Highly Branched Molecules. V.[1] The Solvolysis of Tertiary Carbinyl *p*-Nitrobenzoates from Tri-*t*-butyl to Trineopentyl

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Abstract: The first-order solvolysis rate constants for the *p*-nitrobenzoate esters of tri-*t*-butylcarbinol, di-*t*-butylneopentylcarbinol, *t*-butyldineopentylcarbinol, and trineopentylcarbinol relative to *t*-butyl *p*-nitrobenzoate in 60% dioxane (by weight) containing 0.1 *M* $NaClO_4$ at 40.0° have been found to be 13,000, 19,000, 68,000, and 560 sec^{-1}, respectively. The products of these solvolyses are predominantly of unrearranged carbon skeletons in the last two cases. The results are interpreted as showing that the rates are accelerated by relief of steric strain and that alkyl participation does not occur. No evidence can be seen in models for greater hindrance to solvation or to the escape of the anion in the last case than in the others. The major product from the tri-*t*-butyl compound is 2-methyl-3,3-di-*t*-butylbutene-1. This compound has a temperature-dependent nmr spectrum with a coalescence of peaks near room temperature that is apparently due to the freezing out of two conformations of the compound at low temperature.

Structural modifications in tertiary butyl halides or ionizable esters which increase the hindrance near the functional group produce changes in the rate of solvolysis which become larger as the molecule becomes more crowded. The first of these effects to be clearly recognized was the rate-enhancing "B strain," a repulsive interaction between bulky groups which is relieved when the central carbon atom passes from tetrahedral bonding to the trigonal bonding of a tertiary carbonium ion.[2-4]

In a number of instances it has been observed[1,5] that the greatest accelerations in systems of this sort were accompanied by prevalent or total molecular rearrangement. In most such cases no proof was at hand that the migration of neighboring groups was not itself contributing to the rate enhancement through participation in the ionizing process. This reservation was the more serious since the groups with the highest migratory aptitudes tended to produce the largest reaction rates.[6]

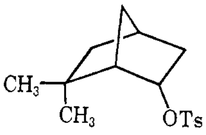
Brown and Kornblum, however,[7] correlated the occurence of rearrangements not alone with the proximity of migrating groups, but also with hindrance in the carbonium ion affecting the rate of access of nucleophiles.

In addition to these two rate-accelerating mechanisms are two possible *rate-retarding* effects of bulky groups which have been considered, but which are obviously on balance less important than the accelerating effects. The first of these to be considered was the Baker–Nathan phenomenon,[8,9] whereby some small loss in hyperconjugative stabilization of the carbonium ion is expected as the hydrogen atoms of the *t*-butyl cation are replaced by hydrocarbon groups. In those few cases where the inductive and hyperconjugative effects of groups have been quantitatively resolved,[10] it has appeared that C–C hyperconjugation is not greatly inferior to that at the C–H bond, and any contribution of the Baker–Nathan effect to the large rate changes now being discussed must be negligible.

The more interesting rate-retarding effect is that of solvent exclusion. Simple alkyl substitution in the benzene ring makes phenol a weaker acid and aniline a stronger base; yet *t*-butyl groups flanking the OH or NH_2 group make the amine a weaker base[11,12] and the phenol a much weaker acid.[13]

Since in the one case it is the formation of a new bond, but in the other case the *breaking* of such a bond, which is rendered unfavorable at equilibrium, no direct steric weakening of this bond can be responsible. In fact, the unfavorable side of the equation is in both cases that in which an ion is formed, and it must be the high requirement of an ion for solvation which determines the direction of the steric effect. In some of the earlier work on highly branched molecules a solvent-exclusion effect in solvolysis was considered, but no clear evidence for it was found.

In more recent studies of the solvolysis of the *endo*-tosylates **1**, **2**, and **3** (solvolytic rate constants relative



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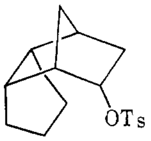

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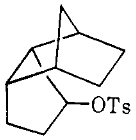

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[1] Part IV: P. D. Bartlett and R. M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955).

[2] (a) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949); (b) *ibid.*, **73**, 1317 (1951).

[3] P. D. Bartlett, *Bull. Soc. Chim. France*, [5] **18**, 104C (1951).

[4] P. D. Bartlett, *J. Chem. Educ.*, **30**, 22 (1953).

[5] P. D. Bartlett and M. S. Swain, *J. Am. Chem. Soc.*, **77**, 2801 (1955).

[6] M. Stiles and R. P. Mayer, *ibid.*, **81**, 1497 (1959).

[7] H. C. Brown and R. B. Kornblum, *ibid.*, **76**, 4510 (1954).

[8] (a) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935); (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 90–92.

[9] M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, pp 9–13.

[10] For example, N. N. Lichtin and P. D. Bartlett, *J. Am. Chem. Soc.*, **73**, 5530 (1951), and P. D. Bartlett, *J. Chem. Educ.*, **30**, 22 (1953), compared the effects of the methyl and *t*-butyl groups in the *meta* and *para* positions on the ionization constant of triphenylmethyl chloride in liquid sulfur dioxide, concluding that the *p*-CH_3 group contributes 1.11 kcal, and the *p*-$(CH_3)_3C$ group 0.84 kcal of hyperconjugative free energy to the ionization process. In Table 4 of the latter reference the last two columns are incorrect; they are easily corrected by performing the indicated arithmetic on the figures of the preceding column.

[11] W. J. Sheppard, Thesis, Harvard, 1958, pp 93–100.

[12] J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *Rec. Trav. Chim.*, **77**, 506 (1958).

[13] (a) G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Am. Chem. Soc*, **67**, 303 (1945); G. H. Stillson, *ibid.*, **68**, 722 (1946); (b) C. H. Rochester and B. Rossall, *J. Chem. Soc.*, *B*, 743 (1967).

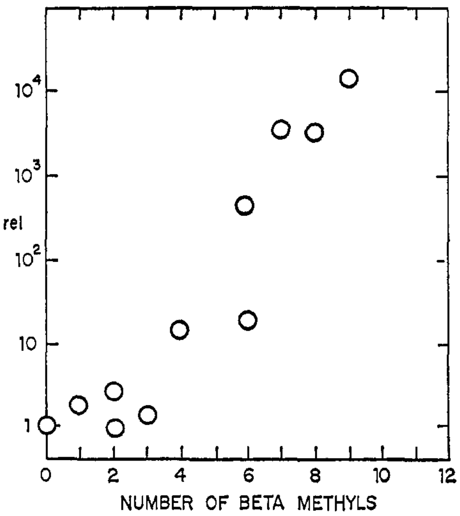


Figure 1. Relative solvolysis rates of tertiary alkyl halides or *p*-nitrobenzoates as a function of branching. The methyl-substituted compounds are those of Table I.

to *endo*-norbornyl tosylate 0.054, 0.10, and 0.19, respectively)[14] it was concluded from the Foote–Schleyer correlation scheme that these rate ratios must be actually the resultant of large theoretically expected (accelerating) ground-state destabilizations and still larger (retarding) transition-state destabilization factors of 8000, 10,000, and 100,000, respectively. The transition-state destabilization could be due to a physical barrier to departure of the anion, or to steric hindrance affecting the large solvation requirement of the anion;[15] of the two, the latter would appear to be the more general effect and to have the greater potential influence on the rate of ionization.

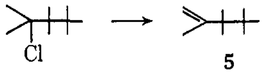
Table I and Figure 1 summarize some existing information on the relative solvolysis rates of compounds derived from *t*-butyl chloride by successive substitution of methyl for β-hydrogen. For the sake of comprehensiveness relative rates have also been included for the highly branched compounds which were examined not as chlorides in 80% ethanol but as *p*-nitrobenzoates in aqueous dioxane. This comparison would be of limited validity in a series where the *m* values of the Grunwald–Winstein equation changed very much with structure. We introduce it to illustrate the increasing steepness of the dependence of solvolytic rate upon degree of crowding, up as far as tri-*t*-butylcarbinyl *p*-nitrobenzoate. The curve is inviting to further exploration with respect to γ substitution.

Table I. Relative Rate Constants for Solvolysis, Referred to *t*-Butyl at the Same Temperature and in the Same Solvent (Compared at 25° and in 80% Ethanol unless Otherwise Indicated)

Compound	k_{rel}	Ref
t-BuCl	1.0	
Me_2EtCCl	1.7	*a*
Me_2-*n*-BuCCl	1.4	*a*
Me_2-*i*-PrCCl	0.88	2
Me_2-*t*-BuCCl	1.21	2
$MeEt_2CCl$	2.6	*a*
Me-*i*-Pr_2CCl	13.6	2
Me-*t*-Bu_2CCl	18.4	16
i-Pr_3CO-*p*-NB	403	*b*
i-Pr_2-*t*-BuCO-*p*-NB	3,440	*b*
i-Pr-*t*-Bu_2CO-*p*-NB	3,330	*b*
t-Bu_3CO-*p*-NB	13,500	*b*

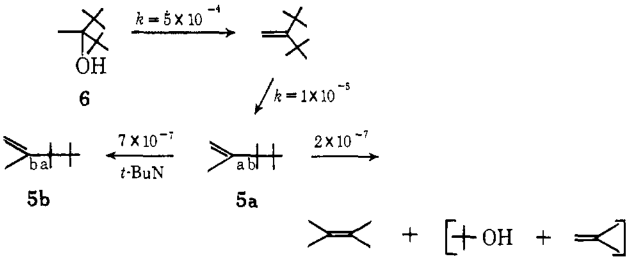
[a] H. C. Brown and H. L. Berneis, *J. Am. Chem. Soc.*, **75**, 10 (1953). [b] Compared with one another in 60% dioxane at 40° by Bartlett and Stiles.[1] For the comparison with *t*-butyl *p*-nitrobenzoate see this paper, Results.

An early attempt[5] to observe the effect of high branching on solvolysis rates was conducted with the chlorides made from a series of trialkylcarbinols up to tri-*t*-butyl. No method was then available to determine the structures of the mixtures of chlorides formed, although it was noted that their reactivities varied widely. From methyldi-*t*-butylcarbinol (**6**), for example, two chlorides were obtained which underwent solvolysis in 90% acetone at rates of 24 and 27,900, respectively, relative to *t*-butyl chloride. In an important paper, Shiner and Meier[16] carried the study of this system forward with nmr identification of the chlorides and their reaction products, and with the use of isotopic tracers to measure the rate constants of successive rearrangements of the olefins. They found that the fast chloride of the pair was 2-chloro-2,3,3,4,4-pentamethylpentane (**4**) (dimethyltriptylcarbinyl chloride) and that it was solvolyzed in 1:2 water–dioxane exclusively to unrearranged olefin **5**. They also determined the competitive rates



4 **5**

at which rearrangements and eliminations took place in a standard acid medium. From their study it



became clear that the chloride **4**, one of the most reactive saturated chlorides known, undergoes solvolysis without molecular rearrangement and without the formation of any ion having symmetrical methyl or *t*-butyl bridging. Thus in an important and probably representative open-chain case, participation of neighboring alkyl groups was ruled out as a factor in the relief of steric strain attending ionization.

The present work was done before this convincing elimination of alkyl bridging as a factor in the solvolysis rates. One of the purposes of the work was to learn whether the course of the curve of Figure 1 would continue upward as if a single force were at work, or show a maximum as if opposing forces were competing.

Results

Trialkylcarbinols were prepared from the appropriate dialkyl ketones (di-*t*-butyl, *t*-butyl neopentyl, or dineopentyl) and *t*-butyl- or neopentyllithium; *p*-nitro-

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[14] H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

[15] H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); H. C. Brown and W. J. Hammar, *J. Am. Chem. Soc.*, **89**, 6378 (1967), and following communications.

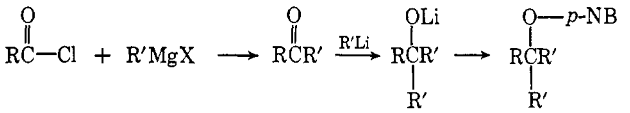
[16] V. J. Shiner, Jr., and G. F. Meier, *J. Org. Chem.*, **31**, 137 (1966).

Table II. Measured Rate Constants for Trialkylcarbinyl *p*-Nitrobenzoates ($R_1R_2R_3CO$-*p*-NB, 60% Dioxane (by weight), 0.1 *M* $NaClO_4$)

			40.0°		50.2°				
R_1	R_2	R_3	k_1, $sec^{-1} \times 10^5$ [c]	k_{rel}	k_1, $sec^{-1} \times 10^5$ [c]	k_{rel}	ΔH^*	ΔS^*	$\Delta\Delta F^*$
Me	Me	Me	0.000727[a]	1.0	0.00332[a]	1.0	29.3	−2.3	0.0
t-Bu	*t*-Bu	*t*-Bu	9.80[b]	13,500	31.6[b]	9,500	22..3	−5.9	5.9
Np	*t*-Bu	*t*-Bu	14.11	19,400	48.0	14,500	23.3	−1.8	6.2
Np	Np	*t*-Bu	49.2	68,000	153	46,000	21.6	−4.8	7.0
Np	Np	Np	0.408	560	1.42 (4)	430	23.8	−7.2	4.0

[a] Extrapolated. Measured rate constants are 8.34×10^{-5} at 115.3° and 1.249×10^{-5} at 97.3° (rates for the solvolysis of *t*-butyl *p*-nitrobenzoate in aqueous acetone solutions at 100.0° have been obtained by C. F. Wilcox, Jr., and M. E. Mesirov, *J. Am. Chem. Soc.*, **84,** 2757 (1962)). The rate constant without $NaClO_4$ was 6.95×10^{-5} at 115.3°. For comparison these were extrapolated to 60% (wt) dioxane (by the somewhat dubious procedure of applying the mY equation (A. H. Fainberg and S. Winstein, *ibid.*, **78,** 2770 (1956) at 100° instead of 25°) to give the value of 1.54×10^{-5} sec^{-1}. The corresponding value calculated from the data in this work (including a correction for zero concentration of $NaClO_4$) was 1.40×10^{-5} sec^{-1}. [b] These rates have been remeasured for calibration purposes and are slightly different from those reported previously[1] (9.05 at 50.0° and 31.7 at 50.0°). [c] Average of two or more runs, average deviation 0.6–6.0%.

benzoate esters were prepared by reaction of the lithium alkoxides with *p*-nitrobenzoyl chloride. The necessary ketones were known compounds obtainable by the coupling of acyl chlorides and Grignard reagents.

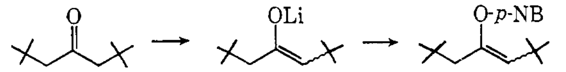


$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-Cl} + \mathrm{R'MgX} \longrightarrow \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R'} \xrightarrow{\mathrm{R'Li}} \mathrm{R}\underset{\mathrm{R'}}{\underset{|}{\overset{\mathrm{OLi}}{\overset{|}{\mathrm{C}}}}}\mathrm{R'} \longrightarrow \mathrm{R}\underset{\mathrm{R'}}{\underset{|}{\overset{\mathrm{O-}p\text{-NB}}{\overset{|}{\mathrm{C}}}}}\mathrm{R'}$$

R,R′ = *t*-Bu or neopentyl (Np)
p-NB = *p*-nitrobenzoyl

7, R = Np; R′-*t*-Bu
8, R = *t*-Bu; R′ = Np
9, R,R′ = Np

Dineopentyl ketone also reacted with the alkyllithiums by enolization as shown by the isolation of 2-*t*-butyl-1-neopentylvinyl *p*-nitrobenzoate (**10**) as a by-product



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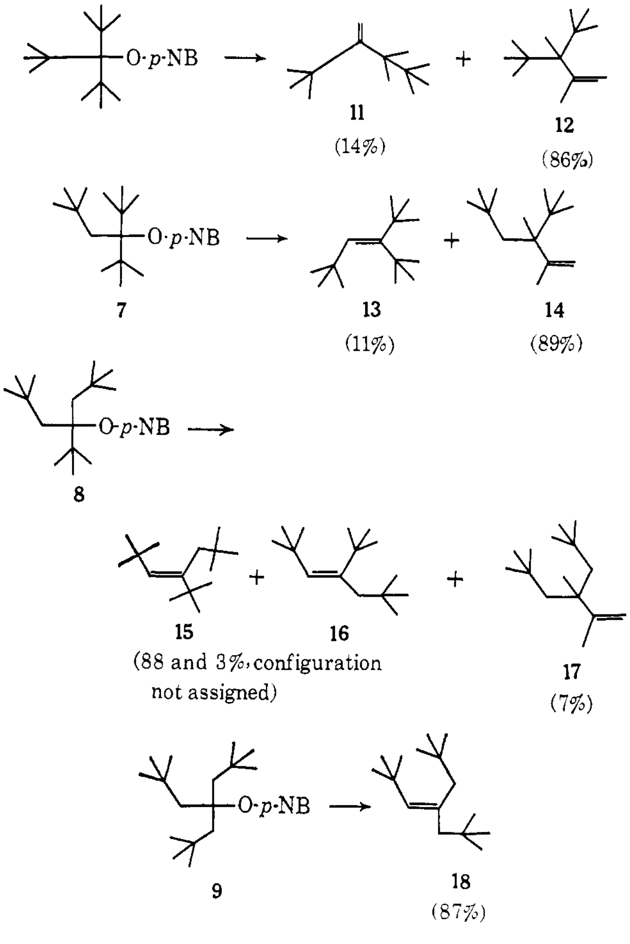
from the reaction of the ketone with neopentyllithium followed by *p*-nitrobenzoyl chloride. Similarly, some dineopentyl ketone was recovered after treatment with excess *t*-butyllithium and hydrolysis, indicating partial enolization.[17]

Solvolysis rates of the highly branched tertiary *p*-nitrobenzoates were measured in 60% (by weight) aqueous dioxane (0.1 *M* in $NaClO_4$) at 40 and 50° using titrimetric and spectrophotometric[18] methods. Rate constants obtained by the two methods were in close agreement. Titrimetric rate constants were also obtained for *t*-butyl *p*-nitrobenzoate at 115 and 97° using degassed solutions. Degassing was necessary because otherwise the titration end points were not stable, apparently on account of slow reaction of the base with oxidation products from the dioxane. The hydrolysis without $NaClO_4$ at 115° was found to be 17% slower, about the same salt effect as was previously observed for tri-*t*-butylcarbinyl *p*-nitrobenzoate.[1] The rate constants are given in Table II.

In order to ensure that *t*-butyl *p*-nitrobenzoate was reacting by alkyl oxygen cleavage a sample of methyl *p*-nitrobenzoate was subjected to the solvolytic conditions and was found to have a rate constant at least 400 times less than that of *t*-butyl *p*-nitrobenzoate at 115°. The rates would be expected to be similar if acyl oxygen cleavage occurred, and hence the *t*-butyl *p*-nitrobenzoate must react predominantly by alkyl oxygen cleavage.

Product studies were carried out by heating the esters in 60% dioxane containing a slight excess of sodium hydroxide. That the presence of base did not affect the rate-determining step in the reaction was demonstrated by a rate measurement on the di-*t*-butylneopentyl derivative with an equivalent amount of sodium hydroxide, which gave the same rate constant within experimental error as the same reaction without base. The base was probably unnecessary to prevent product isomerization as its absence did not affect the ratio of products from the tri-*t*-butyl derivative. The products of the reactions were separated and collected by vpc

Chart I. Products from Highly Branched *p*-Nitrobenzoates (relative yields in parentheses)



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(17) This ketone has also been found to be enolized by crowded aryl Grignard reagents, as evidenced by the isolation of the enol acetate after treatment with acetic anhydride: H. G. Hauthal, P. Kluge, and H. Schmidt, *J. Prakt. Chem.*, **29**, 296 (1965).

(18) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

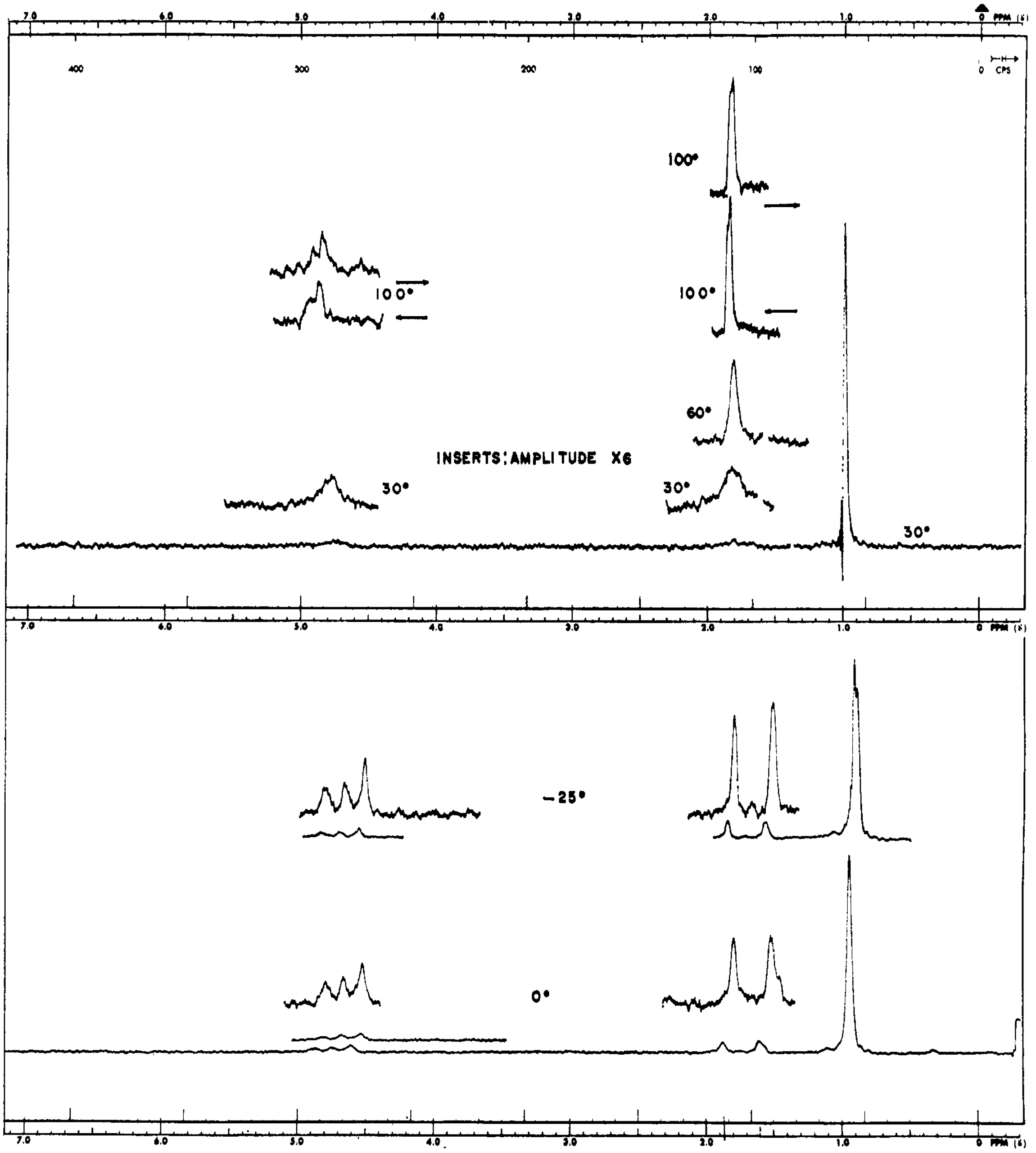

Figure 2. Nmr spectrum of 2-methyl-3,3-di-*t*-butylbutene-1 (**12**) from −25 to 100°.

and identified by their nmr and infrared spectra. The product identifications are shown in Chart I with the relative yields. Total yields of products isolated by vpc varied from 38 to 66% and collection efficiencies on recycled material varied from 18 to 82%. The identifications of the trisubstituted olefins (**13**, **15**, **16**, **18**) are thought to be unambiguous, except for the differentiation of the isomers **15** and **16**, aided by the distinctive patterns of *t*-butyl, methylene, and vinyl resonances (all unsplit) in the nmr.[19] As further proof of structure 1,1-dineopentyl-2-*t*-butylethylene (**18**) was subjected to ozonolysis and gave the expected dineopentyl ketone. The compounds designated as *gem*-disubstituted ethylenes (**11**, **12**, **14**, and **17**) show the strong infrared band around 11.0 μ characteristic of the terminal methylene group, while the trisubstituted ethylenes do not. The latter olefins have a much weaker carbon–carbon stretch around 6.2 μ than *gem*-disubstituted ones do.

Previously,[1] only olefin **11** had been identified as arising from tri-*t*-butylcarbinol, as *t*-butyl triptyl ketone was the product formed on oxidation of the total product. But the oxidation occurred in a very low conversion, and the recovered starting material was resistant to further oxidation. At the time, gas chromatography and nmr techniques were not available, but with their advent it is clear that a mixture of olefins was formed, and that **12** was inert toward the oxidation procedure used to cleave **11**.[20]

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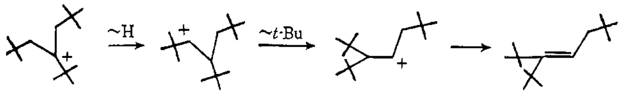
[19] Another possible isomer of **15** and **16**, 1,1-di-*t*-butyl-2-neopentylethylene, is mechanistically unlikely and would be expected to show a coupling constant of 4–10 cps. Its formation would proceed, if at all, through the steps



[20] W. J. Sheppard, ref 11, pp 8–13.

Compound **12** (2-methyl-3,3-di-*t*-butylbutene-1) had a temperature-dependent nmr spectrum (Figure 2) with coalescences at room temperature in the regions near δ 2 and 5. At $-25°$ there are singlets of equal intensities, totaling three protons, at δ 1.71 and 1.99, seen as a doublet at 100° with a splitting of the order of 1 cps. In the unsaturation region at $-25°$ there are three peaks, δ 4.71, 4.85, and 5.00, of relative intensities 2:1:1, totaling two protons; these became a broad, irregular multiplet at 100°.

The 100° spectrum is consistent with the normal[21] coupling constant of about 1.4 cps between the protons of a methyl group and hydrogen *trans* to it on a double bond and the similar or slightly smaller coupling between the protons of a terminal methylene group. The spectrum at $-25°$ indicates about equal populations of two conformations in which the chemical shifts of the isopropenyl CH_3 differ by 0.28 ppm. The unsaturation signal at $-25°$ might mean either that in one conformation the two methylene hydrogens are equally shielded or that the upfield member of the pair of signals due to methylene is at the same position in each conformation.

The restricted rotation giving rise to this temperature dependence of the nmr spectrum must be that of the isopropenyl group around the C_2–C_3 bond. The rotational barrier in propylene is threefold, with each energy minimum corresponding to eclipsing between the vinyl group and a hydroxygen atom.[22] However, this type of electronically based barrier is far too low to produce the effects observed here. A Stuart model of compound **12** suggests that steric hindrance is here imposing a sixfold rotational barrier, with the six staggered conformations, S1–S6, representing deeper energy wells than the three propylene-like, eclipsed conformations, E1–E3 (Figure 3). The identical barriers between S1 and S2 and between S5 and S6 (Figure 3) involve a methyl group rotating past a *t*-butyl group, and should be the highest of the barriers between conformations. When partial freezing of rotation first sets in, then the molecules may be divided into the groups S1–E1–S6, with the two *t*-butyl groups straddling a methyl, and the assembly of all other conformations, interconversion of which will still be rapid compared to those over the principal barrier. The near equality of populations must be fortuitous, and further spectral changes may well occur at still lower temperatures.

At the coalescence temperature the calculated[23] mean lifetime of a conformation group, 0.027 sec, corresponds to a rotational barrier of about 15 kcal.

Discussion

The product compositions from the new series of *p*-nitrobenzoates extend the evidence of Shiner and Meier that rearrangement is not essentially involved in the ionization process of highly branched compounds which show rate acceleration. Among these compounds there is no correlation between solvolysis rate and rearrangement; the fastest ester, **8**, yields 91% of unrearranged olefins, the slowest gives completely unrearranged product, while the two having intermediate rates of solvolysis give 100 and 89% rearrangement. It seems likely, then, that the highly branched tertiary esters, like other acyclic ionizing systems, ionize with only steric, not anchimeric, assistance from neighboring groups. In any case, it is in accord with long-known principles that the only migrations seen in these compounds are of groups moving from quaternary carbon atoms to yield new tertiary cations.

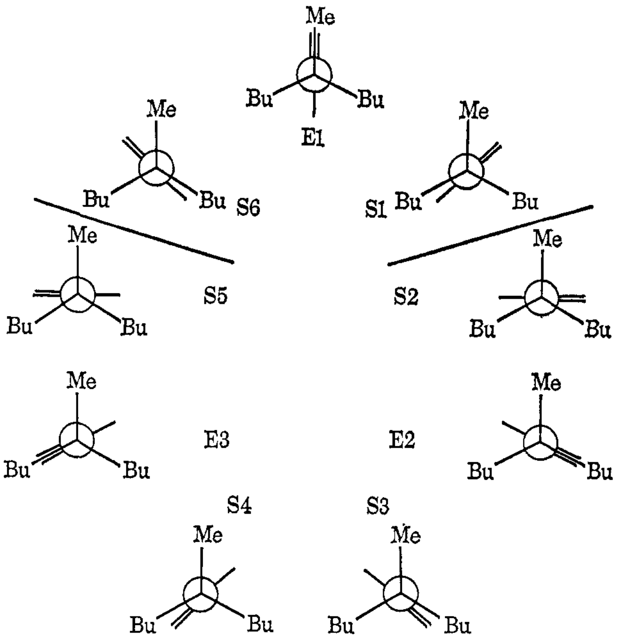
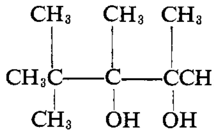


Figure 3.

Stiles and Mayer[6] observed that the pinacol rearrangement involving *t*-butyl migration from 2,3,4,4-tetramethyl-2,3-pentanediol (**19**) was more than 4000 times as fast as the rearrangement involving the migration of a similarly situated methyl group in pinacol. Either the diol **19** undergoes ionization at the position remote from the *t*-butyl group at least 100 times as fast as does pinacol, or else a preformed ion–water pair is induced to rearrange by participation of the migrating *t*-butyl with the observed great speed. Because of the magnitude of the rate difference between **19** and pinacol, Stiles and Mayer favored the latter mechanism. Compound **19**, however, is an isostere of Shiner and Meier's **4**, whose solvolysis rate exceeds that of the corresponding isostere of pinacol by a factor of 73,000 without any molecular rearrangement being involved in its ionization. That case, together with the large accelerations without rearrangement found in the present work, appears to reverse the balance of evidence so as to favor nonanchimeric ionization as the rate-determining step in the pinacol rearrangement of **19**.



$$\begin{array}{ccccc} CH_3 & & CH_3 & & CH_3 \\ | & & | & & | \\ CH_3C & — & C & — & CCH_3 \\ | & & | & & | \\ CH_3 & & OH & & OH \end{array}$$

19

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[21] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p 242.

[22] (a) J. E. Kilpatrick and K. S. Pitzer, *J. Res. Natl. Bur. Std.*, **37**, 163 (1946); (b) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

[23] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

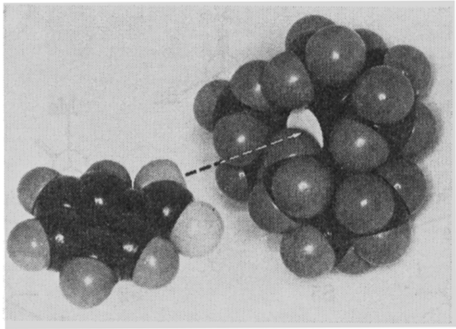

Figure 4. Fisher–Hirschfelder–Taylor model of the *t*-butyldineopentylcarbinyl group, showing hindrance to attachment of a benzoate group.

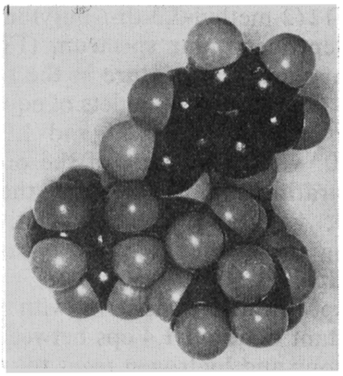

Figure 5. Model of trineopentylcarbinyl benzoate (*p*-nitro group omitted) (**9**), showing diminished hindrance relative to **8**.

Figure 1 shows a fairly consistent, if rough, logarithmic increase in solvolysis rate with increasing β substitution in *t*-butyl chloride or *p*-nitrobenzoate. The rates of **7** and **8** allow the impression that in its effect on ground-state strain the neopentyl group is more hindering than the *t*-butyl. Why then is there a sudden drop of more than a hundredfold in the solvolytic rate as the third *t*-butyl group is replaced by neopentyl?

It is extremely difficult to assemble a Stuart model of tri-*t*-butylcarbinol. With the Fisher–Hirschfelder–Taylor version of these models the insertion of the final methyl group even into the tri-*t*-butylcarbinyl radical invariably causes fission of one or more of the bonds already formed. In the wooden models this severe B strain still leaves room for the attachment of an ester group, although this room must be reduced in the actual molecule by angular distortion as the *t*-butyl groups are pushed away from one another.

In attempting to make a model of the most reactive ester, **8**, it is possible to assemble the *t*-butyldineopentylcarbinyl group, but not to put on the *p*-nitrobenzoate group. The central carbon atom of the tertiary radical is buried deep in the model and overlaid by the methyls of two neopentyl groups (Figure 4). The tertiary butyl, with its inflexible space demand adjacent to the central carbon atom, forces both neopentyl groups to extend over the "front" face of the radical. In this model, five or six of the nine methyl groups are so closely packed that they are unable to rotate. With an ester group present the compression is obviously greater than the models are able to reproduce.

Trineopentylcarbinyl *p*-nitrobenzoate (**9**) is the only ester of the present series of which a complete Fisher–Hirschfelder–Taylor model can be made. In the complete ester model only about three methyl groups are prevented from rotating. The models thus reflect the experimental finding that **9** shows the least steric acceleration of the series (Figure 5).

Unfortunately, it is not possible by the use of models to achieve any convincing resolution of the effects of groups into opposing contributions of steric acceleration and hindrance to solvation. By comparison of the most and least reactive esters **8** and **9** it is seen that the more reactive one has the greater hindrance around the leaving group as well as the greater hindrance on the back side. Thus any steric effect which the neopentyl group is capable of providing appears to be associated with acceleration of ionization, and solvent exclusion effects have yet to be recognized separately in highly branched open-chain compounds. The maximum in hindrance attained by one *t*-butyl and two neopentyl groups is best described in terms of incompatibility of shapes: the neopentyl group is bulkier than the *t*-butyl in that direction in which its quaternary atom extends, and two neopentyls are forced into a competition for space by the presence of *t*-butyl which limits the directions in which they may extend more than a neopentyl group would do in the same position.

It should be noted that the *possible* repulsive energies from close crowding in highly branched molecules are very large. In tri-*t*-butylcarbinol the nongeminal methyl groups are much closer together than in *cis*-2-butene; even the interaction energy deduced from that mild case (1.29 kcal/mol)[24] would account for $6 \times 1.29 = 7.7$ kcal from an estimated six such nearest-neighbor interactions. This is reduced by the angular deformability of the inner bonds, not revealed in the models. In addition, if closest packing should ever demand that an internal rotation be frozen in the unfavored eclipse conformation, there would be about 3-kcal destabilization for each of these rotations, with a maximum of 12 such possibilities. The reaction rates would further respond to any diminution of entropy associated with these restrictions and relieved at the transition state. It is evident from the size of these possible energies, compared with the highest observed $\Delta\Delta F^*$ of about 7 kcal, that we are nowhere near the upper limit of possible steric effects in highly branched molecules.

It should probably be remarked that the study of highly branched molecules in solvolysis has shed no special light on the phenomena of so-called nonclassical ions of the norbornyl, norbornenyl, bicyclohexyl, bicyclobutonium, phenonium, homotropylium, or other types. Our conclusion that there is no participation of neighboring saturated groups in the accelerated ionization of the highly branched acyclic esters might be paraphrased by saying that these solvolyses show none of the special characteristics which are regarded as indicative of the formation of nonclassical ions in the above cases.

Experimental Section

General. Analyses were performed by the Schwarzkopf Microanalytical Laboratory. Melting points (capillary) and boiling points are not corrected. Infrared spectra were determined in carbon tetrachloride solutions on a Perkin-Elmer 137 "Infracord" spectrophotometer. Ultraviolet spectra were recorded on a Perkin-

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[24] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 876 (1935).

Elmer 202 ultraviolet–visible spectrophotometer. Nmr spectra were obtained with a Varian A-60 instrument equipped with a variable-temperature probe and are reported in units of δ (parts per million, ppm) relative to tetramethylsilane. All gas chromatographic analyses and separations were carried out on an F & M Model 300 instrument with an 8 ft × 0.25 in. UCON LB 550X column.

Di-*t*-butyl ketone,[25] ***t*-butyl neopentyl ketone,**[26] **and dineopentyl ketone**[27] were prepared by methods described in the literature.

***p*-Nitrobenzoyl chloride** was obtained commercially and recrystallized from heptane just before use.

Di-*t*-butylneopentylcarbinol[28] was prepared by adding neopentyllithium in pentane to di-*t*-butyl ketone in pentane. After one crystallization from pentane the product was obtained in 68% yield melting at 42–45°. Further recrystallization gave mp 45.6–46.6°; ir: 2.6 μ; nmr: singlet (δ 1.08), 27 *t*-butyl H; singlet (δ 1.38), 1 OH; singlet (δ 1.60), 2 H of the methylene.

***t*-Butyldineopentylcarbinol** was prepared by adding dineopentyl ketone in pentane to excess *t*-butyllithium (Lithium Corporation of America) in pentane. Distillation gave first dineopentyl ketone and then the product in 54% yield; ir: 2.8 μ; nmr: singlet (δ 0.94), 9 H of the *t*-butyl group; singlet (δ 1.05), 1 OH; singlet (δ 1.09), 18 *t*-butyl H of two neopentyl groups; singlet (δ 1.46), 2 H, one from each methylene;[29] singlet (δ 1.59), 2 H, one from each methylene.[29] The same carbinol was also prepared from *t*-butyl neopentyl ketone and neopentyllithium.

Trineopentylcarbinol was prepared by adding dineopentyl ketone in pentane to neopentyllithium in pentane. The oily product was sublimed at 100° (10 mm) to give 27% of crystals which melted at room temperature; ir: 2.6 μ; nmr: singlet (δ 0.96), 1 OH; singlet (δ 1.07), 27 H of three *t*-butyls; singlet (δ 1.58), 6 H of three methylenes.

***t*-Butyl *p*-nitrobenzoate** was prepared from potassium *t*-butoxide and *p*-nitrobenzoyl chloride in *t*-butyl alcohol giving thin yellow plates after recrystallization from ether at −10°, mp 116.5–118.5° (lit.[30] 115–116°).

Methyl *p*-nitrobenzoate was prepared from *p*-nitrobenzoic acid in refluxing methanol with a catalytic amount of sulfuric acid with recrystallization from methanol, mp 94.0–96.5° (lit.[31] 95.1).

Tri-*t*-butylcarbinyl *p*-nitrobenzoate was prepared by Dr. W. J. Sheppard[11] by the method reported previously.[1]

Di-*t*-butylneopentylcarbinyl *p*-Nitrobenzoate (7). Neopentyllithium (0.167 mol) (prepared from neopentyl chloride and lithium wire at −10° in 220 ml of ether) was added over 15 min to di-*t*-butyl ketone (28.2 g, 0.198 mol) in 400 ml of ether. After stirring overnight at room temperature the lithium alkoxide was added to *p*-nitrobenzoyl chloride (36.5 g, 0.20 mol) in 200 ml of ether over 30 min. The precipitate was filtered off, the filtrate poured into sodium carbonate solution and separated, and the ether layer washed with sodium chloride solution, dried over sodium sulfate, and evaporated. Crystallization of the residue from ether at −25° gave 37.1 g (51%) of yellow crystals, mp 100–104°. The analytical sample (large yellow prisms from pentane at −25°) began melting at 97.6°, resolidified, and melted at 234° (*p*-nitrobenzoic acid mp 242°); ir: 5.80 μ; uv: $\lambda_{\max}$ (cyclohexane) 258 mμ (ϵ 12,000); nmr: singlet (δ 1.10), 9 *t*-butyl H of the neopentyl ; singlet (δ 1.33), 18 H of the two *t*-butyls; singlet (δ 2.48), 2 H of the methylene; doublet (δ 8.28 and 8.30), 4 aromatic H.

Anal. Calcd for $C_{21}H_{33}NO_4$: C, 69.39; H, 9.15; N, 3.85. Found: C, 69.44; H, 9.20; N, 3.70.

***t*-Butyldineopentylcarbinyl *p*-Nitrobenzoate (8).** *t*-Butyldineopentylcarbinol (10.3 g, 0.045 mol) in 50 ml of ether was added over 20 min to a solution of 0.051 mol of *n*-butyllithium in 33 ml of pentane (Foote Mineral Co.) and 250 ml of ether. After 40 min of stirring, the alkoxide solution was added over 30 min to *p*-nitrobenzoyl chloride (9.3 g, 0.045 mol) in 100 ml of ether, stirred 2 hr, filtered, and evaporated. The residue was fractionally crystallized from pentane at −25 and 0° to give 2.87 g (0.00765 mol, 17%) of yellow crystals, mp 57–60°. The analytical sample (large yellow prisms from pentane at −25°) gave mp 57.4–60.2° (resolidification); ir: 5.80 μ; $\lambda_{\max}$ (cyclohexane) 258 mμ (ϵ 14,000); nmr: singlet (δ 1.14), 18 *t*-butyl H of the two neopentyls; singlet (δ 1.18), 9 H of the *t*-butyl; quartet (AB system centered at δ 2.00 and 2.53, *J* = 16 cps), 4 H of the two methylenes; doublet (δ 8.20 and 8.22), 4 aromatic H.

Anal. Calcd for $C_{22}H_{35}NO_4$: C, 69.99; H, 9.35; N, 3.71. Found: C, 70.18; H, 9.31; N, 3.96.

Trineopentylcarbinyl *p*-Nitrobenzoate (9). The crude product was prepared by the method employed for di-*t*-butylneopentylcarbinyl *p*-nitrobenzoate, from 0.133 mol of neopentyllithium in 175 ml of ether, 22.6 g (0.133 mol) of dineopentyl ketone, and 25 g (0.135 mol) of *p*-nitrobenzoyl chloride. Fractional crystallization from ether at −25° gave 8.19 g (0.0256 mol, 19%) of material identified as **2-*t*-butyl-1-neopentylvinyl *p*-nitrobenzoate (10)** (*see below*), mp 119–124°. Fractional crystallization of the residue, first from carbon tetrachloride at −25° and then from pentane at −25°, eventually gave 11.24 g (0.0287 mol, 22%) of the desired ester, mp 86–89°. The analytical sample (large yellow prisms from pentane at −25°) had mp 86.6–88.8°; ir: 5.80 μ; uv: $\lambda_{\max}$ (cyclohexane) 258 mμ (ϵ 15,000); nmr: singlet (δ 1.10), 27 H of three *t*-butyls; singlet (δ 2.24), 6 H of three methylenes; doublet (δ 8.14 and 8.20), 4 aromatic H.

Anal. Calcd for $C_{23}H_{37}NO_4$: C, 70.55; H, 9.53; N, 3.58. Found: C, 70.74; H, 9.62; N, 3.63.

2-*t*-Butyl-1-neopentylvinyl *p*-nitrobenzoate (10, configuration indeterminate) as obtained above was recrystallized from pentane at −25° to give pale yellow needles, mp 125.6–126.0°; ir: 5.79 (moderate) and 5.92 μ (strong);[32] uv: $\lambda_{\max}$ (cyclohexane) 263 mμ (ϵ 15,000); nmr: singlet (δ 0.94), 9 *t*-butyl H of the neopentyl; singlet (δ 1.11), 9 H of the *t*-butyl; singlet (δ 2.39), 2 H of methylene; singlet (δ 4.50), 1 vinyl H; doublet (δ 8.13, 8.26), 4 aromatic H.

Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.48; H, 7.79; N, 4.44.

Saponification equivalents were 288 and 298 (calcd 319). The organic residue from these determinations was extracted, distilled, and identified as dineopentyl ketone by comparison of its infrared spectrum and vpc retention time with those of authentic material. The enol ester (0.55 g) resisted refluxing for a week with 90 ml of acetone, 25 ml of water, and 20 ml of concentrated HCl. On cooling a solid precipitate formed which was filtered off, washed, and dried to give 0.486 g (88%) of starting material with an unchanged spectrum.

Solvolysis Product Studies. The ester (about 0.5 g, 1 mmol) was dissolved in 145 ml of dioxane and an equivalent amount of sodium hydroxide solution was added, followed by enough water to make the total volume of water 100 ml. In the case of di-*t*-butylneopentylcarbinyl *p*-nitrobenzoate, twice this volume of solvent was used for a run with 4 mmol of ester. The solutions, in which the esters were insoluble at room temperature and from which the products sometimes separated at bath temperatures, were placed in constant-temperature baths and agitated until the esters completely dissolved. After the specified time, the flasks were removed from the bath, cooled, diluted with aqueous NaCl solutions, and extracted three times with pentane and the combined pentane layers washed eight times with water. The pentane was distilled away and the residues were subjected directly to vpc separation. The products were collected in tubes in a Dry Ice bath at the exit port of the chromatograph. The details of the gas chromatographic separations are given in Table III, and structure proofs of the various products are considered individually. In a control experiment the parent carbinol was shown by vpc to be absent from the solvolysis product of the di-*t*-butylneopentylcarbinyl ester.

Products from Tri-*t*-butylcarbinyl *p*-Nitrobenzoate. The first product from this ester, previously identified, was 1-*t*-butyl-1-triptylethylene (**11**); nmr (unchanged at −25 and 90°): singlet (δ 0.91), 9 H of three methyls γ to the double bond; singlet (δ 1.21), 15 H of five methyls β to the double bond; doublet (δ 4.89, 5.23), 2 methylene H.

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[25] N. C. Cook and W. C. Percival, *J. Am. Chem. Soc.*, **71**, 4141 (1949).

[26] F. C. Whitmore, *et al.*, *ibid.*, **63**, 643 (1941).

[27] F. C. Whitmore, C. D. Wilson, J. V. Capinjola, C. O. Tongberg, G. H. Fleming, R. V. McGrew, and J. N. Crosby, *ibid.*, **63**, 2035 (1941).

[28] This compound was mentioned with no details as to preparation or physical properties by H. D. Zook, J. March, and D. F. Smith, *ibid.*, **81**, 1617 (1959).

[29] Different chemical shifts of the two members of a geminal grouping due to the three different substituents on the adjacent carbon; see J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 58–60. So-called "diastereotopic" groups; see K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967.

[30] J. H. Brewster and C. J. Ciotti, Jr., *J. Am. Chem. Soc.*, 77, 6214 (1955).

[31] M. D. Armstrong and J. E. Copenhaver, *ibid.*, **65**, 2252 (1943).

[32] Typical of enol esters; see K. Nakanishi, "Infrared Absorption Spectroscopy-Practical," Holden-Day, Inc., San Francisco, Calif., 1962, p 181.

Table III. Vpc Product Separation from Ester Solvolyses

p-Nitrobenzoate	Wt, g	Mmoles	Col temp, °C	Product	Ret time, min	% of product	Wt isolated, g	Mmoles isolated	Mol % isolated
Tri-*t*-butylcarbinyl	0.532	1.53	145	**11**	16.4	14[b]	0.010	0.056	3.7
				12	24.4	86[b]	0.173	0.95	62
Di-*t*-butylneopentylcarbinyl (**7**)	1.46	4.02	140	**13**	8.0	11	0.023	0.117	2.9
				14	13.2	89	0.383	1.96	49
t-Butyldineopentylcarbinyl (**8**)	0.34	0.94	135	**15** or **16**	21.2	88	0.158	0.759	47.8
				...	22.0[a]	2	...	...	...
				16 or **15**	24.0	3	0.009	0.041	2.6
				17	28.4	7	0.0215	0.102	6.4
Trineopentylcarbinyl (**9**)	0.519	1.33	140	...	8.8[a]	8	...	...	...
				...	14.8[a]	5	...	...	...
				18	18.8	87	0.113	0.503	37.8

[a] These products were not examined further. [b] Product ratio unchanged when base omitted from solvolysis solution.

The second product was identified as 2,3,4,4-tetramethyl-3-*t*-butylpentene-1 (**12**); ir: 6.20 and 11.07 μ (terminal methylene); nmr: singlet (δ 1.08), 21 H of two *t*-butyls and one methyl removed from the double bond, unchanged at 100° but split about 1 cps at $-25°$; singlet (broad, δ 1.85), 3 H on the 2-methyl group, split about 1 cps at 100° and split into two peaks (δ 1.71, 1.99) at $-25°$; singlet (broad, δ 4.86), 2 methylene H, became an irregular multiplet at 100° and split into three peaks (δ 4.71, 4.85, 5.00; intensity, 2:1:1) at $-25°$. This material was hydrogenated as previously[1] and sublimed to give a white solid, mp 127–134° (lit.[1] 116–118°); nmr: singlet (δ 0.87), 3 H of a methyl; singlet (δ 1.12), 21 H of two *t*-butyls plus half of the isopropyl doublet; singlet (δ 1.26), 3 H of half the isopropyl doublet; multiplet (δ 1.8–2.5), methine H of the isopropyl.

Product from Di-*t*-butylneopentylcarbinyl *p*-Nitrobenzoate (7). The first product was identified as impure tri-*t*-butylethylene (**13**); ir: no bands at 6.2 or 11 μ; nmr: three singlets (δ 1.16, 1.18, 1.30), each 9 H of a *t*-butyl; singlet (δ 5.28), 1 ethylenic H; impurity peaks from δ 0.84 to 1.10.

The second product was identified as 2,3,5,5-tetramethyl-3-*t*-butylhexene-1 (**14**); ir: 6.22 and 11.14 μ; nmr: singlets (δ 0.87, 0.93), each 9 H of a *t*-butyl; singlet (δ 1.11), 3 H of 3-methyl singlet (δ 1.79, slightly split), 3 H of 2-methyl; doublet (δ 4.79, 4.96, both slightly split), 2 olefinic H. The AB system of the saturated methylene group accounts for several small peaks appearing in the aliphatic region.

Products from *t*-Butyldineopentylcarbinyl *p*-Nitrobenzoate (8). The first product was identified as one of the 1,2-di-*t*-butylneopentylethylenes (**15** or **16**); ir: no bands at 6.2 or 11.0 μ; nmr: singlets (δ 1.00, 1.09, 1.10), each 9 H of a *t*-butyl group; singlet (δ 2.20), 2 H of the methylene; singlet (δ 5.31), ethylenic H. The second product was identified as the other isomeric 1,2-di-*t*-butylneopentylethylene (**16** or **15**); nmr: singlets (δ 0.90, 0.97, 1.07), each 9 H of a *t*-butyl group; singlet (δ 1.95), 2 H of the methylene; singlet (δ 4.90), ethylenic H. The third product was identified as 2,3,5,5-tetramethyl-3-neopentylhexene-1 (**17**); nmr: singlet (δ 0.91), 18 H of the two *t*-butyls; singlet (δ 1.76), 3 H of the 2-methyl; singlet (broad, δ 4.72), 2 ethylenic H. There were small singlets ($\sim$1–2 H each) at δ 0.97, 1.08, 1.22, and 1.42 and a larger (2–3 H) peak at δ 1.37 to account for the AB pattern of the two methylenes[29] and the remaining methyl group.

Products from Trineopentylcarbinyl *p*-Nitrobenzoate (9). The small product was identified as 1,1-dineopentyl-2-*t*-butylethylene (**18**); ir: no bands at 6.2 or 11.0 μ; nmr: singlets (δ 0.88, 0.96, 1.09), each 9 H of a *t*-butyl; singlets (δ 1.88, 2.17), each 2 H of a methylene; singlet (δ 5.04), olefinic H. This product was also obtained in 66% yield after twice distilling the crude product through a short-path column at 135° (0.25 mm) (pot) and was shown to be more than 98% pure by vpc. Treatment of this material in methylene chloride with ozone and then triphenylphosphine, followed by distillation, gave a liquid with six peaks in the vpc, one of which had the same retention time as dineopentyl ketone. Collection gave material with infrared and nmr spectra identical with those of dineopentyl ketone.

Rate measurements were carried out in 60% (by weight) aqueous dioxane (dioxane purified by the method of Fieser)[33] 0.100 *M* in sodium perchlorate (reagent grade sodium perchlorate was dried several days at 100° under an aspirator vacuum). Bath temperatures were measured with NBS thermometers; they varied within $\pm 0.05°$. Concentrations used in titrimetric runs were all limited by solubility. As a control in one run with trineopentylcarbinyl *p*-nitrobenzoate the starting material was recovered after partial reaction and was found to be unchanged.

In a typical run with *t*-butyl *p*-nitrobenzoate a solution was prepared with 0.524 g (0.00235 mol) of ester and 1.23 g (0.0100 mol) of sodium perchlorate in 58.36 ml (60.0 g) of dioxane and 40 ml of water. Aliquots (10 ml) were placed in tubes which were sealed under helium after a degassing routine involving evacuation during three freezes and subsequent thaws using Dry Ice–acetone or liquid nitrogen. The tubes were placed in the bath and after equilibrating approximately 15 min were successively withdrawn and titrated to a phenolphthalein end point.

In a typical run with a highly branched ester 0.260 g (0.000716 mol) of di-*t*-butylneopentylcarbinyl *p*-nitrobenzoate was dissolved in 145.9 ml (150.0 g) of dioxane and 3.07 g (0.0251 mol) of sodium perchlorate was dissolved in 100 ml of water. The solutions were equilibrated in the constant temperature bath for 30 min and then the aqueous solution was poured into the dioxane solution and thoroughly mixed. Then 25-ml aliquots were withdrawn at intervals, discharged into ice water, and titrated to phenolphthalein end points.

Spectrophotometric runs[18] were carried out as were the titrimetric runs except that 58.36 ml (60.0 g) of dioxane was used with 40 ml of water and 1.23 g of sodium perchlorate. The weights of ester used averaged about 10 mg. Aliquots (5 ml) were removed and shaken 1 min with a solution of 10 ml of 10% sodium bicarbonate and 10 ml of cyclohexane. After standing several minutes the water layer was let out of the separatory funnel and, after standing a few minutes more, a portion of the cyclohexane solution was pipetted out and the absorbance at 258 mμ determined with a Beckman DU instrument. The blank cell was filled with a solution prepared as above except for the ester and the treatment in the constant temperature bath.

Rate constants and activation parameters were computer calculated using least-squares programs written by Drs. J. M. Wright and J. M. McBride and Mr. M. C. Kohn.

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(33) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 285.