TABLE III

PROPERTIES OF 1-(X-BENZYL)-4-CARBOMETHOXYPYRIDINIUM SALTS

| X | Salt | M.p., °C. | Color | Analyses, %, Calcd. C | Calcd. H | Calcd. N | Found C | Found H | Found N |
|---|---|---|---|---|---|---|---|---|---|
| 4-H | $I^-$ | 165–168 d. | Yel. | 47.34 | 3.97 | 3.94 | 47.47 | 3.73 | 3.79 |
|  | $ClO_4^-$ | 178–180 | White | 51.31 | 4.31 | 4.27 | 51.42 | 4.09 | 4.20 |
| 4-Cl | $I^-$ | 173–175 d. | Yel. | 43.16 | 3.36 | 3.59 | 43.39 | 3.44 | 3.49 |
|  | $ClO_4^-$ | 158–159 | White | 46.43 | 3.62 | 3.87 | 46.55 | 3.80 | 3.85 |
| 2,6-$Cl_2$ | $I^-$ | 158–161 d. | Yel. | 39.74 | 2.62 | 3.31 | 39.82 | 2.90 | 3.09 |
|  | $ClO_4^-$ | 185–187 | White | 42.50 | 2.80 | 3.54 | 42.54 | 3.13 | 3.44 |
| 4-$NO_2$ | $I^-$ | 152–154 | Org.red | 42.02 | 3.28 | 7.00 | 42.21 | 3.33 | 7.04 |
|  | $ClO_4^-$ | 187–189 | White | 45.11 | 3.52 | 7.52 | 45.32 | 3.66 | 7.74 |
| 4-$OCH_3$ | $I^-$ | 136–140 d. | Yel. | 46.77 | 4.19 | 3.64 | 46.68 | 4.20 | 3.60 |
|  | $ClO_4^-$ | 142–144 | White | 50.36 | 4.51 | 3.92 | 50.38 | 4.59 | 4.15 |

as follows: The alcohol, *p*-methoxybenzyl alcohol (50 g.) was dissolved in dry ether (150 ml.) and dry hydrogen chloride was passed through the solution for 2 hours. The ether was evaporated under nitrogen at room temperature. The colorless residue was dissolved in acetone (250 ml.; previously distilled and dried by passage through neutral Wölm alumina) and refluxed for 2 hours with sodium iodide (56 g.) under nitrogen. The sodium chloride produced was filtered off in a tent under nitrogen. Methyl isonicotinate (50 g.) was added to the warm solution, the temperature maintained at 50° for an hour, the solution allowed to cool overnight, then left at 0° for 40 hours. The yellow crystals were filtered off and washed with ice-cold methanol; yield 80 g. (89%, based on the *p*-methoxybenzyl alcohol used).

The benzylpyridinium perchlorates were prepared by reaction of the iodides with silver perchlorate in methanol.

Data on the iodides and perchlorates are summarized in Table III. Without exception, all salts were recrystallized from methanol to constant m.p.

The solvent, *cis*-1,2-dichloroethylene, was purchased from the Aldrich Chemical Co., Milwaukee, Wis., and was purified by fractionation through a large column packed with stainless steel saddles. The fraction boiling at 60° was poured through a neutral Wölm alumina column immediately before use.

Spectra.—Solutions of the iodides were prepared by weighing *ca.* 1.6 mg. on a Cahn Electrobalance, model M10, and dissolving in 50 ml. of *cis*-1,2-dichloroethylene. All manipulations were carried out in a dry-box under argon through iris ports using rubber gloves. After the quartz cells (5 or 10 cm.) were filled, spectra were measured on a Cary recording spectrophotometer, model 14 or model 11. Each peak position was estimated from slow reruns over the maximum and each compound was measured several times.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

# Driving Forces in the Solvolysis of Dimethylcyclobutylcarbinyl *p*-Nitrobenzoate and Related Systems

BY CHARLES F. WILCOX, JR., AND MICHAEL E. MESIROV[1]

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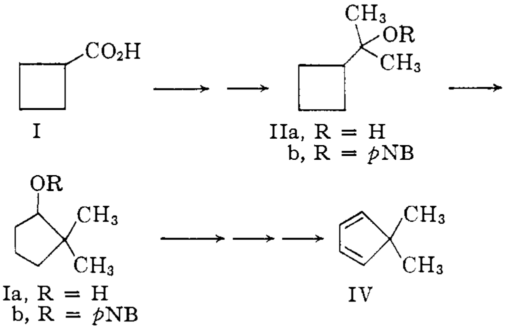
Dimethylcyclobutylcarbinyl *p*-nitrobenzoate was solvolyzed in 60 and 70% aqueous acetone at 100.0° and the driving force for ring expansion calculated to be 2.0 kcal./mole. The driving forces of other three- and four-membered ring expansions are calculated and compared. A linear relation exists between driving force and number of α-methyl groups present at the reacting carbon atom. From a consideration of the products formed in the present solvolyses it is concluded that dimethylcyclobutylcarbinyl *p*-nitrobenzoate forms a bridged non-classical ion and that the driving force is primarily a relief of strain and not a polarizability stabilization.

## Introduction

There has appeared recently a synthesis of 5,5-dimethylcyclopentadiene (IV) by an unambiguous but tedious route.[2] While this synthesis was being developed, a considerably easier synthesis was also considered. In outline form, the alternate plan was to convert the readily synthesized[3] cyclobutanecarboxylic acid (I) into dimethylcyclobutylcarbinol (II) followed by ring enlargement to 2,2-dimethylcyclopentanol (III). The latter alcohol could then be converted into the desired diene.



I

IIa, R = H
b, R = *p*NB

IIIa, R = H
b, R = *p*NB

IV

*p*NB = *p*-nitrobenzoate

Further consideration of the ring enlargement step (II → III) led to the calculation that, according to the Winstein driving force treatment[4] and a tentative estimate[5] for the cyclobutyl $L_0$ value, roughly one-half of the molecules would react by way of non-classical ions. This calculated equality of classical and non-classical routes arises from the balancing of the non-classical cyclobutyl driving

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[1] Taken from the dissertation submitted by M. E. Mesirov to Cornell University in partial completion of the requirements for the Ph.D. degree, Sept., 1961.

[2] C. F. Wilcox, Jr., and M. Mesirov, *J. Org. Chem.*, **25**, 1841 (1960).

[3] G. B. Payne and C. W. Smith, *ibid.*, **22**, 1681 (1957).

[4] S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 821 (1948), and later papers.

[5] S. Winstein, Notes of the Baker Lectures, Cornell University, Spring, 1957.

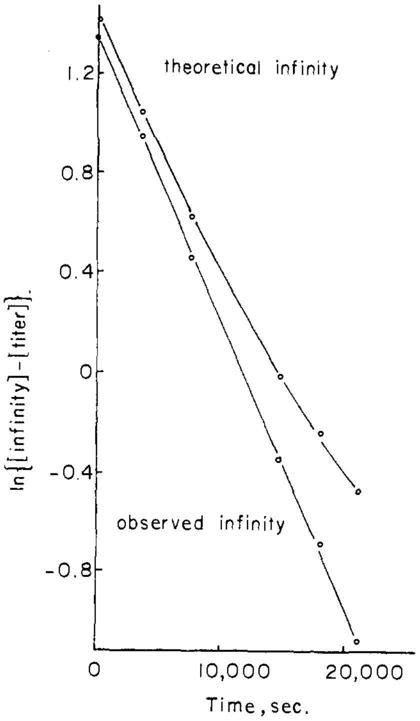

Fig. 1.—Typical rate data plot using theoretical and observed infinity.

force by the net acceleration of the two $\alpha$-methyl groups on the classical ion. Because of this intriguing coincidental equality and the timely appearance of another useful route to IV[6] as well as a potential one,[7] our emphasis was refocused on determining the actual driving force in this system.

The results presented in this paper are primarily concerned with the driving force occurring in the dimethylcyclobutylcarbinyl system, the resulting product composition, and the consequent mechanistic interpretation. Solvolysis data on other cyclobutylcarbinyl and cyclopropylcarbinyl systems have been collected for comparison with the dimethylcyclobutylcarbinyl system.

**Kinetics.**—The sovolysis of dimethylcyclobutylcarbinyl *p*-nitrobenzoate (IIb) in 60 vol. % aqueous acetone at 100.0° liberated only 87.5 ± 1.0% of the stoichiometric acid. When the theoretical infinity was used to calculate a first-order rate constant a diminishing constant was obtained; however, if the observed infinity was employed the first-order rate constant for disappearance of ester IIb was steady at $(1.16 \pm 0.01) \times 10^{-4}$ sec.$^{-1}$. A typical rate run is shown in Fig. 1. In 70 vol. % aqueous acetone at 100.0° the situation was similar with 90.0 ± 1.0% of the stoichiometric acid liberated and a first-order rate constant based on the observed infinity of $(4.22 \pm 0.02) \times 10^{-5}$ sec.$^{-1}$. This kinetic behavior is accounted for by assuming solvolysis to acidic products accompanied by concurrent arrangement to a new ester which is inert under the reaction conditions. When a separate sample of ester IIb was solvolyzed in 60% acetone at 100° for fourteen half-lives, an 11.0% yield of nearly pure 2,2-dimethylcyclopentyl *p*-nitrobenzoate (IIb) was obtained. This secondary neopentyl-type ester would be expected to be inert under the present conditions.

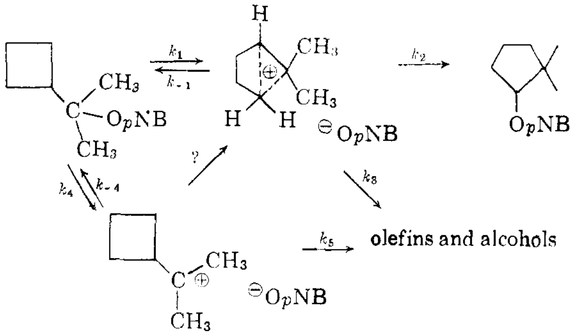

Fig. 2.—Solvolysis scheme.

A reasonable working hypothesis to account for these data is that of Fig. 2. Here, the apparent first-order rate constant, $k_{\text{obs}}$, is a sum of a rate constant giving titratable products, $k_{\text{tit}}$, and a rearrangement rate constant $k_r$. The definitions of $k_{\text{tit}}$ and $k_r$ in terms of the separate rate constants of Fig. 2 are given at the bottom of this figure.

$$k_{\text{tit}} = \frac{k_1k_3}{k_{-1} + k_2 + k_3} + \frac{k_4k_5}{k_{-4} + k_5}$$

$$k_r = \frac{k_1k_2}{k_{-1} + k_2 + k_3}$$

$$k_{\text{obs}} = k_{\text{tit}} + k_r$$

$$\frac{k_{\text{tit}}}{k_{\text{obs}}} = \text{fraction of stoichiometric acid liberated at apparent infinity}$$

Although other ions such as solvent separated ion pairs may well intervene in these solvolyses, it will be shown that the scheme of Fig. 2 is sufficient to account for the products as well as the rate data.

**Driving Force.**—The definition[4] of driving force, $L$, is $RT \ln k_\Delta/k_c$ where $k_\Delta$ is the rate constant for the reaction involving neighboring group participation and $k_c$ is the rate constant for the classical reaction without neighboring group participation but including any inductive effects the neighboring group might exert. The value of $k_c$ for ester IIb was estimated by the method of Streitwieser[8] which employs a Taft[9] $\rho^*\sigma^*$ inductive correction to a reference system such as *t*-butyl. A value of $\rho^*$ appropriate for *p*-nitrobenzoate solvolyses in 60% acetone at 100° was estimated to be −2.2. The solvolytic data determined employed for the estimation are presented in Table I. It should be noted that the present value of −2.2 is considerably less than the $\rho^*$ of −3.4 ± 0.1 observed by Streitwieser[8] for the limiting solvolysis of secondary brosylates and tertiary chlorides. The difference presumably reflects the statistical uncertainty associated with the present limited range of $\Sigma\sigma^*$ values,[10] although conceivably it might represent a

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(6) R. Rouse, 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960; R. Rouse and W. E. Tyler III, *J. Org. Chem.*, **26**, 3525 (1961).

(7) H. Kwart and J. A. Ford, Jr., *ibid.*, **24**, 2060 (1959).

(8) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **78**, 4935 (1956).

(9) R. Taft, Jr. in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

lesser development of positive charge in the *p*-nitrobenzoate transition states. The Streitwieser value is favored. However, in order to accommodate both possibilities, both $\rho^*$ values have been used and the resulting *range* in driving force is given. Fortunately, the driving force is rather insensitive to the choice. A $\sigma^*$ for cyclobutyl has not been reported, but from the acid dissociation data of Roberts[11] it would appear that it is similar to that for cyclopropyl which has been quoted[12] as $+0.11 \pm 0.03$.[13] This value combined with the *t*-butyl *p*-nitrobenzoate rate gives a calculated $k_c$ for IIb of $0.68 \times 10^{-5}$ to $0.92 \times 10^{-5}$ sec.$^{-1}$ depending on the above choice of $\rho^*$.

TABLE I

SOLVOLYSIS RATE CONSTANTS OF TERTIARY *p*-NITROBENZOATES IN 60 VOL. % AQUEOUS ACETONE AT 100.0°

| $R_1$ | $R_2$ | $R_3$ | $10^5 k_1$, sec.$^{-1}$ | $\Sigma\sigma^*$ |
|---|---|---|---|---|
| $CH_3$ | $CH_3$ | $CH_3$ | 1.61 | 0.00 |
| $C_2H_5$ | $CH_3$ | $CH_3$ | 3.12 | .10 |
| $C_6H_{11}$ | $CH_3$ | $CH_3$ | 6.22 | .27 |
| *i*-$C_3H_7$ | $CH_3$ | $CH_3$ | 2.97 | .19 |
| $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | 7.07 | .30 |
| $CH_3$ | $C_2H_5$ | *n*-$C_3H_7$ | 5.80 | .22 |

TABLE II

DRIVING FORCES OF CYCLOBUTYL COMPOUNDS

| Compound | $k_{\text{tit}}$, sec.$^{-1}$ | Cyclobutyl solvent | Temp., °C. | $\Delta\Sigma\sigma^*$ | $\rho^*$ | *L*, kcal. |
|---|---|---|---|---|---|---|
| Cyclobutylcarbinyl bromide[15] | $1.66 \times 10^{-5}$ | 60 vol. % aq. ethanol | 75 | +0.41 | −3.4 | 6.5 |
| Neopentyl bromide[a] | $3.8 \times 10^{-8}$ | | | | | |
| Cyclobutylcarbinyl tosylate[18] | $3.56 \times 10^{-5}$ | HOAc | 75 | + .41 | −3.4 | 6.5 |
| Neopentyl tosylate[19] | $8.35 \times 10^{-7}$ | | | | | |
| Methylcyclobutylcarbinyl brosylate[20] | $1.24 \times 10^{-3}$ | HOAc | 25 | + .11 | −3.4 | 4.3 |
| Isopropyl brosylate[19] | $2.43 \times 10^{-1}$ | | | | | |
| Dimethylcyclobutylcarbinyl *p*-nitrobenzoate, IIb | $1.02 \times 10^{-4}$ | 60 vol. % aq. acetone | 100 | + .11 | −3.4 | 2.0 |
| *t*-Butyl *p*-nitrobenzoate | $1.61 \times 10^{-5}$ | | | | (−2.2) | (1.7) |
| Ester IIb | $3.80 \times 10^{-5}$ | 70 vol. % aq. acetone | 100 | + .11 | −3.4 | 2.0 |
| *t*-Butyl *p*-nitrobenzoate | $6.81 \times 10^{-6}$ | | | | | |

[a] The rate constant was estimated from the data of Dostrovsky and Hughes[16] for the solvolysis of neopentyl bromide at 95° and 115° in 50% and 70% ethanol–water mixtures. The solvent correction was made by the Winstein–Grunwald treatment.[17]

The calculation of $k_\Delta$ offers an additional complication. The theoretically desirable expression for $k_\Delta/k_c$ is, in the symbolism of Fig. 2, just $k_1/k_4$. In order to extract this ratio from the available experimental data, it is necessary to make some further assumptions about the magnitudes of the remaining rate constants. Many assumptions are possible, but in this paper it will be arbitrarily taken that $k_{-4}/k_5 = (k_{-1} + k_2)/k_3$ which requires that the ratio of rates of total anion collapse to solvent collapse is a constant in a given solvent independent of the detailed distribution of charge in the intermediates. This assumption would be exact if the rate constants were determined by the magnitude of the positive charge alone. On this basis $k_1/k_4$ is given by $(k_{\text{tit}} - k_c)/k_c$ which leads to a calculated $k/k_c$ ratio of 10–14 or a driving force of 1.72–1.97 kcal.[14]

**Driving Forces in Other Cyclobutylcarbinyl and Cyclopropylcarbinyl Systems.**—For comparison with the foregoing results the driving forces associated with several other cyclobutylcarbinyl and cyclopropylcarbinyl systems have been calculated from data available in the literature. The data used in these calculations and the derived driving forces are collected in Tables II and III. The method of calculation was identical with that described in the previous section and involved selection of an appropriate non-participating reference with a $\rho\sigma^*$ correction for any difference in inductive effects. In Tables II and III the column entitled $\Delta\Sigma\sigma^*$ refers to the difference in the sum of $\sigma^*$ constants between the reference and participating compounds. The column entitled $\rho^*$ gives the value(s) of $\rho^*$ employed in that particular calculation.

These tables with their footnotes are largely self-explanatory; however, two comments are in order concerning the choice of reference systems. First, from the acetolysis of neopentyl tosylate at 118° Saunders and Paine[21] have concluded that about one-third of the products involved methyl migration. If it is assumed that all of this methyl shift arises from neighboring methyl participation, rather than formation of the neopentylcarbonium ion followed by a methyl shift, and that each participating methyl group goes on to rearrange, then at 75° the neopentyl system would itself have a driving force of about 0.11 kcal. Since it is

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(10) If the slope is constrained to −3.4, the standard deviation of the $\Sigma\sigma^*$ values is 0.05 which is only twice the average standard deviation of the individual $\sigma^*$ values.

(11) J. D. Roberts and Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

(12) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

(13) The exact value and source seems to be in some doubt; compare T. L. Brown, *Chem. Revs.*, **58**, 581 (1958).

(14) Another simple experimental definition of driving force is that based on $(k_{\text{obs}} - k_c)/k_c$. The equality of this ith $k_1/k_4$ requires that $k_4/k_5 = k_1/k_2 + k_3$, which seems more difficult to rationalize.

It cannot be emphasized too strongly that these are only simplifications of a presumably much more complicated kinetic situation. Some of these complications have been elucidated in the case of three- to four-membered ring expansions (see J. D. Roberts, *et al.*, *J. Am. Chem. Soc.*, **83**, 2719 (1961)).

(15) H. Kuivila and W. Masterson, *ibid.*, **74**, 4953 (1952).

(16) I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 166, 171 (1946).

(17) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(18) J. Meinwald and P. Gassman, private communication.

(19) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

(20) S. Winstein and J. Holness, *ibid.*, **77**, 3054 (1955).

(21) W. H. Saunders, Jr., and R. H. Paine, *ibid.*, **83**, 882 (1961).

TABLE III

DRIVING FORCES IN CYCLOPROPYL SYSTEMS

| Compounds | $k_{\mathrm{tit}}$/sec.$^{-1}$ | Solvent | Temp., °C. | $\Delta\Sigma\sigma^*$ | $\rho^*$ | $L$, kcal. |
|---|---|---|---|---|---|---|
| Cyclopropylcarbinyl benzenesulfonate[22] | $6.0 \times 10^{-5}$ | EtOH | 20.1 | +0.41 | −3.4 | 11.4 |
| Neopentyl benzenesulfonate[a] | $3.3 \times 10^{-12}$ | | | | | |
| Cyclopropylcarbinyl chloride[24,b] | $1.30 \times 10^{-4}$ | 50 vol. % aq. ethanol | 50 | + .41 | −3.4 | 11.2 |
| Neopentyl chloride[c] | $1.06 \times 10^{-10}$ | | | | | |
| Methylcyclopropylcarbinyl *p*-nitrobenzoate[25] | $4.53 \times 10^{-5}$ | 60 vol. % aq. acetone | 100 | + .11 | −3.4 | 8.3 |
| Isopropyl *p*-nitrobenzoate[d] | $1.6 \times 10^{-9}$ | | | | (−2.2) | (8.1) |
| Diisopropylcyclopropylcarbinyl *p*-nitrobenzoate[12] | $7.7 \times 10^{-4}$ | 80 wt. % aq. dioxane | 70 | + .30 | −3.4 | 5.9 |
| Triisopropylcarbinyl *p*-nitrobenzoate[12] | $6.8 \times 10^{-6}$ | | | | (−2.2) | (4.3) |
| Triisopropylcarbinyl *p*-nitrobenzoate[12] | $7.4 \times 10^{-4}$ | 70 vol. % aq. acetone | 100 | − .57 | −3.4 | 0.16 |
| *t*-Butyl *p*-nitrobenzoate | $6.81 \times 10^{-6}$ | | | | (2.2) | (1.35) |

[a] Calculated from the solvolysis data for neopentyl tosylate[19] assuming that the benzene sulfonate solvolyzes 1.54 × as fast.[23] [b] This is $k_{\mathrm{tit}}$. [c] Estimated from solvolysis data for neopentyl bromide[16] by applying a correction of $^1/_{36}$ for the average rates in limiting cases.[17] [d] Calculated by assuming that the secondary *p*-nitrobenzoate solvolyzed $10^{-4}$ × as fast as *t*-butyl *p*-nitrobenzoate.[4]

uncertain whether methyl migration occurs during or after the rate-determining step, it will be assumed here that the neopentyl system does not show participation and that it is a suitable standard without an extra correction. The second comment concerns the possible choice of *t*-butyl *p*-nitrobenzoate as a reference for the diisopropylcyclopropylcarbinyl *p*-nitrobenzoate solvolysis. The isopropyl groups might be expected to show considerably different steric phenomena from those of methyl groups. However, from the data in Table III it can be seen that triisopropylcarbinyl *p*-nitrobenzoate gives a similar driving force so that this difference is not significant here.

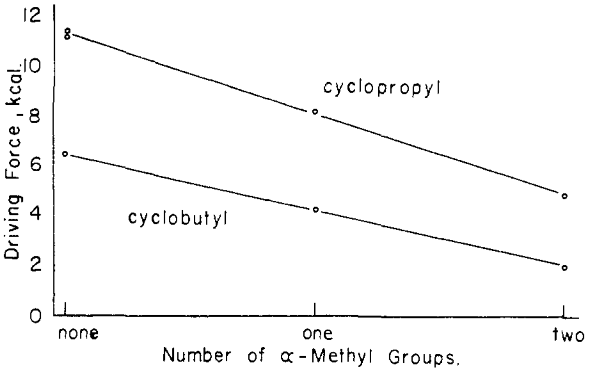

Fig. 3.—Driving forces in cycloalkylcarbinyl systems.

The calculated driving forces for cyclopropyl and cyclobutyl groups as a function of the number of α-methyl groups are plotted in Fig. 3. It is interesting that where more than one example of a given system is available, the agreement is excellent in spite of the wide range of leaving groups, solvents and temperatures represented and the mechanistic approximations made in the calculations. Interesting too is the essential linearity of both of these plots.

The marked difference in slope and intercept ($L_0$) of these two lines deserves some comment. The slope of such a plot is a measure of the extra stabilization α-methyl groups provide for the classical ionization process, $k_c$, compared to the participation process. A steep slope implies a large degree of neutralization of charge by the neighboring group. The slope of the cyclobutyl plot is −2.3 which agrees well with the average value of −2.27 found by Winstein and Grunwald[4] to fit most of the neighboring groups they studied. By contrast, however, the slope of the cyclopropyl plot is −3.3 which indicates a somewhat greater neutralization of charge by the cyclopropyl group than by the cyclobutyl group.

It is possible to visualize two ways in which a particularly large $L_0$ value can occur for a given group. It could correspond to either extensive charge transfer of the usual sort or large polarization which stabilizes an adjoining charge without actual transfer of charge to the site. For the present cyclobutyl and cyclopropyl examples there is no evidence to require a polarization effect. Polarization appears to play a role in the examples cited by Hahn.[26] This point will be returned to later.

**Product Analysis.**—As has been indicated, the solvolysis of dimethylcyclobutylcarbinyl *p*-nitrobenzoate in 60 and 70 vol. % aqueous acetone is accompanied by some 10 to 13% rearrangement to the solvolytically inert 2,2-dimethylcyclopentyl *p*-nitrobenzoate. In order to identify the remaining products, the solvolyses were repeated with the addition of a twofold excess of calcium carbonate to neutralize the liberated *p*-nitrobenzoic acid and prevent incidental rearrangements. It was established that without this added insoluble base the products were slowly isomerized by the acid and that with the base the products were stable for at least the time of reaction. The products were qualitatively analyzed by (1) a comparison of their retention times on gas-liquid chromatography with those of authentic samples, and (2) individual isolation with gas-liquid chromatography and a comparison of infrared spectra and refractive indices with authentic samples. The quantitative analyses were also carried out by gas-liquid chromatography with the assumption that the peak area was proportional to the quantity present. As

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(22) C. G. Berstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).

(23) R. Robertson, *J. Can. Chem. Soc.*, **31**, 589 (1953).

(24) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(25) R. A. Sneen and A. L. Baron, *ibid.*, **83**, 614 (1961).

(26) R. Hahn, Abstracts of the Division of Organic Chemistry of the American Chemical Society, March, 1961, p. 35.

was expected from the data of Messner[27] and verified by preparation and analysis of synthetic mixtures, this assumption was valid within ±2% of total composition. The results of these analyses are given in Table IV. Four possible rearrangement products (*cis*- and *trans*-1,2-dimethylcyclopentanol, 1,2- and 1,5-dimethylcyclopentene) were sought and shown to be apparently absent. It was established with authentic samples that these four compounds had retention times sufficiently different from the identified products that they would have been observed if present in more than about 0.5% concentration.

TABLE IV

PRODUCT ANALYSIS OF SOLVOLYSIS OF IIb IN 60 AND 70 VOL. % AQUEOUS ACETONE AT 100.0%

| Compound | % in 60 vol. % | % in 70 vol. % |
|---|---|---|
| Isopropenylcyclobutane | 30.7 | 40.5 |
| Isopropylidenecyclobutane | 12.1 | 13.5 |
| Dimethylcyclobutylcarbinol | 35.5 | 29.0 |
| 2,2-Dimethylcyclopentanol | 9.2 | 7.0 |
| 2,2-Dimethylcyclopentyl *p*-nitrobenzoate | 12.5 | 10.0 |

**Solvolysis Scheme for Dimethylcyclobutylcarbinyl *p*-Nitrobenzoate.**—The solvolytic scheme shown below could account for the observed rate acceleration if it were assumed that the cyclobutyl group stabilized the carbonium ion by polarizability interactions. With the proper choice of rate constants this scheme could also account for the nearly constant fraction of rearrangement in 60 and 70 vol. % aqueous acetone. There are, however, several arguments against this kind of scheme. First, Hahn[26] has measured the limiting hydrolysis of *p*-cycloalkylphenyldimethylcarbinyl chlorides at 25° in 90% aqueous acetone and found that *p*-cyclobutyl was slower than *p*-cyclopentyl and only 5% faster than *p*-cyclohexyl. If there were some special polarization factor associated with the cyclobutyl ring such as can be ascribed to the cyclopropyl ring a significant rate acceleration would have been expected. A second argument is that the sensitivity of the cyclobutyl driving force to the number of $\alpha$-methyl groups is the same as other normal groups which presumably stabilize by charge transfer. Finally, and most compellingly, when 2,2-dimethylcyclopentyl tosylate was solvolyzed in 80% acetone at 75°, methyl rearranged olefins were formed. The composition and partial identification of this product mixture is summarized in Table V. None of these rearranged olefins appeared in the solvolysis of IIb so that ion V cannot intervene significantly thus excluding this mechanism since it does not then account for the five-membered ring products.

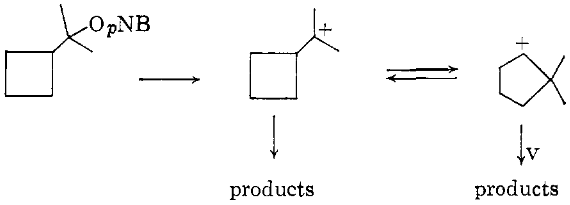

TABLE V

SOLVOLYSIS PRODUCTS OF 2,2-DIMETHYLCYCLOPENTYL TOSYLATE IN 80% AQUEOUS ACETONE AT 75°

| Compound | % |
|---|---|
| Unidentified olefin[a] | 12 |
| 3,3-Dimethylcyclopentene | 12 |
| 1,5-Dimethylcyclopentene | 16 |
| 1,2-Dimethylcyclopentene | 54 |
| Unidentified alcohol[b] | 6 |

[a] From its relative retention time this olefin appears to be acyclic. [b] This alcohol did not correspond to any of the known cyclopentanols and is presumably acyclic.

The simplest solvolysis scheme for IIb consistent with the kinetic *and* product data is that shown in Fig. 2. This scheme accommodates (1) the observed rate acceleration of IIb over that expected for a classical ion, (2) the nearly constant yield of rearranged ester independent of a 2.6-fold change in reaction rate and (3) products which are mostly derived from an intermediate having a large positive charge on the carbon atom bearing the methyl groups. This scheme means that the driving force in these solvolyses results primarily from a relief of strain and not from a polarizability stabilization.

## Experimental

**Kinetics.**—The rate measurements were carried out by the usual sealed ampule techniques. Five-milliliter aliquots were taken and all solutions were approximately 0.03 *N*. Carvacrol sulfonephthalein indicator was used with the titration of the *p*-nitrobenzoates and brom thymol blue was used with the tosylates.

**Product Analyses.**—After the esters had been solvolyzed for a minimum of 10 half-lives in the presence of a twofold excess of $CaCO_3$ the solution (*ca.* 7 ml.) was diluted with 10 ml. of water and then saturated with sodium chloride. The resulting mixture was extracted three times with a total of 2 ml. of pentane and the combined pentane extract analyzed directly by gas–liquid chromatography. The boiling points of compounds isolated in this manner were determined by the micro technique of Siwoloboff.[28]

**Dimethylcyclobutylcarbinol.**—Cyclobutanecarboxylic acid, prepared in 25–30% yield by the method of Payne and Smith,[3] was converted into its ethyl ester using a Dean–Stark water separator according to the usual procedure.[29] The resulting ester was heated with a twofold excess of methyl Grignard to give an 85% yield of dimethylcyclobutylcarbinol, b.p. 143–145°, $n^{23}\mathrm{D}$ 1.4431 (lit.[30] b.p. 144–145°, $n^{14.5}\mathrm{D}$ 1.4483).

**The *p*-nitrobenzoate** of the alcohol was prepared using 5% molar excess of freshly recrystallized *p*-nitrobenzoyl chloride and 15 ml. of Karl Fisher anhydrous pyridine for each gram of alcohol. After this mixture had reacted for 24 hr. at room temperature, it was poured into an equal volume of water and the resulting precipitate removed by filtration. This precipitate was washed well with 5% $Na_2CO_3$ solution and then recrystallized from hexane to give the desired *p*-nitrobenzoate, m.p. 101–102°.

*Anal.* Calcd. for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 64.00; H, 6.51; N, 5.29.

**Alcohols for the Determination of $\rho^*$.**—All of the alcohols involved in the determination of $\rho^*$ (Table I) were synthesized by addition of a twofold excess of the appropriate Grignard reagent to a ketone.

Dimethylethylcarbinol was prepared in 46% yield using ethylmagnesium bromide, b.p. 102–105°, $n^{20}\mathrm{D}$ 1.4045 (lit.[31] b.p. 66° (165 mm.), $n^{20}\mathrm{D}$ 1.4052).

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Dimethylisopropylcarbinol was prepared in 40% yield using isopropylmagnesium bromide, b.p. 121–123°, $n^{20}$D 1.4253 (lit.[32] b.p. 118°).

Triethylcarbinol was prepared in 80% yield using ethylmagnesium bromide; b.p. 69° (50 mm.), $n^{25}$D 1.4252 (lit.[33] b.p. 72.5° (50 mm.), $n^{25}$D 1.4281).

Methylethylpropylcarbinol was prepared in 88% yield, b.p. 74° (60 mm.), $n^{25}$D 1.4198 (lit.[34] b.p. 142°, $n^{21}$D 1.4224).

***p*-Nitrobenzoates for Determination of $\rho^*$.**—All of the *p*-nitrobenzoates solvolyzed in the determination of $\rho^*$ (Table I) were prepared in the manner described under dimethylcyclobutylcarbinyl *p*-nitrobenzoate: dimethylethyl-*p*-nitrobenzoate, m.p. 83–84° (lit [31] m.p. 83.5–84.5°); dimethylisopropylcarbinyl *p*-nitrobenzoate, m.p. 78–79° (lit.[32] mp. 82°); triethylcarbinyl *p*-nitrobenzoate, m.p. 38–39° (lit.[35] m.p. 42.5–43.5°); methylethylpropylcarbinyl *p*-nitrobenzoate, m.p. 41–42°. (*Anal.* Calcd. for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.02; H, 7.44; N, 5.25); *tert*-Butyl *p*-nitrobenzoate, m.p. 114.5–115° (lit.[36] 115–117°).

**2,2-Dimethylcyclopentanol.**—Two grams of dimethylcyclobutylcarbinol and 1 ml. of 25% $H_2SO_4$ were mixed with cooling and then stirred for 12 hr. at room temperature. The reaction mixture was diluted with 2 ml. of water and the organic layer separated. The aqueous layer was extracted with 2 ml. of pentane and the combined organic layers were washed with 10% $Na_2CO_3$ solution, dried over $MgSO_4$, and then distilled to give 1.4 g. (70%) of IIIa, b.p. 149–152° (lit.[2] b.p. 151–152° (744 mm.)). The infrared spectrum of the alcohol was superimposable on that of an authentic sample.[2]

**The *p*-toluenesulfonate** of the alcohol was prepared in a manner analogous to the dimethylcyclobutylcarbinyl *p*-nitrobenzoate using *p*-toluenesulfonyl chloride in place of the *p*-nitrobenzoyl chloride to give a 51% yield, m.p. 50–51°.

*Anal.* Calcd. for $C_{14}H_{20}O_3S$: C, 62.65; H, 7.54; S, 11.95. Found: C, 62.50; H, 7.58; S, 12.12.

**2-Methylcyclopentanone.**—In a flask containing 1000 ml. of absolute alcohol was added 178 g. (1.14 moles) of 2-carbethoxycyclopentanone[37] and 64 g. (1.19 moles) of $NaOCH_3$. The reaction mixture was cooled to −10 to 0° and 170 g. (1.2 moles) of $CH_3I$ diluted with an equal volume of absolute ethanol was added over a 3-hour period. The reaction mixture was then stirred at room temperature for an additional 12 hours. After this time 1 l. of water, 600 ml. of diethyl ether and 400 ml. of benzene were added to the flask and the organic layer separated. The aqueous layer was extracted once with 400 ml. of ether. The combined organic layers were washed with 200 ml. of cold 10% KOH and then dried over magnesium sulfate. After the solvent was removed, the product, b.p. 101–113° (13 mm.), $n^{20}$D 1.4281, was collected by distillation.

This material was refluxed for 14 hours with 600 ml. of 20% sodium hydroxide and then neutralized with concd. HCl. The reaction mixture was extracted five times with 300-ml. portions of ether and the combined extracts dried over $MgSO_4$. The ether was removed and the resulting acyclic diacid used directly in the next step.

The diacid was cyclized by the method of Blanc.[38] A mixture of 118 g. of the crude diacid was heated at 155° with 240 g. of acetic anhydride until all of the acetic acid had distilled. Pyrolysis of the resulting anhydride at 235° yielded 50 g. of crude ketone. This product was washed with 10% $Na_2CO_3$ solution, dried over $K_2CO_3$ and then distilled to give 34 g. (43%) of 2-methylcyclopentanone, b.p. 138°, $n^{27.5}$D 1.4303 (lit.[39] b.p. 139–142°, $n^{20}$D 1.4347).

***cis*- and *trans*-1,2-Dimethylcyclopentanol.**—The 2-methylcyclopentanone was treated with methyl Grignard to give a mixture of *cis–trans*-alcohol in 71% yield. The two isomers were separated by gas–liquid chromatography at 138° on a silicone oil column. The ratio of *trans* to *cis* was 1:1.2. The physical constants of the two fractions were: *trans*, b.p. 142°, $n^{25}$D 1.4448 (lit.,[40] b.p. 58.4° (25 mm.), $n^{25}$D 1.4463) and *cis*, $n^{25}$D 1.4516 (lit.,[40] $n^{25}$D 1.4523).

**1,2- and 1,5-Dimethylcyclopentene.**—Four grams of the *cis–trans* mixture of 1,2-dimethylcyclopentanol was dehydrated at 115° by addition of 0.1 ml. of concd. sulfuric acid and removal of the olefins by distillation as formed. The distillate was washed with 1 ml. of 10% $Na_2CO_3$ solution and then dried over $K_2CO_3$ to give 3.1 g. (91%) of an olefin mixture.

This olefin mixture was separated by gas–liquid chromatography on a silicone oil column and found to contain 90% 1,2-dimethylcyclopentene and 10% 1,5-dimethylcyclopentene. The 1,5-isomer was identified by the characteristic band at 12.5 μ for trisubstituted olefins and the 1,2-isomer was identified by its lack of characteristic olefin hydrogen bands as well as its physical constants; b.p. 105°, $n^{26}$D 1.4408 (lit.[41] 105.8°, $n^{25}$D 1.4420).

**Isopropylene- and isopropylidenecyclobutane.**—In the manner of Kazanskii[42] a mixture of 2 g. of dimethylcyclobutylcarbinol and 0.02 ml. of concd. $H_2SO_4$ was heated at 125° and the volatile products collected as they distilled from the reaction flask. The distillate was washed and dried. Gas–liquid chromatography showed that two olefins, present in equal amounts, composed 92% of the distillate (60% over-all yield). The physical constants of these two olefins were: isopropylenecyclobutane, $n^{21}$D 1.4332, b.p. 98.5° (742 mm.) (lit.[42] $n^{20}$D 1.4347, b.p. 98.5) and isopropylidenecyclobutane, $n^{21}$D 1.4441, b.p. 107° (742 mm.) (lit.[42] $n^{21}$D 1.4452, b.p. 107.3°).

As further proof of structure the two olefins were separately reduced with Adams catalyst to give the same product, isopropylcyclobutane, whose infrared spectrum, refractive index and boiling point agreed with those reported.[42,43]

**3,3-Dimethylcyclopentene** was prepared by the procedure of Kwart and Ford.[7]

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