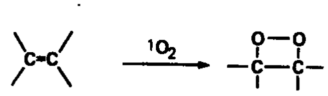
The low difference in reactivity in hydration between *Z*- and *E*-**24** is perhaps surprising, in view of the 10 kcal greater strain in the former. It would be anticipated that bond rotation would occur after protonation so that the first intermediate from either isomer would be the same, and the extra strain present in *Z*-**24** would be lost. The results may be explained by the transition

$$Z\text{-}\mathbf{24} \xrightarrow{H^+} t\text{-Bu}\overset{+}{C}HCH_2\text{-}t\text{-Bu} \xleftarrow{H^+} E\text{-}\mathbf{24}$$

state model shown. There is still substantial double bond character in this transition state so rotation around the central C–C bond does not occur. Rehybridization at C(β) results in little net decrease in the distance between the R groups so there is little strain relief in the transition state.



Oxidation of crowded alkenes produces unusual results. The reaction of ozone with adamantylideneadamantane (**17**),[57a] or tetraisopropylethylene (**8**),[57b] or of **15** with *m*-chloroperbenzoic acid[16] yields epoxides, as well as the normal ozonide in the case of **17**.[57a] By contrast only the normal cleavage product was detected from ozonololysis of tri-*tert*-butylethylene (**41**).[57c] It has been found that tetrasubstituted alkenes which lack reactive β-hydrogens, such as **17** and norbornylidenenorbornane react with singlet oxygen to give 1,2-dioxetanes (eqn 26).[18b,57e,f] However, attempts

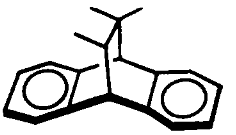

(26)

to prepare the dioxetane of **8** in this way have so far been unsuccessful.[57d] The X-ray structure of the dioxetane of **17** indicates steric hindrance to cleavage of this molecule.[57h]

Steric crowding also affects the photochemical reactivity of alkenes. In particular alkenes such as *Z*-4,4-dimethyl-2-pentene are reactive quenchers of acetophenone triplets, but have low quantum yields for isomerization or formation of new products, in contrast to less hindered alkenes.[59a] Attempts to define the geometries of the intermediates by use of the available structure-reactivity data have not been completely satisfying,[59a] and further attention to this topic is required. Steric inhibition of fluorescence quenching by *cis*-piperylene of substituted benzenes is observed with very bulky substituents, such as in 1,3,5-tri-*tert*-butylbenzene.[59b]

FREE-RADICAL REACTIONS OF CROWDED SUBSTRATES

In hydrogen atom abstraction α- to the methyl group, an acceleration of a factor of 14 was observed for **53** relative to **54**.[60] This was ascribed to relief of *B*-strain in **53**.[60]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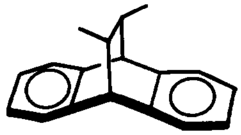
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Rate effects due to crowding in free radical formation have been reported from thermolysis of perester (eqn 27),[61] diazene (eqn 28),[45,48b,62] and hexasubstituted ethane (eqn 29)[63] precursors.

$$R_1R_2R_3CCO_3\text{t–Bu} \xrightarrow[-\text{t–BuO}\cdot]{-CO_2} R_1R_2R_3C\cdot \qquad (27)$$

$$R_1R_2R_3CN{=}NCR_1R_2R_3 \xrightarrow{-N_2} 2R_1R_2R_3C\cdot \qquad (28)$$

$$(R_1R_2R_3C)_2 \longrightarrow 2R_1R_2R_3C\cdot \qquad (29)$$

Rate effects on the first two types of radical formation are compared with rates of carbonium ion formation (from ester or chloride solvolysis) in Table 4. It has been pointed out[48b] that the square roots of the rates of the azo compounds are the proper quantity to compare with the carbonium ion data, since two equivalent groups with multiplicative *B*-strain effects are involved in the case of diazenes.

A fairly good correlation of the rates of the diazenes with carbonium ion formation is found, with a somewhat larger effect of *B*-strain on the solvolysis reaction. Three

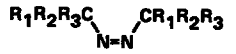
Table 4. Comparative rates of radical and cation formation

R	Radicals		Cations
	RCO_3t-Bu	RN=NR	
t-$BuMe_2CMe_2C$	—	—	8.9×10^{4e}
Np_3C	—	—	560[f]
t-Bu_2MeC	—	—	230[g]
Np_2MeC	5.7[a]	5.7×10^{4c}	580[c]
$NpMe_2C$	3.5[b]	1.3×10^{3c}	14[h]
i-Pr_3C	32[b]	206[d]	80[h]
Et_3C	3.2[i]	3.6[d]	6.4[j]
t-$BuMe_2C$	4.1[b]	5.3[d]	3[h]
t-Bu	1.0	1.0	1.0

[a]Ref. 62*c*. [b]Ref. 61*a*. [c]100°, Ref. 62*c*. [d]180°, Ref. 48b. [e]Ref. 65*a*. [f]Ref. 34*b*. [g]Ref. 49*a*. [h]Av. value, see Ref. 61*a*. [i]Ref. 65[b]. [j]Ref. 48*b*.

carbonium ion precursors for which rates of radical formation are not available are included in Table 4. It is to be hoped that the appropriate radical precursors will be examined, as these cases will provide a valuable test of the interrelationship of these reactivities.

Recently the reactivities of *cis*-diazenes (**55**) have also been reported.[62a] These are enormously more reactive



$R_1R_2R_3C\text{–}N{=}N\text{–}CR_1R_2R_3$

55

than the *trans* isomers, with kinetics of the *Z* isomers conveniently followed at 200°C lower temperatures than the *E*-isomers. The *Z*-isomers also show much greater increases in reactivity with increasing bulk of the groups R than the *E*-isomers. Evidently the strain in the *Z*-isomers, comparable to that in *Z*-alkenes such as *Z*-di-*tert*-butylethylene (10 kcal/mol) is partly relieved in their decomposition.

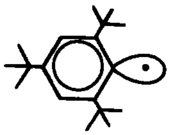
The greatest effects of steric bulk on rate of radical formation are observed for the hexasubstituted ethanes (eqn 29).[63a] Hexaethylethane is 5×10^7 more reactive than hexamethylethane. A correlation between the rates of reaction and the steric parameters E_s of the groups was also observed. In the ethanes the F-strain interactions between the groups are evidently the dominant influence on the reactivity, as the *B*-strain effects would be little different than those in peresters.

The crowded alcohol **7** has also been reported to undergo C–C bond scission with formation of free-radicals on heating to 180–240° (eqn 30).[64] The strain in **7** was

$$t\text{-}Bu_3COH \xrightarrow{\Delta} t\text{-}Bu_2\dot{C}OH + t\text{-}Bu^{\cdot} \qquad (30)$$

evident from the X-ray structure of the corresponding *p*-nitrobenzoate which showed the C–C bonds to the central carbon elongated to an average of 1.62 Å.[24b] It may be anticipated that other known crowded structures with weak C—C bonds will form free radicals on pyrolysis at relatively low temperatures.

Radicals substituted with bulky groups have been found to be amazingly long-lived. It has been proposed by Ingold[66] that the proper designation for these species that are long-lived in a kinetic sense is persistent, as opposed to stable, which implies electronic stabilization in a thermodynamic sense. Electron spin resonance (ESR) provides a convenient means to study these species, and some of the more noteworthy examples include **4**,[7] **5**,[7] **6**,[67] **56**[68] and **57**.[69] The reason for the great longevity of these species is the absence of accessible decay pathways. These radicals show no tendency to dimerize and self-disproportionate. Even **6**, which has



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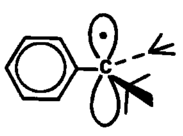


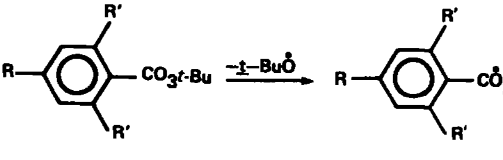
57

three β-hydrogens, yields no detectable tri-isopropylmethane, apparently since the β-hydrogens lie in the plane orthogonal to the p-orbital carrying the unpaired electron and are inaccessible to the bulky radical. The corresponding methanes are formed from **4** and **5**, apparently by abstraction of hydrogen from solvent. Di-isopropyldimethylethylene is formed from **6** indicating a disproportionation with solvent radicals. The phenyl radical **56** undergoes intramolecular hydrogen abstraction from a *tert*-butyl group to give a phenethyl radical as one decay path.[68] The di-*tert*-butylbenzyl radical **57** is interesting because the phenyl ring is twisted perpendicular to the adjacent p-orbital so that there is hardly any spin density in the aromatic ring. The persistance of this species in the absence of resonance stabilization emphasizes that a major reason for the persistence of triphenylmethyl (**2**) is the crowding which blocks decay of this radical.

Rate acceleration with increasing bulk of the ortho substituents was observed for a series of substituted *tert*-butyl perbenzoates (Table 5).[70] These compounds each gave some of the corresponding carboxylic acid in the reaction product, a result that indicates that each is reacting with rate limiting formation of a carboxylate radical (eqn 31). This result was ascribed[70] to ground

Table 5. Reactivities of substituted *tert*-butylperbenzoates **58** in cumene at 100°C

R	R'	k_{rel}	$\Delta H^{\ddagger}$(kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
H	H	1.0	34.0	9.3
Me	H	1.3	32.2	4.8
Me	Me	11	31.9	8.4
t–Bu	t–Bu	29	32.9	13.0

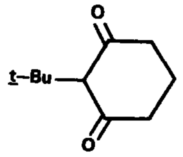


58 **59** (31)

state destabilization of the more crowded esters due to twisting of the percarboxyl group out of conjugation with the ring. Conjugation between the carboxyl radical group and the ring would also be precluded, but this was argued to be less significant than conjugation in the ground state. Supporting evidence for this contention is provided by a report that benzoyloxy and formyloxy radicals are Σ-type radicals,[71] a situation that would preclude delocalization of the radical into the ring in **59**.

STERIC EFFECTS OF BULKY GROUPS ON CARBANION REACTIVITY

This is largely a neglected area. It may be anticipated that to the extent that large groups hamper solvation of Carbanions, they will inhibit formation of these species. Also if Carbanions are hybridized sp^3 the groups attached to the carbanion center will not move apart on ionization and there will be no reduction in *B*-strain. However in enolate formation the groups will move apart when the carbon α to the carbonyl rehybridizes to sp^2 and some reduction in strain may result. One case that has been reported is 2-*tert*-butylcyclohexane-1,3-dione (**60**).[72] This compound was reported to have no tendency toward enol formation, and further did not exchange the proton on C-2 on treatment with base. We have examined[51] the reaction of ketone **61** with bases such as $NaCD_2SOCD_3$ in DMSO-d_6 and *t*-BuOK in *t*-BuOD at 195°. No deuterium incorporation into **61** was observed under any conditions, although fenchone (**63**) readily undergoes homoenolization and deuterium incorporation in the methyl groups on the same treatment.[73] It is probable that the enolate **62** that would be formed from **61** would be highly strained, presumably by as least as much as the 30 kcal/mol strain calculated for tri-*tert*-butylethylene. This strain apparently prevents formation of the enolate. Steric hindrance to approach of the base is probably not a decisive factor, as ketene formation from di-*tert*-butylacetyl chloride is readily accomplished on treatment with triethylamine (eqn 32).[74] Di-*tert*-butyl ketone on treatment with *t*-BuOK-*t*-BuOD at 185° undergoes homoenolization and rearrangement (eqn 33).[73d]



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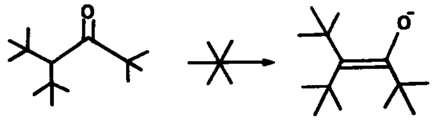

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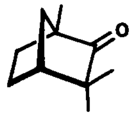

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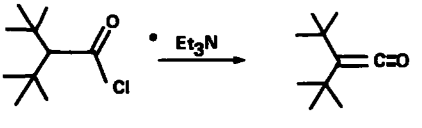

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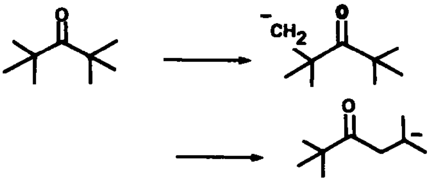

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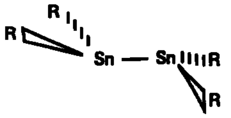
INORGANIC ANALOGS

Inorganic analogs of strained carbon structures have also been reported. Some of the notable examples are tri-*tert*-butylsilane (**64**, eqn 34)[75] and the ditin compound **66** (eqn 35). The latter compound is particularly interesting because it has some of the properties predicted for tetra-*tert*-butylethylene (**11**). The X-ray structure of **65** shows that the tin atoms to have a pyramidal arrangement, but the substituents are *anti* to one another (**66**), indicating no effective π-bonding.

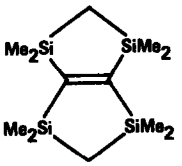
$$t\text{-BuSiCl}_3 + t\text{-BuLi} \longrightarrow \underset{\mathbf{64}}{t\text{-Bu}_3\text{SiH}} \qquad (34)^{75b}$$

$$((\text{Me}_3\text{Si})_2\text{N})_2\text{Sn} \xrightarrow[\text{2) SnCl}_2]{\text{1) Et}_2\text{O}} \underset{\mathbf{65}}{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{SnSn}[\text{N}(\text{SiMe}_3)_2]_2} \qquad (35)^{76}$$



66

An ethylene substituted with 4 quaternary silicon atoms, analogous to tetra-*tert*-butylethylene (**11**) has also been reported (**67**),[77] as well as a methane substituted with 4 trialkyltin groups (**68**).[78]



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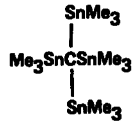
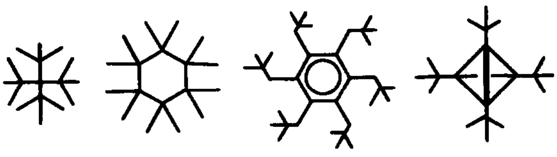


68

CONCLUSION

The future for the study of crowded compounds appears to be bright, as advances in synthetic methodology and improvements in the techniques of structure determination should make many hitherto new species available for study. In the field of hydrocarbons some challenging goals are **11** and the other structures shown. Some species not isolable under ordinary conditions may nevertheless be observable by the techniques of matrix isolation or in the gas phase. Improved computational techniques will allow an appreciation of the structures of known compounds and also those which have still not yielded to synthesis. The fascination of steric crowding will continue to encourage its devotees to use their ingenuity to crowd even more atoms in a limited volume (not unlike a competition to stuff maximum numbers of people into a telephone booth) and ever greater accomplishment may be anticipated.



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