Acetolysis Studies of Pinacolyl-Type Tosylates. Rapid Solvolysis Rates of Possible Steric Origin

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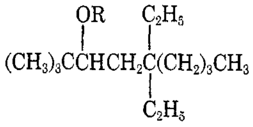
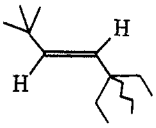
The acetolysis rates of a series of pinacolyl-type tosylates have been studied. The acetolysis of 5,5-diethyl-2,2-dimethyl-3-nonyl tosylate (**1**, R = Ts) has been found to yield 58% of olefin **2** of unrearranged carbon skeleton. Tosylate **1** (R = Ts) and 2,2,5,5-tetramethyl-3-hexyl tosylate (**3**, R = Ts) undergo acetolysis 119 and 71.5 times faster, respectively, than 2,2-dimethyl-3-nonyl tosylate (**4**). It is suggested that these rate enhancements are steric in origin.

It recently has been reported that 5,5-diethyl-2,2-dimethyl-3-nonanol (**1**, R = H) yields a single olefin **2** on dehydration with potassium hydrogen sulfate.[2] This dehydration, without rearrangement, of a pinacolyl-type alcohol is of considerable interest in that systems of this general type are prone to undergo rearrangement on dehydration. While the mechanism of the dehydration of **1** (R = H) with potassium hydrogen sulfate is uncertain (probably of some ionic character), the related 2,2,5,5-tetramethyl-3-hexanol (**3**, R = H) has been shown to lead to a mixture of olefins on dehydration under the same conditions utilized for **1** (R = H).[2] It has been suggested that the carbonium ion from **1** (R = H) is more crowded than the corresponding cation from **3** (R = H). Steric factors were proposed as controlling the formation of the single olefin **2** from **1** (R = H) since any rearrangement of the carbonium ion from **1** (R = H) would lead to a more sterically crowded ion.

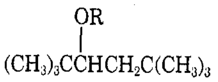


$(CH_3)_3C\overset{OR}{C}HCH_2\underset{C_2H_5}{\overset{C_2H_5}{C}}(CH_2)_3CH_3$

1



2



$(CH_3)_3C\overset{OR}{C}HCH_2C(CH_3)_3$

3

It was therefore of considerable interest to study the solvolysis of the tosylates **1** (R = Ts) and **3** (R = Ts) in order to make rate and product comparisons to other pinacolyl-type systems.

Results

The acetolysis data and the activation parameters for the tosylates **1** (R = Ts) and **3** (R = Ts) along with those for several model compounds are tabulated in Table I. In order to make rate comparisons with the tosylates studied here and other related systems, comparative rate data are presented in Table II.

The products obtained from **1** (R = Ts) are of interest in that 87% olefinic material and 13% acetate were produced (nmr area ratios). Of the olefinic material, 67% was the unrearranged olefin of, readily identified by its characteristic AB quartet at δ 4.2.[2] The other olefinic product was that of rearranged carbon skeleton and exhibited in the nmr a pattern at δ 4.6 representative of a terminal methylene group. The acetate product was also that of a rearranged carbon skeleton since the acetate protons appeared at δ 1.9, while the nmr signal for the unrearranged acetate appeared at δ 1.6 [prepared from **1** (R = H) *via* acetic anhydride in pyridine]. It should be noted that 58% of the acetolysis product from **1** (R = Ts) is the olefin of unrearranged carbon skeleton. In contrast, the acetolysis products from 2,2-dimethyl-3-nonyl tosylate (**4**) were predominantly of rearranged skeletons (85%). The products consisted of 15% unrearranged olefin, 17% rearranged acetate, and 68% an olefin mixture resulting from methyl transposition (1-ene to 2-ene ratio, 1.4:1).

As can be seen from the data presented in Table II, the tosylates **1** (R = Ts) and **3** (R = Ts) undergo acetolysis considerably faster than the model *tert*-butyl *n*-alkylcarbinyl tosylates **4** and **5**. The acetolysis rate of **1** (R = Ts) is the fastest one in the series despite the formation of a substantial amount of olefin of unrearranged carbon skeleton (58%).

Discussion

The interpretation of the data presented herein raises the question of whether the solvolysis of these pinacolyl-related esters proceeds *via* a concerted or a stepwise pathway. The same question has also been asked regarding neopentyl arenesulfonates.[3] The solvolysis rates of pinacolyl brosylate have been compared to those of isopropyl brosylate[4] in several solvents and methyl participation has been discussed. However, the use of isopropyl brosylate as a comparative standard is open to question.[5] If isopropyl arenesulfonates solvolyze with considerable nucleophilic solvent assistance at the transition state (k_s) with no contribution from k_Δ, this would be a poor model for comparison with pinacolyl esters since the large steric hindrance to backside solvent approach in the latter would make the k_s contribution unimportant and the solvolysis would proceed either through a k_Δ or a k_c pathway (nucleophilic solvent and neighboring group unassisted).

Deno and Newman have reported that *d*-pinacolyl hydrogen sulfate racemizes faster than it rearranges in

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[1] Department of Chemistry, University of Missouri, Columbia, Mo. 65201.

[2] N. Rabjohn and C. A. Drake, *J. Amer. Chem. Soc.*, **88**, 3154 (1966).

[3] (a) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969). (b) A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, **91**, 5637 (1969). (c) P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969). (d) S. H. Liggero, R. Sustmann, and P. von R. Schleyer, *ibid.*, **91**, 4571 (1969). (e) V. J. Shiner, Jr., and W. Dowd, *ibid.*, **91**, 6528 (1969).

[4] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

[5] (a) P. von R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969), and papers cited therein. (b) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. von R. Schleyer, *ibid.*, **92**, 2538 (1970). (c) J. L. Fry, J. M. Harris, R. C. Bingham, and P. von R. Schleyer, *ibid.*, **92**, 2540 (1970). (d) P. von R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970). (e) A. Streitwieser, Jr., and C. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

TABLE I

ACETOLYSIS RATES OF PINACOLYL-TYPE TOSYLATES

Tosylate[a]	Temp, °C[b]	$k_t \times 10^4$ sec^{-1}[c]	ΔH^*, kcal	ΔS^*, eu
1 (R = Ts)	15.0	0.45 ± 0.10	22.6 ± 1	+0.3 ± 3
	25.0	1.75 ± 0.14		
3 (R = Ts)	25.0	1.05 ± 0.03		
4, $(CH_3)_3C\overset{OTs}{C}H(CH_2)_5CH_3$	40.0	0.128 ± 0.006	26.0 ± 1	+2.1 ± 3
	60.0	1.66 ± 0.08		
5, $(CH_2)_3C\overset{OTs}{C}H(CH_2)_7CH_3$	40.0	0.120 ± .004	26.4 ± 1	+3.1 ± 3
	60.0	1.63 ± 0.08		

[a] Performed in acetic acid in solutions 0.04–0.07 *M* in ester and 0.1 *M* in sodium acetate. [b] Temperature deviation of ±0.05°. [c] Average of two kinetic runs using the least squares rate constants; the error is the average standard deviation.

TABLE II

RELATIVE RATE COMPARISONS FOR PINACOLYL-TYPE TOSYLATES

Tosylate	k_t (sec^{-1})[a]	Relative k (25°)
1 (R = Ts)	1.75×10^{-4}[b]	119
3 (R = Ts)	1.05×10^{-4}[b]	71.5
4	1.47×10^{-6}[d]	1.0
5	1.36×10^{-6}[d]	0.93
6, $(CH_3)_3C\overset{OTs}{C}HCH_3$	1.92×10^{-7}[c]	0.13
7, $(CH_3)_3C\overset{OTs}{C}HCH_2CH_3$	1.37×10^{-6}[c]	0.93
8, $(CH_3)_3C\overset{OTs}{C}H(CH_2)_2CH_3$	2.10×10^{-6}[c]	1.4

[a] All rate constants are tabulated at 25°. [b] Experimentally determined at 25°. [c] Calculated at 25° from data at other temperatures (data taken from the thesis of J. J. Harper, Princeton University, 1968). Performed in unbuffered acetic acid. [d] Calculated from data at other temperatures. Performed in buffered acetic acid.

sulfuric acid solutions.[6] It was proposed that the ionization proceeds to carbonium and bisulfate ions followed by reassociation to racemic pinacolyl hydrogen sulfate. The trifluoroacetolysis of pinacolyl brosylate has been interpreted as proceeding through rate-determining formation of a tight ion pair while the trifluoroacetolysis of isopropyl brosylate is thought to proceed through rate-determining dissociation of a tight ion pair.[7] Pinacolyl brosylate has been proposed as a useful reference compound for estimating unassisted ionization rates of secondary substrates in the absence of ion pair return.

In the series of alkyl-substituted *tert*-butylcarbinyl arenesulfonates, it is of interest to look at the response of the solvolysis rate as a function of the alkyl substituent. In these systems the solvolysis should proceed through a k_Δ or a k_c pathway (k_s contribution expected to be unimportant). The appropriate data for the Taft[8] correlation (log k_t *vs.* $\Sigma\sigma^*$) is graphically illustrated in Figure 1.

Since the substrates **4**, **5**, **6**, **7**, and **8** listed in Table II have no branching in the alkyl side chain (all have a common *tert*-butyl grouping), the steric influence of this group can probably be neglected. Although only five compounds have been utilized to determine the line, and the linearity is questionable, the estimated ρ^* of -8 (acetic acid, 25°) is of considerable speculative interest. The ρ^* value of -2.6 (acetic acid, 70 and 100°)[9] found for simple secondary systems with no β-alkyl branching is to be contrasted with this value. The increased negative ρ^* value for the *tert*-butyl-*n*-alkylcarbinyl esters is consistent with a diminished backside solvent stabilization effect at the transition state, in comparison to the simple secondary esters which probably solvolyze with considerable nucleophilic solvent assistance.[5]

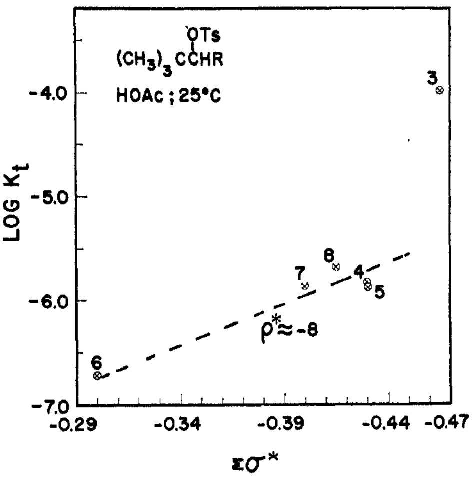

Figure 1.—Acetolysis rates (25°) of the alkyl-substituted *tert*-butylcarbinyl tosylates listed in Table II *vs.* the $\Sigma\sigma^*$ constants.

In the absence of complicating steric effects, the $\Delta\rho^*$ of about -5 may perhaps be taken as a measure of the difference in the degree or amount of positive charge at the reaction site in the transition state in the two series. A k_c route would be expected to exhibit a pronounced response to the inductive contribution of an alkyl group. However, it might be noted that partial methyl bridging (k_Δ route) at the transition state might also exhibit a high group response dependent on the degree of participation at the transition state (both routes k_c and k_Δ would proceed without backside nucleophilic solvent stabilization of the transition state).

The simple Taft treatment is clearly not sufficient to rationalize the rate enhancements found in **1** (R = Ts)

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(6) N. C. Deno and M. S. Newman, *J. Amer. Chem. Soc.*, **73**, 1920 (1951).

(7) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

(8) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556 ff.

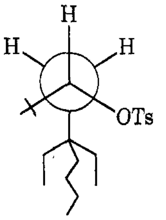
(9) (a) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965). (b) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967). (c) W. Pritzkon and K. H. Schoppler, *Chem. Ber.* **95**, 834 (1962). (d) C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969).

and **3** (R = Ts) as is illustrated for **3** (R = Ts) in Figure 1. No apparent rate correlation exists based solely on the Foote–Schleyer[10] "angle-effect," since the ν_{CO} for the ketone corresponding to **1** is 1705 cm^{-1}, while that for pinacolone is 1709 cm^{-1}.

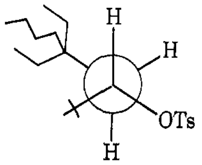
In the comparison of **1** (R = Ts) to the model system **4** (R = Ts) one sees a rate enhancement of 119 (Table I). If methyl participation is the major solvolytic pathway in **4** (R = Ts), then the magnitude of this participation effect should be comparable to that of compound **1** (R = Ts), and, indeed, the bridging at the transition state **1** (R = Ts) may be sterically less favorable than the comparable bridged transition state in **4** (R = Ts). This comparison might lead to predicting a lower rate for **1** (R = Ts) than for **4** (R = Ts) if k_Δ is the major solvolytic pathway. One can then conclude in the case of system **1** (R = Ts) that the major rate *increase* over the model pinacolyl system is *steric* in origin.

In the solvolyses of several highly branched tertiary carbinyl esters such as 2-chloro-2,3,3,4,4-pentamethylpentane, the products were predominantly of unrearranged carbon skeletons and it was proposed that alkyl participation did not occur.[11] A Taft plot of $\Sigma\sigma^*$ *vs.* log relative *k* for tertiary carbinyl halides (80% aqueous ethanol) seems to indicate that polar effects may account for the solvolysis rates of simple tertiary halides, and even for di-*tert*-butylmethyl carbinyl chloride, but that neopentyl groups introduce marked rate accelerations ascribed to ground-state steric congestion.[12]

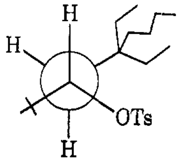
In **1** (R = Ts) the bulky alkyl group interacts sterically with the *tert*-butyl group of the neopentyl system in two conformations **1a** and **1b**, and with the tosylate group in two conformations **1a** and **1c**. Conformation **1c** might be expected to be the predominant conformation due to the lesser steric repulsions between groups. However, steric bumping is indicated in conformation **1c** as the bulky side chain interacts with the oxygen atom of the tosylate group. The increased rate of **1** (R = Ts), relative to the model systems in Table I, could be readily rationalized by release of ground-state strain (F strain) at the transition state.[13] The relative decrease in rate of **3** (R = Ts) in comparison to **1** (R = Ts) might simply reflect a greater steric strain release in **1** (R = Ts) than in **3** (R = Ts) due to the greater bulk of the groups in the former compound.



1a



1b



1c

It is possible that the solvolysis of **1** (R = Ts) proceeds *via* a k_c route. In this route proton loss at the ion pair stage or the carbonium ion stage would lead to **2** and competitive methyl transposition would lead to products of rearranged carbon skeleton. If an ion pair mechanism is assumed, less internal return (steric assistance to anion departure) might be expected in the comparison of **1** (R = Ts) to **4** (R = Ts) and a rate enhancement for **1** would result.[7] Steric factors would seem to control the formation of the trans olefin **2** as this would be formed from the lower energy trans-like transition state from conformation **1c**. The products from **1** (R = Ts) could also arise *via* a bridged species. A steric bias for methyl migration could produce **2** as the major product *via* proton loss from a bridged ion and partial competitive methyl migration to a tertiary cation followed by reaction of this cation with solvent or proton loss could lead to rearranged acetate and terminal olefin, respectively. The products from the acetolysis of **3** (R = Ts) have not been determined.

In conclusion, the fast rates of acetolysis of **1** (R = Ts) and **3** (R = Ts) are steric in origin even if the exact mechanism of solvolysis can be questioned. No definite conclusion can be reached from the present data as to whether these compounds or the other model systems solvolyze *via* the k_Δ or k_c routes (k_s sterically inhibited) although we favor the k_c route. Further investigations will be necessary to establish these points.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 21 infrared spectrophotometer. All infrared spectra of solids were taken from a CCl_4 solution and all liquids were taken in the neat phase. The nuclear magnetic resonance spectra were determined on a Varian A-60 nuclear magnetic resonance spectrophotometer. Both solids and liquids were examined in CCl_4 solutions with an internal tetramethylsilane standard. Boiling and melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by the Microanalytical Laboratory at the University of Massachusetts, Amherst, Mass.

Synthesis of the Alcohols. A. 2,2,5,5-Tetramethyl-3-hexanol (3, R = H).—This sample was prepared by the procedure of Drake (Ph.D. Thesis, University of Missouri, 1967).[2]

B. 5,5-Dimethyl-2,2-dimethyl-3-nonanol 1 (R = H).—This sample was prepared by the procedure of Drake (Ph.D. Thesis, University of Missouri, 1967).[2]

C. 2,2-Dimethyl-3-nonanol.—Magnesium turnings (2.4 g, 0.1 g-atom) were placed in a 100-ml flask fitted with a condenser, a nitrogen inlet tube, and an addition funnel. The vessel was flushed with nitrogen, and a solution of *n*-hexyl bromide (16.5 g, 0.1 mol) in 50 ml of dry ether was added slowly, to maintain a slow reflux rate. The mixture was allowed to reflux an additional 15 min, and a solution of freshly distilled 2,2-dimethylpropanal (7.74 g, 0.09 mol) in 30 ml of dry ether was added slowly, with cooling. After addition was complete, the reaction mixture was stirred for an additional 10 min, poured into ice water, and extracted with ether. The extract was washed with saturated aqueous sodium bicarbonate and aqueous sodium chloride, dried over anhydrous magnesium sulfate, and the ether was removed on an aspirator. The residue was distilled at reduced pressure to yield 7.35 g (48%) of *tert*-butyl-*n*-hexylcarbinol, bp 45° (0.2 mm).

Anal. Calcd for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.99; H, 13.90.

The nmr spectrum showed absorption at δ 3.12 (m, 1 H, -CHOH), 1.92 (s, 1 H, -CHOH), 1.31 (m, 10 H, $-CH_2-$), and 0.85 (s, 12 H, $-CH_3$).

D. 2,2-Dimethyl-3-undecanol.—The procedure above was used to convert *n*-octyl bromide (19.3 g, 0.1 mol) to 9.4 g (52%) of *tert*-butyl-*n*-octylcarbinol. The product distilled at 71° (0.2 mm).

Anal. Calcd for $C_{13}H_{28}O$: C, 77.93; H, 14.08. Found: C, 77.95; H, 14.34.

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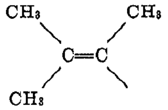
(10) (a) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); (b) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(11) (a) V. J. Shiner, Jr., and G. F. Meier, *J. Org. Chem.*, **31**, 137 (1966). (b) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968), and papers cited therein.

(12) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 124–125. The point scatter is significant and the correlation is poor.

(13) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 323.

TABLE III

	$-CH{=}CH-$	Rearranged CH_3CO_2-	$CH_2{=}C<$		$CH_3{-}\overset{\|}{C}{-}$		
Chemical shift, δ	5.38	1.88	4.67			1.62	
Protons	2	3	2		3		9
Nmr area ratios	50	86	131			624	
	50	86	131		196.5		427.5
Mole ratios	25	28		66			47
Product %	15	17		40			28

Synthesis of the Tosylates. General Procedure.[14]—In a three-necked flask fitted with an addition funnel, a rubber septum and a reflux condenser was placed up to 3 g of alcohol dissolved in absolute ether. By means of a syringe, a 10% mol excess (with respect to the alcohol) of methyllithium in ether was added with stirring to the solution of the alcohol. After allowing the resulting solution to stir for approximately 5 min, an ethereal solution of tosyl chloride was added dropwise with stirring. A nitrogen atmosphere was maintained throughout the course of the reaction. After stirring from 2 to 24 hr, depending on the particular alcohol, the lithium chloride was filtered through a sintered glass funnel. The filtrate was concentrated by means of a rotary evaporator and placed in a freezer to induce crystallization. Recrystallization was from pentane or a pentane–ether mixture.

A. **5,5-Diethyl-2,2-dimethyl-3-nonyl Tosylate (1, R = Ts).**—The general procedure was employed to convert 5,5-diethyl-2,2-dimethyl-3-nonanol (2.9 g, 0.013 mol), using tosyl chloride (2.65 g, 0.014 mol), and 8.5 ml of 1.6 *M* methyllithium to 1.7 g (37% yield) of 5,5-diethyl-2,2-dimethyl-3-nonyl tosylate, mp 50–52°. The analytical sample was crystallized from pentane, mp 51–52°.

Anal. Calcd for $C_{22}H_{38}O_3S$: C, 69.08; H, 10.02. Found: C, 69.00; H, 10.01.

The infrared spectrum showed strong bands characteristic of the tosylate at 1355 and 1175 cm^{-1}. The nmr spectrum showed signals at δ 7.50 (A_2B_2 quartet, 4 H, J = 8 Hz, aromatic protons), 4.7 (m, 1 H, -CHOTs), 2.44 (s, 3 H, aromatic CH_3), 0.92 (s, 9 H, protons of *tert*-butyl), and 0.5–1.7 (complex multiplets, 21 H).

B. **2,2,5,5-Tetramethyl-3-hexyl Tosylate (3, R = Ts).**—The general procedure described above was employed to convert 2,2,-5,5-tetramethyl-3-hexanol (0.50 g, 0.0022 mol), using tosyl chloride (0.62 g, 0.0022 mol), and 2.0 ml of 1.6 *M* methyllithium, to 2,2,5,5-tetramethyl-3-hexyl tosylate (0.362 g, 38% yield), mp 62–64°. The analytical sample was recrystallized from pentane, mp 63–64°.

Anal. Calcd for $C_{17}H_{28}O_3S$: C, 65.31; H, 9.02. Found: C, 65.20; H, 8.99.

The infrared spectrum showed strong bands characteristic of the tosylate at 1350 and 1175 cm^{-1}. The nmr spectrum showed signals at δ 7.50 (A_2B_2 quartet, 4 H, aromatic protons, J = 8 Hz), 4.7 (m, 1 H, -CHOTs), 2.45 (s, 3 H, aromatic CH_3), 1.6 (d, 2 H, $-CH_2-$), and 0.9 (s, 18 H, $-CH_3$).

C. **2,2-Dimethyl-3-nonyl Tosylate (4).**—The general procedure was used to convert 3.0 g (0.0174 mol) of the parent alcohol to 2,2-dimethyl-3-nonyl tosylate in a 69% yield (3.94 g). The product was an oil at room temperature.

Anal. Calcd for $C_{18}H_{30}O_3S$: C, 66.22; H, 9.26. Found: C, 66.24; H, 9.14.

The nmr spectrum showed absorption at δ 7.50 (A_2B_2 quartet, 4 H, aromatic protons), 4.34 (m, 1 H, -CHOTs), 2.37 (s, 3 H, aromatic CH_3), 1.18 (broad pattern, 10 H, $-CH_2-$), and 0.88 (broad s, 12 H, CH_3).

D. **2,2-Dimethyl-3-undecyl Tosylate (5).**—The general procedure was utilized to convert the parent alcohol (3.58 g, 0.0174 mol) to the tosylate 5 in a 57% yield (3.53 g). The product was an oil at room temperature and was not further purified. The nmr spectrum showed absorption at δ 7.50 (A_2B_2 quartet, 4 H, J = 8 Hz, aromatic protons), 4.36 (m, 1 H, -CHOTs), 2.42 (s, 3 H, aromatic CH_3), 1.23 (broad split peak, 14 H, $-CH_2-$) and 0.87 (broad s, 12 H, CH_3).

Acetolysis Kinetics.—The acetolysis procedures were the same as those used by previous investigators.[15] The infinity titer technique was utilized in which aliquots were taken at appropriate intervals from approximately 0.05 *M* solutions of the sulfonate ester in buffered acetic acid (approximately 0.1 *M* in sodium acetate) in the thermostated bath. Each aliquot was titrated with a standardized perchloric acid solution in acetic acid using a 1% solution of crystal violet in acetic acid as the indicator. The sample was taken as zero time and the infinity titer was taken after at least 12 half-lives had elapsed.

Treatment of Experimental Data.—The first-order rate constants were calculated according to the standard procedures.[16] The calculations were performed on an IBM 1130 computer and the least squares average rate constant was calculated along with the standard deviation and the correlation coefficient for each run. The activation parameters and rates at different temperatures were calculated on the IBM 1130 computer.[17]

Product Studies. Acetolysis of 2,2-Dimethyl-3-nonyl Tosylate (4).—The tosylate 4 (0.52 g) was dissolved in 20 ml of 0.1 *N* sodium acetate in acetic acid and kept at 60° for 12 half-lives. The cooled solution was poured into ice water and the products extracted with pentane. The combined pentane extracts were washed with a saturated solution of aqueous sodium bicarbonate, a saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. The pentane was carefully removed and the remaining oil (0.32 g) was identified by nmr analysis. The product data is tabulated in Table III. The vinyl methyl absorption was separated into the two fractions on the basis of the exocyclic methylene protons. Unrearranged acetate was shown not to be present by the absence of the tertiary acetate proton, and by the acetate absorption at δ 1.88; secondary acetates absorb at δ 1.95.

Acetolysis Products of 5,5-Diethyl-2,2-dimethyl-3-nonyl Tosylate (1).—In a round-bottom flask fitted with a reflux condenser was placed a mixture of 0.300 g of 5,5-diethyl-2,2-dimethyl-3-nonyl tosylate and 20 ml of 0.0998 *M* sodium acetate in acetic acid and the solution was stirred at room temperature for 3 days. The mixture was then poured into an equal volume of cold water, extracted with pentane, and washed with water, 5% sodium bicarbonate, and again with water. The pentane solution was dried over potassium carbonate and then concentrated on a rotary evaporator to give 0.150 g of product. The neat infrared spectrum of the product mixture showed strong absorption at 1730 cm^{-1} characteristic of acetates. The nuclear magnetic resonance spectrum showed signals at δ 5.2 (AB quartet, characteristic of olefin 2), 4.6 (broad d, for $=CH_2$ of rearranged olefin) and 1.90 (s, $CH_3{-}\overset{|}{C}{=}O$).

From the relative peak area ratios at 5.2 (unrearranged olefin 2) and 4.6 ($H_2C{=}\overset{|}{C}-$ of rearranged olefin), it can be ascertained that of the total olefin formed 67% of 2 is present and 33% is rearranged olefin.

From the relative peak areas the molar composition of the acetolysis product is 58% unrearranged olefin 2, 29% of the rearranged olefin with a $CH_2{=}C-$ grouping, and 13% of rearranged acetate.

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Reference Samples. 5,5-Diethyl-2,2-dimethyl-3-nonene (2).—In a flask fitted with a reflux condenser was placed a mixture of 5,5-diethyl-2,2-dimethyl-3-nonanol (1, R = H) (0.85 g, 0.0037 mol) and 3.0 g of potassium hydrogen sulfate. The mixture was then heated at 170–180° for 20 hr. After allowing the mixture to cool, it was distilled at reduced pressure to give 0.70 g (89% yield) of 5,5-diethyl-2,2-dimethyl-3-nonene (**2**), bp 63–65° (1.0 mm) [lit.[2] bp 120–121° (40 mm)]. The nmr showed signals at δ 5.2 (AB quartet, 2 H, J = 16 Hz), 1.0 (s, 9 H, *tert*-butyl group), and 0.5–1.8 (m, 19 H).

5,5-Diethyl-2,2-dimethyl-3-nonyl Acetate.—The acetate was prepared by refluxing 5,5-diethyl-2,2-dimethyl-3-nonanol (0.5 g, 0.0022 mol) with acetic anhydride (2.0 g, 0.019 mol) in 5.0 ml of dry pyridine for 2 hr. The mixture was cooled, poured onto ice water, and extracted with pentane. The pentane layer was washed with 10% hydrochloric acid, 5% sodium bicarbonate, and finally with water. The pentane solution was dried over magnesium sulfate and then distilled to give 0.3 g (50% yield) of 5,5-diethyl-2,2-dimethyl-3-nonyl acetate, bp 80–82° (0.5 mm). The infrared spectrum showed evidence of slight alcohol impurity, but the characteristic strong acetate absorption was present at 1735 cm^{-1}. The nmr spectrum showed signals at δ 4.8 (q, 1 H, -CHOH), 1.95 (s, 3 H, $CH_3C{=}O$), 0.9 (s, 9 H, *tert*-butyl group), and 0.7–1.5 (m, 21 H).

Registry No.—**1** (R = Ts), 25966-57-8; **3** (R = Ts), 25966-58-9; **4**, 25966-59-0; **5**, 25966-60-3; **6**, 25966-61-4; **7**, 25966-62-5; **8**, 25966-63-6; 2,2-dimethyl-3-nonanol, 25966-64-7; 2,2-dimethyl-3-undecanol, 25966-65-8; 2,2-dimethyl-3-nonyl acetate, 25966-66-9; 5,5-diethyl-2,2-dimethyl-3-nonyl acetate, 25966-67-0.

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The Decarboxylation and Rearrangement of 3,3-Dialkyl-2-oxocarboxylic Acids[1]

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The thermal decomposition of 3,3-dialkyl-2-oxocarboxylic acids (**1**) has been shown to lead to decarboxylation and rearrangement. Although 3,3-dimethyl-2-oxobutyric acid (**1e**) undergoes decarbonylation, 2-oxo acids with larger groups in the 3 position, **1a–d**, afforded mixtures of ketones by 1,2 shifts. Ethyl, butyl, and heptyl groups migrated with similar ease, **1b**, while phenyl was found to have essentially the same migratory aptitude as pentyl in 2-oxo-3-pentyl-3-phenyloctanoic acid (**1c**). However, the phenyl group shifted almost exclusively, in preference to ring expansion, in 1-phenylcyclohexaneglyoxylic acid (**1d**). These results are ascribed to the bulk and conformational effects of the groups in the 3 position of **1**. It is suggested that either a zwitterionic or a concerted process (Scheme 1) best explains the experimental observations.

In a related investigation,[3] it was observed that a small amount of a low-boiling material was obtained on distillation of the product from the base-catalyzed autoxidation of ethyl 2-cyano-3,3-dipentyloctanoate. Since vpc analysis of the crude mixture showed that the only volatile products were unchanged cyano ester and the corresponding 2-keto ester, and these are known to be stable at distillation temperatures, it appeared that the pyrolysis of some nonvolatile species in the reaction mixture was responsible for the low-boiling unknown. The latter was present when either DMF or DMSO-*tert*-BuOH was used as the reaction medium, which eliminated condensation products of dimethyl sulfoxide[4] as possible precursors.

The ir spectrum of the crude autoxidation mixture had broad absorptions at 3200–3600 and 2550–2700 cm^{-1} which suggested the presence of a carboxylic acid. This was confirmed by the preparation of 3,3-dipentyl-2-oxooctanoic acid (**1a**) which on attempted distillation gave a 77% yield of the unknown pyrolysate. It was identified as 7-pentyl-6-dodecanone (**2a**) by comparison of its spectral properties with those of an authentic sample of this ketone.

Although the decarbonylation of 2-oxo esters is well known,[5] the decarboxylation of the corresponding acids has received relatively little attention. In those cases which have been studied,[6] aldehydes have been obtained as the common products. The present paper describes the investigation of the thermal decarboxylation and accompanying rearrangement of a number of 3,3-dialkyl-2-oxocarboxylic acids, **1**, to ketones **2**, **3**, and **4**. In

$$\underset{\mathbf{1}}{R_1R_2R_3CCOCO_2H} \xrightarrow{\Delta}$$

$$\underset{\mathbf{2}}{R_2R_3CHCOR_1} + \underset{\mathbf{3}}{R_1R_3CHCOR_2} + \underset{\mathbf{4}}{R_1R_2CHCOR_3} + CO_2$$

1a, $R_1 = R_2 = R_3 = C_5H_{11}$
b, $R_1 = C_2H_5$; $R_2 = C_4H_9$; $R_3 = C_7H_{15}$
c, $R_1 = R_2 = C_5H_{11}$; $R_3 = C_6H_5$
d, $R_1, R_2 = (CH_2)_5$; $R_3 = C_6H_5$
e, $R_1 = R_2 = R_3 = CH_3$
f, $R_1, R_2 = (CH_2)_5$; $R_3 = H$

addition, exploratory experiments were carried out in an attempt to elucidate the mechanism of the reaction.

The pyrolysis of **1a–d** on attempted distillation afforded the corresponding **2**, **3**, and **4**, whereas **1e** was decarbonylated to pivalic acid; the less highly substituted acid, **1f**, produced a mixture of four components.

Attempts to analyze and separate the mixture of ketones from **1b** by vpc on several different columns were not successful, but nmr analysis suggested that **2**, **3**, and **4** were present in the approximate ratio of 40:30:30, respectively. Compound **1c** gave 7-phenyl-6-dodecanone (**2c**, pentyl migration) and 2-pentylheptanophenone (**4c**, phenyl migration) in the ratio of 66:34. The migratory abilities of the phenyl and pentyl groups then are approximately equal in this case since pentyl migration is favored statistically by a factor of 2:1.

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[1] Taken from the Ph.D. Thesis of C. A. Harbert, 1967, and presented in part at the 3rd Midwest Regional American Chemical Society Meeting, Columbia, Mo., Nov 2–3, 1967.

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