All the reactions were carried out under pseudo-first-order conditions and the rate constants were calculated by the use of the equation

$$k_1 = \frac{2.303}{t} \log \frac{A_\infty - A_0}{A_\infty - A_t}$$

wherein A_∞ is the measured infinity absorption, A_0 is the absorbance at $t = 0$, and A_t is the absorbance at time t. Second-order rate constants were obtained by dividing the first-order rate constant by the base concentration.

The reported rate constants from both the titrimetric and spectrophotometric runs were calculated on an IBM 7044 computer using the method of least squares. In most cases duplicate runs were measured.

Ultraviolet Spectra of 1-Aryl-1-propenes and 2-Arylpropenes.—Molar extinction coefficients measured in 95% ethanol were the following: 1-phenyl-1-propene, 18,600 (248 mμ); 1-(4-chlorophenyl)-1-propene, 24,500 (255 mμ); 1-(3-bromophenyl)-1-propene, 20,900 (253 mμ); 1-(4-methoxyphenyl)-1-propene, 22,400 (258 mμ); 2-phenylpropene, 11,400 (243 mμ); 2-(4-chlorophenyl)propane, 15,700 (248 mμ); 2-(3-bromophenyl)-propene, 10,700 (245 mμ); 2-(4-methylphenyl)propene, 13,700 (248 mμ); and 2-(4-methoxyphenyl)propene, 16,200 (257 mμ).

Registry No.—Table I (X = OTs, Y = H), 14135-71-8; Table I (X = OTs, *p*-Cl), 23430-31-1; Table I (X = OTs, *m*-Br), 23430-32-2; Table I (X = OTs, *p*-CH_3), 23430-33-3; Table I (X = OTs, *p*-OCH_3), 898-95-3; Table I (X = Br, H), 2114-39-8; Table I (X = Br, *p*-Cl), 23430-36-6; Table I (X = Br, *m*-Br), 23430-37-7; Table I (X = Br, *p*-CH_3), 2114-40-1; Table I (X = OTs, β-phenylethyl), 4455-09-8; Table I (X = Br, β-phenylethyl), 103-63-9; Table III (X = OTs, Y = *p*-H, Z = H), 23430-41-3; Table III (X = OTs, *p*-Cl, H), 23465-00-1; Table III (X = OTs, *m*-Br, H), 23430-42-4; Table III (X = OTs, *m*-Br, D), 23430-43-5; Table III (X = OTs, *p*-CH_3, H), 23430-44-6; Table III (X = OTs, *p*-CH_3, D), 23430-45-7; Table III (X = OTs, *p*-OCH_3, H), 23430-46-8; Table III (X = Br, H, H), 1459-00-3; Table III X = Br, *p*-Cl, H), 23430-48-0; Table III (X = Br, *m*-Br, H), 23430-49-1; Table III (X = Br, *m*-Br, D), 23430-50-4; Table III (X = Br, *p*-CH_3, A), 23430-51-5; Table III (X = Br, *p*-CH_3, D), 23430-52-6; Table III (X = Br, *p*-OCH_3, H), 23430-53-7.

Electronic Effects in Elimination Reactions. VII. *syn* and *anti* Eliminations of the 3-Phenyl-2-norbornyl Tosylates[1]

C. H. DEPUY,[2] CARTER G. NAYLOR,[3] AND JOSEPH A. BECKMAN[4]

Departments of Chemistry, University of Colorado, Boulder, Colorado 80302, and Iowa State University, Ames, Iowa 50010

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The four isomeric 3-phenyl-2-norbornyl *p*-toluenesulfonates were subjected to elimination in order to study the effect of geometry on the rate. The relative rates in potassium *t*-butoxide–*t*-butyl alcohol at 50° for the four modes of elimination are *exo–syn* (*exo*-β hydrogen–*syn* elimination)/*exo–anti*/*endo–syn*/*endo–anti* = 100:3.1:0.12:0.21. The rate differences are ascribed to a combination of dihedral angle, *endo*-hydrogen removal, and *endo* leaving group effects. The Hammett ρ values for *exo–syn* and *exo–anti* are both much larger than that for an *anti*-coplanar elimination. These results imply that *syn* elimination has an inherently greater demand for carbanion character than *anti* elimination, and that noncoplanar geometry increases the electronic requirements of *anti* elimination.

The usually preferred stereochemistry for bimolecular elimination is an *anti*-coplanar relationship between the acidic hydrogen and the leaving group,[5] but *syn* pathways have been shown to compete effectively with *anti* elimination in certain rigid cyclic systems,[6] and occasionally in flexible cyclic and acyclic systems.[7] It was theorized[6] that the rate of elimination is maximized as the dihedral angle between leaving group and acidic hydrogen approaches 180° (*anti* coplanar) and 0° (*syn* coplanar). Hine[8] has given a semitheoretical justification for this concept based on the "principle of least motion" involving a mechanical model of the E2 transition state. A quantum mechanical argument has been presented by Eliel, *et al.*,[9] to show that *syn*-coplanar elimination should be less favorable than *anti*-coplanar elimination, aside from all other factors such as steric and electrostatic repulsions.

The present study of 3-phenyl-2-norbornyl tosylates is an extension of earlier work[6] on the mechanisms of *syn* and *anti* eliminations of the 2-phenylcyclopentyl tosylates, which gave the first direct comparison of electronic requirements for *syn* and *anti* eliminations in a β-phenylethyl system. The norbornyl system has the advantage of a better defined geometry in which the dihedral angles are accurately known. Cyclopentyl derivatives are more flexible, so the ground-state geometry is not necessarily the same as that for the elimination transition state.

Results

The preparation of the four isomeric 3-phenyl-2-norbornyl tosylates was recently reported by Kleinfelter.[10] The same synthetic route to *endo*-3-phenyl-

(1) Part VI: C. H. DePuy, D. L. Storm, J. T. Frey, and C. G. Naylor, *J. Org. Chem.*, **35**, 2746 (1970). This work was supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of said funds.

(2) To whom correspondence should be addressed at the University of Colorado.

(3) NSF Summer Research Participant, 1966; NIH Predoctoral Fellow, 1966–1968. Taken in part from the Ph.D. thesis of C. G. N., University of Colorado, 1968.

(4) Taken in part from the Ph.D. thesis of J. A. B., Iowa State University, 1965.

(5) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., Amsterdam, 1963.

(6) C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Amer. Chem. Soc.*, **87**, 2421 (1965).

(7) J. Sicher, M. Havel, and M. Svoboda, *Tetrahedron Lett.*, 4269 (1968), and earlier papers.

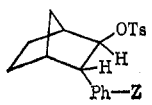
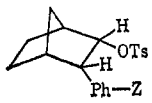
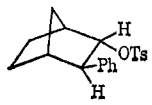
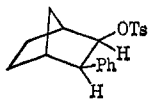
(8) J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

(9) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, p 483.

(10) D. C. Kleinfelter, *J. Org. Chem.*, **32**, 840 (1967); D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *ibid.*, **37**, 1734 (1967).

TABLE I

ELIMINATION RATE DATA FOR 3-ARYL-2-NORBORNYL TOSYLATES AT 50°

	Compound	Z	$k_{E2} \times 10^4$ (l. mol^{-1} sec^{-1}) t-BuOK–t-BuOH	% elimination	$k_{E2} \times 10^4$ (l. mol^{-1} sec^{-1}) EtONa–EtOH	% elimn
			exo–syn			
A		H	15.70 ± 1.50[a]	100		
		H	2.34 ± 0.05 (30°)	100		
		p-CH_3	7.06 ± 0.42	100		
		p-Cl	83.7 ± 0.4	100	1.45	48
		m-Cl	255 ± 12	100	2.37	74
			exo–anti			
B		H	0.482 ± 0.017	92	0.088 ± 0.005	62
		p-CH_3	0.185 ± 0.004	68		
		p-Cl	1.82 ± 0.23	100[b]		
		m-Cl	3.69 ± 0.15	100		
			endo–syn			
C			0.0195 ± 0.0005	94 ± 4		
			endo–anti			
D			0.0335 ± 0.0020	55 ± 3 (Base = 0.400 *M*)		
			0.0334 ± 0.0032	79 ± 2 (Base = 0.915 *M*)		

[a] Average deviation from the mean of two or more runs. [b] Assumed.

exo-2-norbornanol was used in the present work; oxidation of this alcohol to the corresponding ketone was achieved with dimethyl sulfoxide and dicyclohexylcarbodiimides.[11] This procedure yielded an epimeric mixture of 3-phenylnorbornanones, which was then reduced to a mixture of isomeric alcohols. This mixture was partially separable by crystallization and chromatography. (A sample of the least plentiful isomer, *exo*-3-phenyl-*exo*-2-norbornanol, was kindly supplied by Professor Kleinfelter.)

In Table I are given the measured second-order rate constants of the four isomeric tosylates. Included are data for phenyl-substituted tosylates of isomers A and B.

These tosylates gave good second-order kinetics and 100% elimination in most cases in *t*-butoxide–*t*-butyl alcohol. Because of the small quantities of isomers C and D available and their very slow rates, the rate constants are more uncertain. Percentages of elimination were calculated from ultraviolet absorbance infinity values and the measured extinction coefficients of the arylnorbornenes. Although the infinity samples did not discolor, polymerization of the 2-arylnorbornene products was possible because of the long time required for completion of the reactions. Thus the reported percentages are best regarded as minimum values.

Tosylate D gave the same k_{E2} but a higher olefin yield with higher base concentration. This is evidence for competition from a first-order ionization reaction. Simple calculations based on known data suggest that D can undergo processes other than 1,2 elimination. Nickon[12] measured the solvolysis rate of *exo*-norbornyl tosylate in *t*-butyl alcohol at 60° ($k_1 = 1.3 \times 10^{-5}$ sec^{-1}) while Kleinfelter[13] solvolyzed isomer D and *exo*-norbornyl tosylate in acetic acid. Assuming the *exo*-phenyl group decreases the solvolysis rate by the same factor in *t*-butyl alcohol as in acetic acid (128), a first-order rate constant for the solvolysis of D in *t*-butyl alcohol can be estimated ($k_1 = 1 \times 10^{-7}$ sec^{-1} at 60°, $\sim 0.5 \times 10^{-7}$ at 50°). The pseudo-first-order rate constant for D at 50°, 0.40 *M* *t*-butoxide, is 12.6×10^{-7} sec^{-1}. Therefore about 4% of the substrate is estimated to be reacting by an E1–SN1 pathway (2% at 0.915 *M* base), assuming all the olefin product arises from an E2 reaction. Second-order 1,3 elimination is also probably occurring.[12] Until product analyses and more accurate kinetic data are gathered, little more can be said about the non-E2 processes.

endo-Norbornyl tosylates solvolyze much more slowly than *exo*-tosylates;[13] so isomers B and C do not undergo E1–SN1 processes during elimination, but they are subject to 1,3 elimination and direct displacement reactions.[12] Vpc analysis of the reaction mixture of B revealed a product of shorter retention time than 2-phenylnorbornene which is assumed to be phenylnortricyclene. No peak of longer retention time was observed, so apparently no ether was formed. The few per cent nonolefin product from C was not identified.

Table II compares the phenylnorbornyl elimination data with those of 2-phenylcyclopentyl[6] and 2-phenylcyclobutyl[14] tosylates. Included are ρ values calculated from the data in Table I.

Discussion

If the cyclopentane ring were planar, the dihedral angle for *trans*-2-phenylcyclopentyl tosylate would be 0° and that for the *cis* isomer would be 120°. However, eclipsing effects force the ring out of planarity;[15] so that the two dihedral angles being considered are greater than 0° and 120°. Thus *syn* elimination is rendered less favorable, while the *anti* pathway becomes more favorable. Models suggest that the *cis* isomer can

(11) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661 (1965).

(12) A. Nickon and N. H. Werstiuk, *ibid.*, **89**, 3915 (1967).

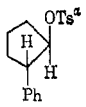
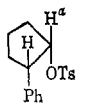
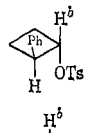
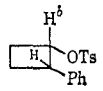
(13) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, **88**, 5350 (1966).

(14) C. H. DePuy and C. H. Hendrickson, unpublished work.

(15) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, p 200.

TABLE II

syn:*anti* RATE RATIOS AND ρ VALUES AT 50°

Compound	Mode	*syn*:*anti*	*t*-BuOK–*t*-BuOH	ρ	EtONa–EtOH	ρ
A	*exo–syn*		15.7	3.12 ± 0.05	1.0[c]	2.1[c]
		30.7				
B	*exo-anti*		0.482	2.56 ± 0.01	0.087	
C	*endo–syn*		0.0195			
		0.58				
D	*endo–anti*		0.0334			
	*syn*		2.9	2.76		
		0.10				
	*anti*		29.1	1.48	24.2	0.99
	*syn*		5.10	2.90		
		0.39				
	*anti*		13.0	2.18	1.16	1.26

[a] Reference 6. [b] Reference 14. [c] Calculated from a plot of two points.

achieve a dihedral angle approaching 180° with little strain. In fact *cis*-2-phenylcyclopentyl tosylate, with low ρ values and high rates in the two base–solvent media used, appears to exhibit behavior normal for an α,β-dialkyl-β-phenylethyl tosylate,[1] which presumably would undergo *anti*-coplanar elimination and show E1-like behavior.

Cyclobutane is puckered 25–30° out of planarity;[16] so dihedral angles are close to 30° and 150° for *cis* and *trans* substituents, respectively. That these angles are closer to 0° and 120° than those in cyclopentane is reflected in the larger *syn*:*anti* rate ratio. The *syn* rate is faster than that in the cyclopentyl system even though a more highly strained olefin is being formed, and the *anti* rate is slower.

The norbornane ring system is more rigid than the cyclobutyl or cyclopentyl system, so that the dihedral angles between hydrogen and leaving groups should be very close to 0° and 120° for *syn* and *anti* elimination, respectively. Torsional effects may prevent exact eclipsing, but the deviation is expected to be small. We, therefore, felt that in isomer A we would have very nearly the best possible model for a *syn* elimination, and in isomer B a similarly good example of a noncoplanar *anti* elimination. By comparing isomer C and D where these angles are equally well determined, with A and B we hoped to be able to separate various steric factors from conformational effects. In this we were only partly successful.

The elimination rates from isomers A and B were fully in accord with predictions made on the basis of the earlier hypotheses.[6] In the first place the *endo*-phenyl *exo*-tosylate (A) undergoes a bimolecular *syn* elimination with *t*-butoxide–*t*-butyl alcohol 30 times more rapidly than its isomer *endo*-phenyl *endo*-tosylate (B) undergoes *anti* elimination under the same conditions. This is by far the largest *syn*:*anti* ratio observed in the β-phenylethyl tosylate system, the corresponding ratio in the cyclopentyl compounds being 0.10.[17] In accordance with predictions we see that the change in ratio from 0.10 to 30 is due to a combination of two factors, a fivefold *increase* in the rate of *syn* elimination, and a 60-fold *decrease* in the rate of *anti* elimination. These changes are in the expected order if, in the norbornyl system, the *syn* elimination is more coplanar and the *anti* elimination is less coplanar, the latter being rigidly constrained to a 120° geometry. Acceleration of elimination due to *endo*-steric interactions in compound B is obviously not a significant factor.

The Hammett ρ values are also in accord with expectations (Table II). We have shown previously[6] that *syn* eliminations are more E1cB-like than *anti* eliminations; their ρ values are relatively high. So, too, ρ for *syn* elimination from the norbornyl tosylates is high. More enlightening is the high ρ value for *anti* elimination from the norbornyl compounds. If we examine a series of compounds 2-aryl-cyclopentyl tosylate, 2-aryl-cyclobutyl tosylate, and *endo*-2-aryl-*endo*-norbornyl tosylate in which the attainment of an *anti*-coplanar transition state becomes progressively more difficult, we find a steady increase in the ρ value for *anti* elimination, the values being 1.48, 2.18, and 2.56, respectively. Presumably these results indicate that, as the *anti* elimination deviates from exact coplanarity, more carbanionic character is needed in the transition state to drive off the leaving group. However, the rate of *anti* elimination is much less sensitive to deviations from coplanarity than is the rate of *syn* elimination.

Our studies of the *endo–syn* and *endo–anti* eliminations (compounds C and D) were hampered by synthetic difficulties, and by the much lower rates of elimination of the compounds, which allowed other reactions pathways to compete. Both *syn* and *anti* rates dropped, probably reflecting the lesser accessibility of

(16) J. D. Roberts and M. C. Caserio, "Modern Organic Chemistry," W. A. Benjamin Inc., New York, N. Y., 1967, p 91.

(17) It should be recalled that the corresponding ratio in the cyclohexyl system is <0.0001, presumably because a boat form would be required for a coplanar *syn* elimination.[6]

the *endo* hydrogen, but the *syn* rate dropped more than the *anti* rate. Nevertheless, the *syn*:*anti* ratio (0.6) is larger than that for any tosylate system so far investigated with the exception of the *exo* eliminations in this same system.

Ordinarily it is not possible to observe *syn* eliminations of tosylates in sodium ethoxide-ethanol solution. Since *syn* eliminations are E1cB-like, their rates are decreased by the use of a weak base like ethoxide, and the polar medium promotes competing solvolysis reactions. Because of the rapidity of *exo*–*syn* elimination, however, we were able to observe *syn* E2 eliminations in activated aryl systems. We have pointed out previously[6] the possible mechanistic significance of *t*-BuO$^-$:EtO$^-$ rate ratios. For this *syn* elimination this ratio is 50–100, while for the corresponding *exo*–*anti* elimination it is only 5, and in coplanar *anti* eliminations it can be considerably less than 1.

The data gathered by LeBel[18] on the elimination reactions of 2,3-dihalonorbornenes show qualitatively the same dependence of relative rate on dihedral angle and proton accessibility. LeBel concluded that the mechanisms are concerted and E1cB-like. The present results, by allowing quantitative comparisons with other cyclic and noncyclic β-phenylethyl systems, strengthen and extend these conclusions.

Experimental Section

Melting points and boiling points are uncorrected. Vapor phase chromatographic analyses were performed on an Aerograph 200 or an F & M 700 instrument. Nmr spectra were measured on a Varian A-60 or A 60A spectrometer; chemical shifts are reported in parts per million from internal standard tetramethylsilane in δ units. Spectra descriptions are as follows: peak multiplicity—s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); peak areas—*n* (*n* protons). Ultraviolet spectra were measured on a Beckman model DK-2A or Coleman–Hitachi 124 spectrometer. Elemental analyses were performed by the Weiler and Strauss Analytical Laboratory, Oxford, England, Dr. A. Bernhardt of the Max-Planck-Institute, Mülheim, Germany, and Huffmann Laboratories, Wheatridge, Colo.

Preparation and Purification of Materials. Preparation of 2-Phenylbicyclo[2.2.1]heptyl Compounds. 2-Arylnorbornenes.—To an ether solution of phenyllithium prepared from 5.0 g (0.721 g-atom) of lithium and 93.0 g (0.592 mol) of bromobenzene was added an ether solution of 50.0 g (0.454 mol) of 2-norbornanone (Aldrich Chemical Co.) at a rate sufficient to maintain gentle reflux. The solution was allowed to stir for 2 hr and water was added slowly to remove excess phenyllithium and hydrolyze the salts. The aqueous phase was separated and extracted three times with portions of fresh ether. The combined ether solutions were dried over $MgSO_4$ and most of the ether was removed by atmospheric distillation. Approximately 0.1 g of *p*-toluenesulfonic acid was added and the contents of the flask were heated vigorously to promote dehydration. The water formed in the dehydration was removed by azeotropic distillation with benzene and the residue was distilled to yield 56.4 g (0.331 mol) of olefin, bp 79–81° (0.7 mm), lit.[19] bp 124–128° (17 mm) 73% yield. Vpc analysis showed the olefin to be about 98% pure, the remainder being a peak of shorter retention time, presumably phenylnortricyclene.

The *p*-methylphenyl compound was made by the same procedure using *p*-bromotoluene. The *m*-chlorophenyl and *p*-chlorophenyl compounds were made by the same procedure using Grignard reagents: 2-*p*-methylphenylnorbornene, bp 89–90° (0.3 mm), 73.4% yield; 2-*m*-chlorophenylnorbornene, bp 99–100° (0.45 mm), 78.3% yield; 2-*p*-chlorophenylnorbornene, bp 106–110° (0.9 mm), mp 55–57°, 73% yield.

endo-**3-Aryl-*exo*-2-norbornanols.**—2-Phenylbicyclo[2.2.1]hept-2-ene, 27.0 g (0.159 mol), and sodium borohydride, 3.2 g (0.085 mol), were dissolved in 150 ml of diglyme. To this solution of 13.0 g (0.092 mol) of boron trifluoride etherate in 40 ml of diglyme was added over a period of 1 hr. The solution was chilled in an ice bath and stirred for 2 additional hr. Water (20 ml) was added cautiously, followed by 40 ml of 3 *M* sodium hydroxide and 40 ml of 30% hydrogen peroxide solution. This mixture was stirred for 1 hr and was then poured into ice–water. The organic material was extracted with ether and the ether solution was dried and distilled to yield 21.8 g of alcohol, bp 111–113° (0.7 mm), 73% yield. Nmr analysis indicated that the hydroxyl group was exclusively in the *exo* position: *endo*-3-*p*-methylphenyl-*exo*-2-norbornanol, bp 130–133° (0.7 mm), mp 81.5–82°, 77% yield; *endo*-3-*m*-chlorophenyl-*exo*-2-norbornanol, bp 153–159° (0.9 mm), mp 75.5–76°, 66% yield; *endo*-3-*p*-chlorophenyl-*exo*-2-norbornanol, bp 124–129° (0.5 mm), 55% yield.

3-Phenyl-2-norbornanone.—To dimethyl sulfoxide (100 ml, distilled from calcium hydride under aspirator pressure) in a dry flask was added 14 g of 100% phosphoric acid and 31.2 g of 3-phenyl-2-norbornal in 100 ml of dry ether. When dicyclohexylcarbodiimide (100 g, Aldrich Chemical Co.) in 50 ml of ether was added, a precipitate began forming and the mixture became warm. After stirring 6 hr the solution was filtered to remove the dicyclohexylurea. To the filtrate was added 25 g of oxalic acid in 70 ml of methanol, and the mixture was again filtered. The solution was washed with aqueous sodium bicarbonate and water, then dried. Solvent removal and vacuum distillation gave 25 g of the ketone (75%): nmr[20] δ 1.3–1.9 (m, 6), 2.5–2.9 (2 m, 2), 3.32 (d, 1), 7.2 (s, 5). *endo*-3 H appears at 2.93 in epimerized ketone mixture.

In the same manner the three phenyl-substituted ketones were prepared: 3-(*p*-methylphenyl)-2-norbornanone, bp 120–130° (0.4 mm); nmr δ 1.1–2.0 (m, 6), 2.23 (s, 3), 2.4–2.8 (m, 2), 2.88 (d, 0.4), 3.25 (d, 0.6), 7.0 (s, 4). The two fractional peaks represent the *endo* and *exo* epimeric benzylic protons, respectively. 3-(*p*-Chlorophenyl)-2-norbornanone had mp 65–66°; nmr δ 1.3–2.2 (m, 6), 2.6–3.0 (2 m, 2), 3.33 (d, 1), 7.2 (s, 4). 3-(*m*-Chlorophenyl)-2-norbornanone had nmr δ 1.0–2.0 (m, 6), 2.3–3.0 (m, 2), 3.25 (d, 1), 7.1 (m, 4). *endo*-3-Phenyl-*endo*-2-norbornanol was obtained from the ketone by lithium aluminum hydride reduction in the manner previously described. Crystallization from petroleum ether gave alcohol with mp 69–70° (lit.[21] 71°); nmr δ 1.2–2.1 (m, 7), 2.4 (broad s, 2), 3.0 (q, 1), 7.25 (s, 5).

exo-**3-Phenyl-*endo*-2-norbornanol.**—The mother liquor above contained three isomeric alcohols by vpc analysis (Carbowax 20 M column at 210°) as well as some ketone and 2-phenylnorbornene. Dry column chromatography over alumina (Alcoa, type F-20) using petroleum ether with increasing amounts of ether eluted the components in the following order: 2-phenylnorbornene, 3-phenyl-2-norbornenone, di-*endo*- and di-*exo*-3-phenyl-2-norbornanol, and *exo*-3-phenyl-*endo*-2-norbornanol. The two *cis* isomers could not be separated. The last isomer was converted into its tosylate without further purification or analysis.

endo-3-(*p*-Methylphenyl)-*endo*-2-norbornanol was obtained from the ketone as described above: mp 109–109.5°; nmr δ 0.9–1.9 (m, 7), 1.9–2.2 (2 m, 2), 2.24 (s, 3), 2.84 (2 d, 1), 4.06 (2 d, 1), 7.0 (s, 4).

endo-3-(*p*-Chlorophenyl)-*endo*-2-norbornanol and *endo*-3-(*m*-chlorophenyl)-*endo*-2-norbornanol were obtained from their corresponding ketones as described above. One major product was obtained in each case, indicating that the ketones were only slightly epimerized: nmr of *p*-chloro alcohol, δ 1.2–2.0 (m, 7), 2.4 (broad s, 2), 3.0 (2 d, 1), 4.25 (2 d, 1), 7.2 (s, 4); nmr of *m*-chloro alcohol, δ 0.9–1.8 (m, 7), 2.3 (broad s, 1), 2.84 (broad s, 1.5), 3.0 (d, 0.5), 4.3 (2 d, 1), 7.2 (m, 4).

Tosylates.—The tosylate esters of the arylnorbornanols were prepared by the method of Tipson.[22] Nmr data below include only the chemical shifts and multiplicity of the 3- and 2-hydrogens, respectively.

endo-**3-(X-Phenyl)-*exo*-2-norbornanol Tosylates.**—The compound with X = H had mp 86–86.5° (reported 94–95°),[13] nmr δ

(18) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.*, **85**, 3199 (1963); N. A. LeBel, P. D. Beirne, and P. M. Subramanian, *ibid.*, **86**, 4144 (1964).

(19) D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

(20) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, **86**, 4913 (1964).

(21) B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).

(22) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

3.02 (t), 4.6 (broad d). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.48. Found: C, 70.11; H, 6.64.

The compound with X = *p*-CH_3 had mp 86.5–87.5°, nmr δ 3.05 (t), 4.6 (d). *Anal.* Calcd for $C_{21}H_{24}O_3S$: C, 70.75; H, 6.79. Found: C, 70.39; H, 6.08.

The compound with X = *p*-Cl had mp 108.5–109°, nmr δ 2.94 (t), 4.43 (d). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.72; H, 5.62. Found: C, 63.94; H, 5.50.

The compound with X = *m*-Cl had mp 87.5–88.5°, nmr δ 3.00 (t), 4.5 (broad s). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.72; H, 5.62. Found: C, 63.44; H, 5.81.

***endo*-3-(X-Phenyl)-*endo*-2-norbornanol Tosylates.**—The compound with X = H had mp 113–114° (reported 111–112°),[13] nmr δ 3.12 (2 d), 5.1 (2 d). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.16; H, 6.48. Found: C, 70.29; H, 6.65.

The compound with X = *p*-CH_3 had mp 109–109.5°, nmr δ 3.03 (2 d), 5.0 (2 d). *Anal.* Calcd for $C_{21}H_{24}O_3S$: C, 70.77; H, 6.79. Found: C, 71.13; H, 7.00.

The compound with X = *p*-Cl had mp 123°, nmr δ 3.18 (2 d), 5.02 (2 d). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.7; H, 5.62. Found: C, 63.6; H, 5.68.

The compound with X = *m*-Cl had mp 123–125°, nmr δ 3.04 (2 d), 5.06 (2 d). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.7; H, 5.62; S, 8.50. Found: C, 63.6; H, 5.60; S, 8.40.

***exo*-3-(X-Phenyl)-*endo*-2-norbornanol Tosylate.**—The compound with X = H had mp 99–100° (reported 96–97°),[13] nmr δ 2.52 [q(?)], 4.82 (t). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.16; H, 6.48. Found: C, 69.6; H, 6.23.

***exo*-3-Phenyl-*exo*-2-norbornyl tosylate** was prepared from the alcohol supplied by Professor D. C. Kleinfelter, University of Tennessee,[10,13] mp 101–102° (reported[13] 102–103°).

Kinetic Procedures.—Kinetic analyses were performed as described previously.[1] Olefin product yields were calculated from the measured extinction coefficients: 2-phenylnorbornene, ε 14,800 at λ_{max} 262.5 mμ (lit.[19] ε 10,715 at λ_{max} 262.5); 2-*p*-methylphenylnorbornene, ε 15,600 at λ_{max} 264.5 mμ (lit.[19] ε 12,023 at 264.0); 2-*p*-chlorophenylnorbornene, ε 18,800 at λ_{max} 267.5 mμ (lit.[19] ε 15,490 at 267.0); 2-*m*-chlorophenylnorbornene, ε 14,100 at λ_{max} 265.0 mμ.

Registry No.—A (Z = H), 23430-74-2; A (Z = *p*-CH_3), 23430-75-3; A (Z = *p*-Cl, 23430-76-4; A (Z = *m*-Cl), 23430-77-5; B (Z = H), 10472-58-9; B (Z = *p*-CH_3), 23430-79-7; B (Z = *p*-Cl, 23430-80-0; B (Z = *m*-Cl), 23430-81-1; C, 23430-82-2; D, 10472-63-6; 2-*p*-methylphenylnorbornene, 23430-54-8; 2-*m*-chlorophenylnorbornene, 23465-01-2; 2-*p*-chlorophenylnorbornene, 23430-55-9; *endo*-3-*p*-methylphenyl-*exo*-2-norbornanol, 23430-84-4; *endo*-3-*m*-chlorophenyl-*exo*-2-norbornanol, 23430-85-5; *endo*-3-*p*-chlorophenyl-*exo*-2-norbornanol, 23430-86-6; 3-(*p*-methylphenyl)-2-norbornanone, 23465-02-3; 3-(*p*-chlorophenyl)-2-norbornanone, 23430-56-0; 3-(*m*-chlorophenyl)-2-norbornanone, 23430-57-1; *endo*-(3-*p*-methylphenyl)-*endo*-2-norbornanol, 23430-87-7.

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Reexamination of Type II Elimination Reactions in the Photolysis of Aliphatic Carboxylic Acids and Amides

COLIN H. NICHOLLS AND PETER A. LEERMAKERS[1]

Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457

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Early and sparse accounts of the type II process in simple aliphatic carboxylic acids and amides have been scrutinized experimentally and conceptually. Little of a photochemical nature is known about these important classes of compounds, owing primarily to experimental problems. We have found the early work on these systems to be incomplete and possibly misleading, and thus present the results of our own study of products, quantum yields, and spectroscopy of the above compounds. The type II process does take place, from a high-lying probably n,π^* state, in butyric and valeric acid. In the case of the amides, in contrast to a previous report, irradiation at 254 nm causes virtually no reaction of unsubstituted propionamide, butyramide, and valeramide. However, the N,N-dimethyl derivatives do decompose, *via* the type I process, relatively efficiently *via* an unspecified electronic state.

The type II photochemical elimination reaction has often been demonstrated to occur readily during the photolysis of such carbonyl compounds as aldehydes, ketones, keto acids, and certain esters; however, evidence for this reaction occurring with aliphatic carboxylic acids and amides is less conclusive. Indeed, very little about the latter processes is known, owing both to experimental difficulty and poor understanding of the relevant spectroscopic states.

Booth and Norrish[2] examined the gaseous products from the photolysis of the aliphatic amides propionamide (C_3), butyramide (C_4), valeramide (C_5), and hexanomide (C_6) dissolved in dioxane or hexane. They obtained some unsaturated hydrocarbon gas, which was established as ethylene (insoluble in concentrated sulfuric acid but soluble in fuming sulfuric acid) for the C_3 and C_4 amides, and inferred as propylene and butylene for the C_5 and C_6 amides, respectively. Despite the fact that more "ethylene" was obtained from propionamide than from butyramide and that none of the unsaturated gases was identified, the authors suggested that evidence for type II elimination existed. On the other hand Volman[3] found no photodecomposition of aliphatic amides in water at 25°. At 92° he found that the quantum yields for the formation of ammonia from acetamide, propionamide, and butyramide were 0.16, 0.023, and 0.029, respectively. He examined only the gaseous products of the photodegradation, but records no evidence for the formation of ethylene from any of the amides.

The gaseous products from the photolysis of butyric acid dissolved in isooctane or water were determined by Borrell and Norrish.[4] They found that ethylene was a

(1) Alfred P. Sloan Fellow, 1967–1970.

(2) G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 188 (1952).

(3) D. H. Volman, *J. Amer. Chem. Soc.*, **63**, 2000 (1941).

(4) P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **262**, 19 (1961).