

UniMelt capillary melting point apparatus. Microanalyses were performed by Mikroanalytisches Laboratorium, Vienna, Austria, and Industrial Testing Laboratories, St. Louis, Mo. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrometer. ^1H NMR spectra were obtained on a Varian A-60A spectrometer, unless otherwise noted, with tetramethylsilane (δ 0 ppm), *tert*-butyl alcohol (δ 1.28 ppm), or 99% dimethyl sulfoxide- d_6 (δ 2.51 ppm) as internal standard, depending on the solvent used. ^{13}C NMR spectra were obtained on a JEOL Model FX-60 spectrometer, with tetramethylsilane as an internal standard; we are indebted to Dr. J. L. Ludwig of the Petrolite Corporation of St. Louis for these determinations. The following abbreviations are used to denote NMR spectral characteristics: s, singlet; br s, broad singlet; d, doublet; t, triplet; m, multiplet. Optical density measurements for the ferric hydroxamate assay were made on a Beckman DU quartz prism spectrometer at 505 nm. pH measurements were made with a Corning Model 12 Research meter using a Corning 07497 glass electrode and a Beckman 39071 calomel electrode with a Carbo-

rumundum frit. The pH meter was standardized against Beckman Buffer 14268 which has a pH value of 6.83 at 50 °C. The rates of acetyl phosphate decomposition were determined in a Fisher Isotemp Bath Model 15-452 at 50 ± 0.05 °C, unless otherwise noted.

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Chemical Effects of Steric Strains. 22. Rates of Solvolysis of Dimethyl(2-norbornyl)carbinyl *p*-Nitrobenzoates and of the Quaternization of 2-Dimethylaminonorbornanes. A Critical Examination of the Significance of Steric Factors in the Chemistry of *exo*- and *endo*-Norbornyl Derivatives

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Abstract: The techniques previously used to explore the effects of steric strains in strained homomorphs were applied to *exo*- and *endo*-norbornyl derivatives in order to examine the importance of steric effects in the behavior of those derivatives. The solvolysis of dimethyl(*endo*-2-norbornyl)carbinyl *p*-nitrobenzoate proceeds 18 times faster than the *exo* isomer. A similar factor is observed in the solvolysis of neopentyl dimethylcarbinyl *p*-nitrobenzoate which also proceeds 18 times faster than *tert*-butyl *p*-nitrobenzoate. These results are readily interpretable in terms of the relief of steric strain facilitating the solvolysis of both the *endo* isomer and the neopentyl dimethylcarbinyl derivative (a homomorph of di-*tert*-butylmethane). Contrariwise, the rate of reaction of *endo*-dimethylaminonorbornane with methyl iodide proceeds at a rate that is 51 times slower than that of the *exo* isomer. Similarly, neopentyl dimethylamine reacts with methyl iodide at a rate that is 150 times slower than that of *n*-butyl dimethylamine. Here reactions proceeding with an increase in steric strain are resisted. Thus, a close parallelism exists between the behavior of the neopentyl dimethylcarbinyl system, homomorphs of di-*tert*-butylmethane, and that of the dimethyl(*endo*-2-norbornyl)carbinyl system: steric strain facilitates solvolysis but hinders amine quaternization, as compared to less sterically demanding systems. The implication of these results to the *exo*:*endo* rate ratios observed in the solvolysis of 2-norbornyl derivatives is examined.

The high *exo*:*endo* rate ratios observed in the solvolysis of highly stabilized tertiary 2-norbornyl derivatives, such as 2-*p*-anisyl-2-norbornyl² (284) and 2-*p*-anisyl-2-camphenyl² (44 000), cannot be attributed to σ participation.³ Such highly stabilized cations cannot possibly form σ bridges involving the 1,6-bonding pair.⁴ The sole alternative interpretation now receiving serious consideration is steric hindrance to ionization in the *endo* isomer.

It has long been apparent from the Goering-Schewene diagram⁵ that the difference in energies of the two transition states must be far larger than the small differences in the energies of the ground states. In terms of the steric interpretation, this is accounted for by the fact that in solvolysis the *endo* leaving group moves from its less strained normal position into the *endo* cavity, increasing the steric strain and diminishing the usual solvation of the developing anion. Hence, a normal *exo* rate coupled with a slow *endo* rate arising from this large increase in the energy of the *endo* transition state satisfactorily accounts for the high *exo*:*endo* rate ratios observed in such stabilized tertiary 2-norbornyl derivatives.^{4,6}

It has been suggested that the same steric explanation should

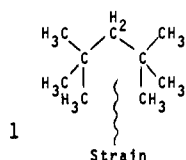
be applicable to the high *exo*:*endo* rate ratios observed in the secondary derivatives.⁴ Recently, Menger and Thanos claimed that the steric explanation is inadequate to account for the observed secondary *exo*:*endo* solvolysis rate ratios.⁷ They compared the rates of NH proton exchange, nitrogen inversion, and amine quaternization of *exo*- and *endo*-2-dimethylaminonorbornanes and stated "the *exo* and *endo* compounds do not display substantial differences as would be expected if the *endo* dimethylamino group were subjected to unusual steric or solvation effects within the *endo* cavity".⁷

It appeared to us that a possible weakness in the Menger and Thanos study was the use of phenomena and reactions which have not been calibrated against other known systems with established major steric requirements. Many years ago we examined the effects of steric strains on the behavior of entire families of strained homomorphs.⁸ We decided to apply the techniques used in that study to the *exo*- and *endo*-norbornyl systems and to compare the results with those realized in the corresponding study of derivatives related to a typical strained homomorph, di-*tert*-butylmethane (1), with established strain of ~ 5.4 kcal mol⁻¹.^{8,9}

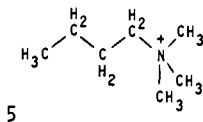
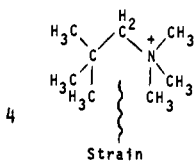
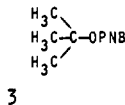
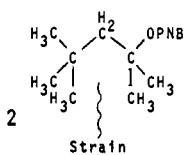
Table I. Rates of Solvolysis of the *p*-Nitrobenzoates in 80% Aqueous Acetone

<i>p</i> -Nitrobenzoate	$10^6 k_1, s^{-1}$		25 °C	$\Delta H^\ddagger,$ kcal mol ⁻¹	$\Delta S^\ddagger,$ eu	Rel rate at 25 °C	
	$T_1, ^\circ C$	$T_2, ^\circ C$					
<i>tert</i> -Butyl ^a	23.3 (125)	1.85 (100)	$7.45 \times 10^{-5} b$	29.2	-7.1	1.00	
Neopentylidimethylcarbonyl	350.0 (125)	29.0 (100)	$1.34 \times 10^{-3} b$	28.8	-2.4	18.0	
<i>exo</i> -2-6	206.0 (125)	16.2 (100)	$6.10 \times 10^{-4} b$	29.4	-2.0	8.2	1.00
<i>endo</i> -2-7	83.1 (100)	6.47 (75)	0.0109 ^b	25.8	-8.5	146.0	18.0

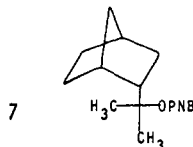
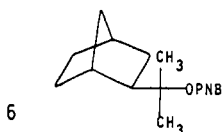
^a H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, **91**, 1226 (1969). ^b Calculated from data at higher temperatures.



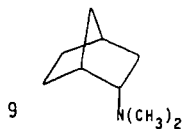
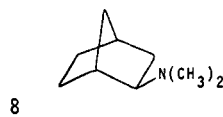
In this study, we examined the rates of solvolysis in 80% aqueous acetone of neopentylidimethylcarbonyl *p*-nitrobenzoate¹⁰ (**2**) with that of the less strained *tert*-butyl derivative (**3**), and the rates of reaction in nitrobenzene of neopentylidimethylamine with methyl iodide with that of the less strained *n*-butylidimethylamine, giving the corresponding quaternary salts (**4**, **5**).



The observed behavior was then compared with that for the relative rates of solvolysis of dimethyl(2-norbornyl)carbonyl *p*-nitrobenzoates (**6**, **7**) and with the relative rates of quaternization of the *exo*- and *endo*-dimethylaminonorbornanes (**8**, **9**).



(Menger and Thanos had determined the relative rates of reaction of the amines, **8** and **9**, with methyl tosylate in acetone.)



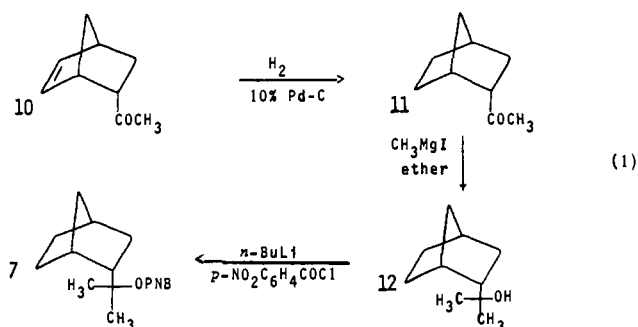
Unfortunately, this reaction does not appear to have been used in other known systems. For that reason, we decided to establish the rates for the well-defined methyl iodide reaction in nitrobenzene solution.)

The question posed was how large might be the effects in a known system, with well-defined strains of ~ 5.4 kcal mol⁻¹, compared with those realized in the 2-norbornyl system itself. Are they comparable, or are they of a totally different order of magnitude, as might be implied by the discussion of Menger and Thanos.⁷

Results

Synthesis. The Diels-Alder reaction between methyl vinyl ketone and cyclopentadiene gave a mixture of *exo*- and

endo-2-acetylnorborn-5-enes.¹¹⁻¹³ Pure *endo* isomer **10** was then hydrogenated and treated with methyl magnesium iodide to yield the tertiary alcohol **12**. The alcohol was converted into *p*-nitrobenzoate **7** by treating the lithium salt with *p*-nitrobenzoyl chloride (eq 1).¹⁴



exo-2-Acetylnorbornane was prepared by the free-radical addition of acetaldehyde to norbornene following the method of Stockmann.¹⁵ The *p*-nitrobenzoate **6** was obtained in the same manner as that outlined in eq 1.

Neopentylidimethylcarbonyl *p*-nitrobenzoate (**2**) was synthesized by oxymercuration-demercuration of 2,4,4-trimethyl-1-pentene, followed by the usual conversion of the alcohol to the *p*-nitrobenzoate. The *exo*- and *endo*-2-dimethylaminonorbornanes (**8**, **9**) were synthesized by the reductive methylation of the corresponding amines with aqueous formaldehyde and sodium cyanoborohydride in acetonitrile.^{7,16} Neopentylidimethylamine was also prepared by the same method.

Kinetic Studies. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% acetone following the standard titrimetric procedure. The rate data and activation parameters are summarized in Table I. The rate of quaternization of amines **8**, **9** with methyl iodide was measured using the literature procedure.¹⁷ The pertinent rate data are tabulated in Table II.

Discussion

The primary objective of the present study was to apply the techniques used previously for the study of strained homomorphs⁸ to an examination of the *exo*- and *endo*-norbornyl systems. The question was whether these techniques would reveal comparable effects of steric strain in *endo*-norbornyl, or would they reveal effects far smaller, as implied by the study and conclusions of Menger and Thanos.⁷

Steric Effects as a Factor in the Chemical Behavior of endo-Norbornyl Derivatives. We selected homomorphs of di-*tert*-butylmethane (**1**) as our comparison system. Here several different approaches had indicated the presence of strains of ~ 5.4 kcal mol⁻¹.^{8,9}

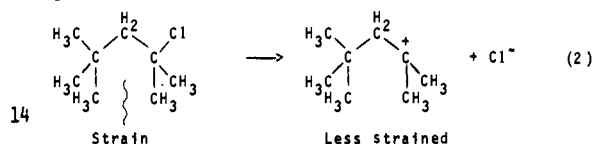
It was previously observed that the solvolysis of neopentylidimethylcarbonyl chloride (**14**) proceeds at a rate 21 times faster than that of *tert*-butyl chloride (**13**) in 80% ethanol at 25 °C.¹⁸ The faster rate was attributed to the relief of steric strain accompanying partial ionization in the transition state

Table II. Rate of Quaternization of the Tertiary Amines with Methyl Iodide in Nitrobenzene

Amine	$k_2, \text{L mol}^{-1} \text{s}^{-1}$		$\Delta H^\ddagger,$ kcal mol^{-1}	$\Delta S^\ddagger, \text{eu}$	Rel rate at 25 °C
	40 °C	25 °C			
<i>N</i> -Butyldimethyl ^a	0.310	0.144	8.4	-34.1	1.00
Neopentylidimethyl	0.00258	9.59×10^{-4} ^b	11.2	-34.6	0.0068
<i>exo</i> -2-Norbornyldimethyl	0.0916	0.0403	9.6	-32.8	1.00
<i>endo</i> -2-Norbornyldimethyl	0.00218	7.94×10^{-4}	11.9	-32.8	0.0196

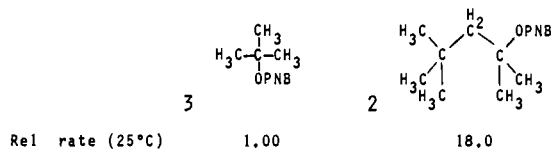
^a Reference 15. ^b Lit.¹⁵ $k_2 = 9.62 \times 10^{-4} \text{L mol}^{-1} \text{s}^{-1}$.

on the way to the less strained neopentylidimethylcarbonyl cation (eq 2).¹⁸



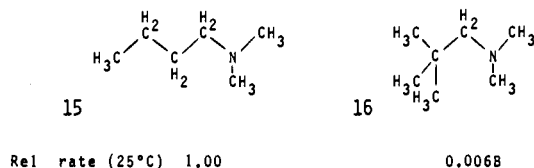
It did not appear practical to use the chlorides corresponding to **6** and **7**. Treatment of such alcohols with hydrogen chloride to form the tertiary chlorides often results in rearrangement involving the neighboring tertiary hydrogen atom.¹⁹ Accordingly, we decided to use the *p*-nitrobenzoates where this uncertainty could be avoided.

Solvolysis of the corresponding *p*-nitrobenzoates **2** and **3** in 80% aqueous acetone revealed a similar factor.



Considerable data has now accumulated that the solvolysis of tertiary derivatives with large bulky groups is assisted by the relief of steric strain (*B* strain) accompanying the transition to a less strained planar carbonium ion.^{19,20} The large increased rates observed in the solvolysis of these neopentylidimethylcarbonyl derivatives do not appear explicable in terms of inductive and hyperconjugative contributions. Relief of steric strain offers a reasonable explanation for these and other enhanced rates.^{18,20}

On the other hand, the reaction of methyl iodide with neopentylidimethylamine (**16**) in nitrobenzene solution at 25 °C proceeds at a rate that is 150 times slower than that of the corresponding reaction with *n*-butyldimethylamine (**15**).

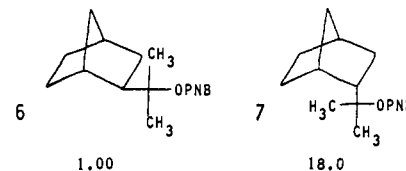


In this case, the reaction of neopentylidimethylamine with methyl iodide would produce the more strained neopentyltrimethylammonium ion **4**, a homomorph of di-*tert*-butylmethane. Such a reaction is resisted and exhibits reduced rates.

It is characteristic of systems with significant steric requirements that the rates of reactions proceeding with a reduction in steric strain are enhanced (steric assistance). Contrariwise, the rates of reactions proceeding with an increase in steric strain are diminished (steric hindrance). What is the situation with respect to the corresponding *exo*- and *endo*-norbornyl derivatives?

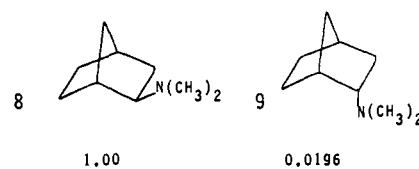
The solvolysis of dimethyl(*endo*-2-norbornyl)carbonyl *p*-nitrobenzoate (**7**) proceeds at a rate 18 times faster than that of the *exo*-2-norbornyl derivative **6**.

It does not appear that anyone has ever argued for an enhanced inductive or electronic effect of the *endo*-norbornyl



group which could be used to account for the enhanced rate observed. On the other hand, relief of steric strain in the *endo* isomer provides a simple, reasonable explanation.

This conclusion is supported by the results of the quaternization study. Here the rate of quaternization is slower for the *endo* isomer **9** than for the *exo* isomer **8** by a factor of 51.



Thus we are observing a consistent pattern of reactivity in both the neopentylidimethylcarbonyl and the norbornyl systems—increases in rates in solvolysis, a reaction which proceeds with a decrease in steric strain, and decreases in rates in quaternization, a reaction which proceeds with increase in steric strain. There appears to be no basis to question the conclusion that *endo*-norbornyl is a sterically crowded system which exerts steric effects anticipated for such a system.

Magnitude of the Steric Effects. The *exo*:*endo* rate ratio in the acetolysis of 2-norbornyl tosylate is 280²¹ (~1600 if we correct for internal return²²). Menger and Thanos argue that an *exo*:*endo* rate ratio of 51, observed for the quaternization reaction, is simply too small to account for the solvolysis factor.

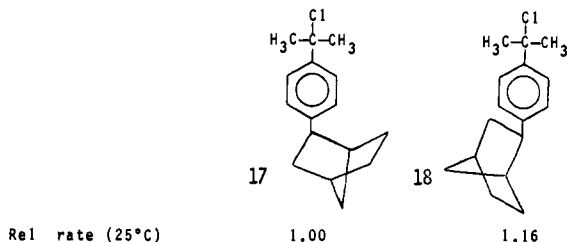
This question was considered much earlier. Is a factor of 150 observed in neopentylidimethylamine reasonable for a system involving generation of a structure containing steric strain of 5.4 kcal mol⁻¹? An increase of 5.4 kcal mol⁻¹ in energy of activation should result in a decrease in rate by a factor of 10⁴. Yet the observed change is only 10²! It was argued that neopentylidimethylamine was itself moderately strained. In addition, the strain was only partially developed in the transition state. Consequently, the factor of 10⁴ must represent the upper limit, and the observed decrease of 10² was indeed reasonable.⁸

In addition, we must consider another factor in comparing the *exo*:*endo* factor of 51 for the quaternization reaction with the factor of 280 (1600) for the solvolysis reaction. In the solvolysis reaction, the alterations in the steric effects involve changes in a ring atom (C₂). In the quaternization, the chemical change is taking place at an atom α to C₂. Surely it is not unreasonable that the steric effects should be somewhat smaller at the more remote position.

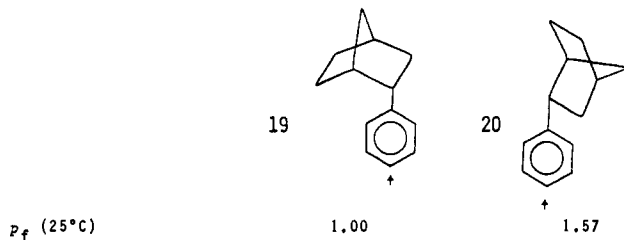
Electronic Effects of the 2-Norbornyl System. Menger and Thanos argued that, since their tests revealed only relatively small differences between *endo*- and *exo*-norbornyl, the much larger *exo*:*endo* rate ratio must be an electronic effect, which operates in the *exo*, but is absent in the *endo*.

Numerous attempts have been made to find such a differ-

ential electronic effect. Thus, we studied the solvolysis of *tert*-cumyl derivatives containing *exo*- and *endo*-norbonyl groups in the para position (**17**, **18**).²³ The effect is minor.



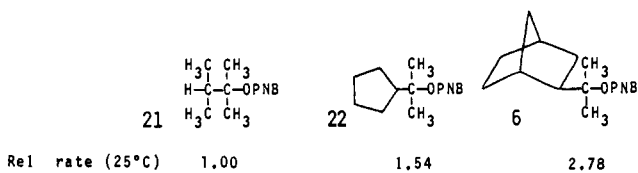
A slightly larger effect was observed by Jensen and Smart for the partial rate factors, p_f , in the benzylation of the phenylnorbornanes **19** and **20**.²⁴



It can be argued that these systems fail to provide a fair test for the proposal. The amount of charge delocalized to the para position is relatively small and can only induce a minor response from the 2-norbonyl structure.

The present study provides a more rigorous test of this proposal. In **6** and **7**, the developing cationic charge is α to the 2-norbonyl system. If the system provides preferential electronic stabilization from the *exo* direction, the rate of the *exo* derivative should be considerably enhanced over the rate of the *endo*, but that is not observed. Clearly such rate enhancement as is observed must be small and greatly overshadowed by the effect of relief of steric strain in the *endo* isomer.

That conclusion is supported by a comparison of the rates of solvolysis of dimethyl(*exo*-2-norbonyl)carbinyl *p*-nitrobenzoate (**6**) with the related isopropyl (**21**) and cyclopentyl (**22**) derivatives. These results fail to support the presence of



any exceptional electronic contribution from the *exo*-norbonyl moiety.

Conclusion

The present study supports the conclusion that steric factors play an important role in the different behavior of *exo*- and *endo*-norbonyl derivatives. Their behavior reveals a consistent pattern of reactivity, very similar to those previously established for strained homomorphs. Very high *exo*:*endo* rate ratios are observed in highly stabilized 2-*p*-anisyl-2-norbonyl (284) and 2-*p*-anisyl-2-camphenyl (44 000) derivatives where σ bridging cannot be a factor.² The proposal of steric hindrance to ionization provides a consistent explanation for the high *exo*:*endo* rate ratios observed in the solvolysis of both secondary and tertiary 2-norbonyl derivatives.

Experimental Section

endo-2-Acetylnorborn-5-ene was prepared by the Diels-Alder reaction of methyl vinyl ketone and cyclopentadiene.¹³ Pure *endo* isomer was obtained by preparative GLC (20% Carobwax 20M on Chromosorb W 60/80 mesh, 95 °C), n_{D}^{20} 1.4839 (lit.¹³ n_{D}^{20} 1.4843).

endo-2-Acetylnorbornane. This compound was obtained by the hydrogenation of *endo*-2-acetylnorborn-5-ene over 10% palladium on carbon at 40 psi in 92% yield, bp 92–93 °C (21 mm), n_{D}^{20} 1.4745 (lit.¹¹ n_{D}^{25} 1.4722).

exo-2-Acetylnorbornane was synthesized by the free-radical addition of acetaldehyde to norbornene following the method of Stockmann in 78% yield, bp 80–81 °C (15 mm) (lit.¹⁵ bp 79–81 °C (15 mm)), n_{D}^{20} 1.4739 (lit. n_{D}^{24} 1.4709).

Dimethyl(endo-2-norbonyl)carbinol. Addition of the ketone to methylmagnesium iodide in ether afforded the tertiary alcohol in 95% yield: ¹H NMR (CCl₄) δ 1.10, 1.18 (2 CH₃), 2.21 (br, bridgehead protons), 0.83–1.70 (remaining protons).

Dimethyl(exo-2-norbonyl)carbinol. Addition of the *exo* ketone to methylmagnesium iodide in ether yielded the *exo* tertiary alcohol (92% yield): ¹H NMR (CCl₄) δ 1.06, 1.13 (2 CH₃), 2.21 (br, bridgehead protons), 0.83–1.67 (remaining protons).

Dimethyl(endo-2-norbonyl)carbinyl p-Nitrobenzoate. This compound was prepared by treating the alcohol with *n*-butyllithium and *p*-nitrobenzoyl chloride in THF;¹⁴ mp 82.5–83 °C; ¹H NMR (CCl₄) δ 1.63, 1.71 (2 CH₃), 2.38 (bridgehead), 1.16–2.20 (br, remaining protons), 8.18 (m, 4H, aromatic). Anal. Calcd for C₁₇H₂₁NO₄: C, 67.32; H, 6.98; N, 4.61. Found: C, 67.47; H, 6.98; N, 4.74.

Dimethyl(exo-2-norbonyl)carbinyl p-Nitrobenzoate. This *p*-nitrobenzoate was obtained by treating the lithium salt of the alcohol with *p*-nitrobenzoyl chloride in THF in the usual manner;¹⁴ mp 102.5 °C; ¹H NMR (CCl₄) δ 1.56 (2 CH₃), 2.33 (bridgehead protons), 1.00–2.00 (remaining protons), 8.13 (m, 4H, aromatic). Anal. Calcd for C₁₇H₂₁NO₄: C, 67.32; H, 6.98; N, 4.61. Found: C, 67.38; H, 6.91; N, 4.64.

Neopentyl dimethylcarbinol. Oxymercuration–demercuration²⁵ of 2,4,4-trimethyl-1-pentene gave the alcohol in 92% yield, bp 112–113 °C (12 mm) (lit.¹⁸ bp 146–146.5 °C (750 mm)).

Neopentyl dimethylcarbinyl p-Nitrobenzoate. The tertiary alcohol was treated with *n*-butyllithium and *p*-nitrobenzoyl chloride to yield the *p*-nitrobenzoate, mp 64.5–65 °C.

Neopentyl dimethylamine. Neopentylamine was reductively methylated with 37% aqueous formaldehyde and sodium cyanoborohydride in acetonitrile following the procedure of Borch and Hassid.¹⁶ The crude product was distilled to give a 84% yield of the pure tertiary amine, bp 94.5–95 °C (749 mm) (lit.¹⁷ bp 94.7–95.2 °C (749 mm)), n_{D}^{20} 1.3970 (lit.¹⁷ n_{D}^{20} 1.3970).

exo-2-Dimethylaminonorbane was synthesized by the reductive methylation of the *exo* amine following the literature procedure¹⁵ in 55% yield, bp 66–67 °C (15 mm) (lit.²⁶ bp 71 °C (20 mm)).

endo-2-Dimethylaminonorbane. *endo*-2-Aminonorbane hydrochloride (Aldrich) was treated with aqueous alkali to generate the free amine and then reductively methylated to yield the tertiary amine (50% yield), bp 64–65 °C (15 mm) (lit.²⁶ bp 68–69 °C (13 mm)).

Rates of Solvolysis. The rates of solvolysis of the *p*-nitrobenzoates were determined following the literature procedure.¹⁴ The rate constants are reproducible to $\pm 1\%$.

Rates of Amine Quaternization. The procedure followed is essentially the same as described in the literature.¹⁷ The concentration of amine and methyl iodide solutions were checked before each run. The rate constants in Table II are the average of at least two kinetic runs.

References and Notes

- Postdoctoral research associate on a grant supported by the Exxon Research and Engineering Co.
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σ Ground State of the Benzoyloxy Radical

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Abstract: The ground state of benzoyloxy radical is examined by two methods: (1) the comparison of the direction cosines of the experimental g tensor reported² with the x-ray crystallographic data of the host molecule in single crystals, and (2) calculation of the g tensors in various possible ground states of acetoxy radical as a model. The two considerations agree and support the assignment of the ${}^2A'$ σ ground state of the benzoyloxy radical, rather than the 2A_2 π state.

Several acyloxy radicals³⁻⁸ have been observed in single crystals by electron spin resonance (ESR) and their g tensors were reported. All of these radicals were found to have σ ground states on the basis of their g tensors. Hyperfine tensors were reported for some of these radicals³⁻⁶ and the same conclusions were obtained from this information. All acyl radicals⁹⁻¹⁶ obtained in single crystals and in polycrystalline matrices are also reported to be σ radicals based on their g tensors and hyperfine tensors.

The most common assumption for utilizing eigenvectors (direction cosines) for spectral assignment in single crystals is that the local symmetry of radicals is fundamentally the same as the radical precursor in the matrix. This assumption has been justified in the case of acyl type radicals by observing a large ${}^{13}\text{C}$ hyperfine splitting constant.^{13,16}

Kikuchi et al.¹⁷ applied the semiempirical NDDO MO method¹⁸ to formyloxy and acetoxy radicals and predicted σ ground states.

Recently, Karch et al.² reported the g tensor of the benzoyloxy radical obtained during the course of the investigation of radical pairs in crystalline acetylbenzoyl peroxide. They tentatively assigned the ground state as a 2A_2 π state of C_{2v} symmetry on the basis of INDO and ab initio STO-3G calculations and ${}^{13}\text{C}$ CIDNP. In view of the characterization of σ ground states for all previously characterized acyl and acyloxy radicals, the π ground state assignment for benzoyloxy radical in single crystal is quite unusual. Since an experimental g tensor was reported² it is possible to characterize the ground state of this radical from experimental data alone.

The reliability of a NDDO prediction of the correct ground state for radicals is not absolute owing to the uncertainties of semiempirical MO calculations of total energies. However, it can reliably predict a variety of molecular properties if the symmetry and ground state are given. The g tensors of several σ -type radicals have been successfully estimated¹⁹ in this way.

We present here (1) a reexamination of the ground state of benzoyloxy radical in single crystal from an analysis of the reported g tensor alone and (2) a calculation of the g tensor of acetoxy radical as a model by the semiempirical NDDO MO method.

Results and Discussion

A. g Tensor Analysis. Table I shows the reported² principal values and direction cosines of the g tensor for the benzoyloxy radical produced by the photolysis of crystalline acetylbenzoyl peroxide and the bond directions of the host molecule calculated from the orthogonal axes (a*, b, c).²⁰ The directions are portrayed against the background of a partial skeleton of acetylbenzoyl peroxide in Figure 1.

Since g_2 is $(\Delta g)_{\min}$ for this radical, the unpaired electron orbital should lie very close to this direction. The g_2 axis of this radical lies 86.5° away from the direction of a π type orbital while the g_3 axis is perpendicular to the carboxyl plane within 7° (see Table I). The sum of the angles of the g_2 and g_3 axes with the O_3C_3 bond is 95.5°, which is 5.5° larger than it should be. This angle deviation is quite consistent with a deviation of g_3 of 7° from the normal to the carboxyl plane. It may originate from distortion from its undamaged position and/or nonplanarity of the radical carbon by the above amount. Thus the unpaired electron orbital cannot be a π orbital unless the carboxyl plane has turned sideways dramatically (~80°) with respect to its undamaged position.

Two extreme cases can be considered for the unpaired electron orbital for this radical: (1) the unpaired electron is located *mostly* along the cleaved bond on O_3 with C_s symmetry; (2) the unpaired electron is equally distributed between O_3 and O_4 with C_{2v} symmetry. The first case is a ${}^2A'$ state and the second case will be either the 2A_1 or 2B_2 states² (Figure 2). Taking case 1 first, an idealized P_σ orbital on the O_3 atom of the radical will make angles of 90 and 20.9° with the $\text{C}_3\text{-O}_3$ and $\text{O}_2\text{-O}_3$ bond directions, respectively, of the host molecule