unsaturation, a band at 10.21 μ indicating N–F bonding, and was generally similar to that of $(CF_3)_2NF$ in the 8 to 11 μ region. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 152 ($C_2F_6N^+$), 59(CFN_2^+), 50(CF_2^+), 31(CF^+), 114($C_2F_4N^+$), 83(CF_3N^+), 64(CF_2N^+) and 133 ($C_2F_5N^+$). The n.m.r. spectrum showed only three peaks at −7.2 (CF_3), at +8.7 (N–F), and at +17.3 ppm. (CF_2), all relative to CF_3COOH. The respective peak areas were also in accord with the proposed structure. The new saturate was colorless and occurred mixed with the corresponding unsaturated VIII in varying proportions. The unsaturate in the mixture could readily be destroyed by hydrolysis, leaving the saturate essentially pure.

Perfluoro-1,3-diazabutane, $CF_3NFCF_2NF_2$ (VII).—A small quantity of this compound was isolated by v.p.c. on Florisil from the more vigorous fluorinations. Its retention time was slightly less than that of its isomer $NF_2CF_2CF_2NF_2$, b.p. −1.6°, indicating that its boiling point was slightly below −2°. The infrared spectrum was complex in the N–F region, showing a strong band at 10.53 μ and a weaker one at 10.82 μ. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 50(CF_2^+), 102(CF_4N^+), 152($C_2F_6N^+$), 31(CF^+), 83(CF_3N^+), 33(FN^+), 64(CF_2N^+), 52(F_2N^+), 12(C^+), 45(CFN^+), 114($C_2F_4N^+$), 97($CF_3N_2^+$), 19(F^+), 147($C_2F_5N_2^+$), 166($C_2F_6N_2^+$), 40(CN_2^+), 95($C_2F_3N^+$), 76($C_2F_2N^+$), 128($C_2F_4N_2^+$), 133($C_2F_5N^+$) and 185 ($C_2F_7N_2^+$). The relative abundance of the peaks at mass 33(NF) and 52(NF_2) strongly suggested the presence of more than one type of N–F bonding in this molecule, as did the infrared spectrum.

Octafluoro-2,4-diazapent-2-ene, $CF_3NFCF{=}NCF_3$ (VIII) was separated in small amounts by v.p.c. from complex mixtures boiling in the 0° to 20° range, and was obtained from the milder fluorinations. Its b.p. as estimated from its retention time was between 15° and 20°. The infrared spectrum showed a strong band at 5.62 μ, indicating internal C=N bonding. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 114($C_2F_4N^+$), 109($C_2F_3N_2^+$), 31(CF^+), 50(CF_2^+), 152($C_2F_6N^+$), 197($C_3F_7N_2^+$), 64(CF_2N^+), 45(CFN_2^+), 216($C_3F_8N_2^+$) parent ion, 128($C_2F_4N_2^+$), 83(CF_3N^+), 12(C^+), 147($C_2F_5N_2^+$), 95($C_2F_3N^+$) 47(FN_2^+), 71($C_2FN_2^+$), 90($C_2F_2N_2^+$), 19(F^+), 59(CFN_2^+), 26(CN^+) and 33(FN^+).

This colorless compound was readily hydrolyzed by water at room temperature. The resulting solution contained no CF_3COOH, but evolved NH_3 on treatment with base. This indicated the absence of terminal C–C bonding, and the presence of a C=N group, thus supporting the proposed structure.

Octafluoro-3-methyl-1,3-diazabut-1-ene, $(CF_3)_2NCF{=}NF$ (IX).—This pure isomer of VIII was separated by v.p.c. from the same complex mixture as above, but had a somewhat shorter retention time indicating a b.p. near 10°. The infrared spectrum showed bands at 5.94 μ (C=N) and 10.56 μ (N–F), as well as at 10.07 μ $(CF_3)_2N$; the last value being well supported by Dresdner.[9] The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 31(CF^+), 59(CFN_2^+), 50(CF_2^+), 45(CFN^+), 128($C_2F_4N_2^+$), 64(CF_2N^+), 166($C_2F_6N_2^+$), 114($C_2F_4N^+$), 33(FN^+), 12(C^+), 147($C_2F_5N_2^+$), 83(CF_3N^+), 95($C_2F_3N^+$), 26(CN^+), 71($C_2FN_2^+$), 19(F^+), 197($C_3F_7N_2^+$), 47.5($C_2F_3N^{++}$), 135(CF_5N_2), 90($C_2F_2N_2^+$), 109($C_2F_3N_2^+$) and 216($C_3F_8N_2^+$) parent ion. The absence of ions at 119($C_2F_5^+$), 100($C_2F_4^+$) and 81($C_2F_3^+$) indicated clearly that there was no C–C bonding in the molecule, and therefore that the carbon and nitrogen atoms were alternately placed.

Acknowledgment.—We wish to thank Dr. Wallace S. Brey, University of Florida, for determining and interpreting the n.m.r. spectra given above. We are also indebted to Dr. John Ruth, Liggett and Myers Research Laboratory, Durham, N. C., for the mass spectroscopic analyses reported here.

(9) J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *J. Am. Chem. Soc.*, **82**, 396 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, AND THE CHEMISCHES LABORATORIUM DER UNIVERSITAT, FREIBURG I. BREISGAU, GERMANY]

Pyridinium Complexes. IV. The Effect of N-Substituents on the Position of the Iodide Charge-transfer Band

BY EDWARD M. KOSOWER,[1a] DIETER HOFMANN[1b] AND K. WALLENFELS

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The positions of the iodide charge-transfer bands for a series of substituted 1-X-benzyl-4-carbomethoxypyridinium ions in *cis*-1,2-dichloroethylene are shown to be correlated by the equation $E_T/2.303RT = \rho_s\sigma$, in which σ is the Hammett constant and ρ_s is a sensitivity parameter comparable to the usual ρ. In the present case, $\rho_s = -1.70$, consistent with the large effect of substitution expected for a charge-transfer band. It is suggested that an intramolecular charge-transfer band (i.c.t.) is observed as a shoulder at 3090 Å. in solutions of 1-(4-methoxybenzyl)-4-carbomethoxypyridinium ion (as the perchlorate).

Previous studies of alkylpyridinium iodide charge-transfer bands have indicated that the transition energies are very sensitive to the nature of the substitution on the pyridinium ring.[2,3] We now report data for a series of 1-X-benzyl-4-carbomethoxypyridinium iodides in which it is clear that the charge-transfer band position is very sensitive to even small changes in the electron affinity of the pyridinium ring. A potentially useful correlation with the Hammett σ-constant is also found for the band positions.

Results

Five 1-(X-benzyl)-4-carbomethoxypyridinium iodides (X = 4-NO_2, 4-Cl, H, 4-OCH_3 and 2,6-Cl_2) were prepared. Their charge-transfer bands were measured in the low-polarity solvent, *cis*-1,2-dichloroethylene (**Z**, 63.4).[4] This solvent has the requisite amount of solvent power for alkylpyridinium iodides combined with low ion pair-dissociating power,[4] thus ensuring adequate quantities of ion-pairs even at low solute concentrations. The absorption maxima for the pyridinium iodides are summarized in Table I. Ultraviolet data for the pyridinium perchlorates are given in Table II.

Discussion

The charge redistribution corresponding to the charge-transfer transition of the benzylpyridinium

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(2) E. M. Kosower, J. A. Skorcz, W. M. Schwarz, Jr., and J. W. Patton, *J. Am. Chem. Soc.*, **82**, 2188 (1960).

(3) E. M. Kosower and J. A. Skorcz, *ibid.*, **82**, 2195 (1960).

(4) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

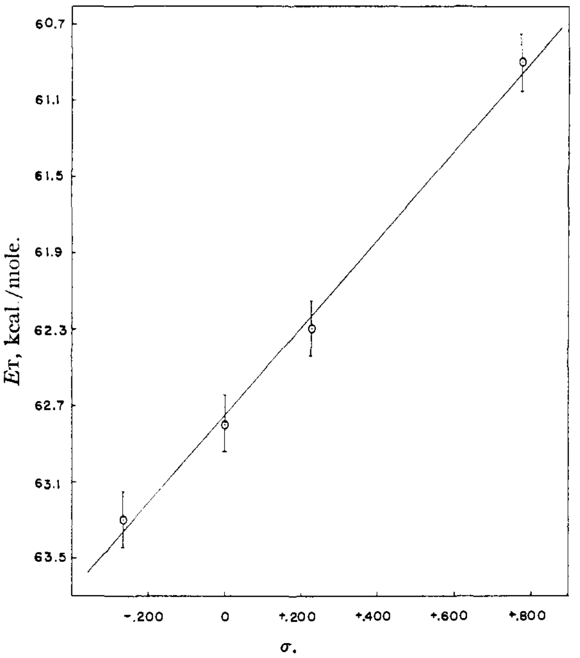
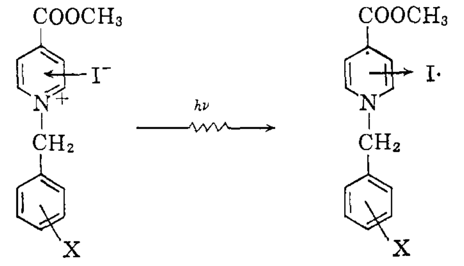


Fig. 1.—A plot of transition energies (E_T) for the charge-transfer band of 1-(X-benzyl)-4-carbomethoxypyridinium iodide against the Hammett σ-constant. The line corresponds to eq. 2.



(1)

iodides is indicated in eq. 1.[2] Electron-withdrawing substituents on the benzyl group should lower the energy of the electronic transition and electron-supplying groups should raise the energy. A plot of the transition energies against the Hammett σ-constant[5] gives an excellent straight line, expressed as eq. 2. A ρ_S-value can be defined (eq. 3), analogous to the equation defining ρ in the

$$E_T = -2.320\sigma + 62.75 \qquad (2)$$

usual Hammett correlations[5] (eq. 4)

$$\frac{E_T^x - E_T}{2.303RT} = \rho_s\sigma \qquad (3)$$

$$\log K/K_0 = \rho\sigma \qquad (4)$$

In this way, substituent effects on certain spectroscopic transitions may be compared to their effects on kinetics and equilibria. Eq. 3 may be written because (a) the empirical correlation of E_T and σ exists, (b) the entropy change on electronic excitation is very small, and (c) the substituents on the benzyl group are far enough away from the absorption center [*i.e.*, the "reaction center"] so that this may be regarded as constant throughout the series. In connection with the last point, a reasonably good correlation is obtained (ρ_S = −13.4) even when the substituents are varied on the 3- and 4-positions of the pyridinium ring.[6]

TABLE I

CHARGE-TRANSFER BANDS OF 1-(X-BENZYL)-4-CARBOMETHOXYPYRIDINIUM IODIDES IN *cis*-1,2-DICHLOROETHYLENE[a]

X	λ_{max}, Å.[b] (ϵ_{max})	E_T, kcal./mole	σ[c]
4-H	4556 (1040)	62.8	0.000
4-Cl	4593 (1070)	62.3	+ .227
4-NO_2	4693 (1180)	60.9	+ .778
4-OCH_3	4516 (960)	63.3	− .268
2,6-Cl_2	4694 (830)	60.9	.....

[a] Z = 63.4 [λ_{max} 4508 Å. (ε 973) for 1-ethyl-4-carbomethoxypyridinium iodide (*cf.* ref. 4)]. [b] ±10 Å. [c] Ref. 5.

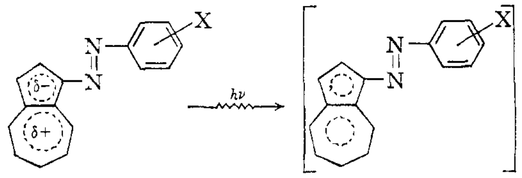
TABLE II

ULTRAVIOLET ABSORPTION DATA FOR 1-(X-BENZYL)-4-CARBOMETHOXYPYRIDINIUM PERCHLORATES IN WATER

X	λ_{max}, Å.[a] (ϵ_{max})	λ_{max}, Å.[b] (ϵ_{max})
4-H	2735 (4390)	2188 (16800)
4-Cl	2732 (4650)	2243 (14400)
4-NO_2	2675 (15100)	2160 (15700)
4-OCH_3[c]	2730 (5300)	2275 (22400)
2,6-Cl_2	2753 (5050)	2208 (23000)

[a] ±5–8 Å. [b] ±6–10 Å. [c] Shoulder at 3090 Å. (ε 540).

The ρ_s value for the charge-transfer band of eq. 1 is −1.70, indicating a moderate substituent effect (Fig. 1). A good correlation of long wave length band displacements caused by substituent changes with σ has been observed by Gerson and Heilbronner[7] for X-phenylazoazulenes. The electronic transition corresponds roughly to the charge redistribution shown in eq. 5, *i.e.*, an intramolecular charge-transfer transition. The data were correlated with the expression $\delta\bar{\nu}$ (in cm.$^{-1}$) = −26 + 810 σ_X, which corresponds to a ρ_s value of +1.72, similar in magnitude to the ρ_s value for eq. 1 but opposite in sign since the direction of charge redistribution is opposite.



(5)

The long wave length shoulder observed in the spectrum of 1-(4-methoxybenzyl)-4-carbomethoxypyridinium perchlorate is tentatively assigned as an i.c.t. band with the *p*-methoxybenzyl group as donor and the pyridinium ring as acceptor.

Experimental

The 1-benzyl-4-carbomethoxypyridinium iodides were prepared by reaction of the appropriate benzyl iodide with methyl isonicotinate in methanol. 2,6-Dichlorobenzyl iodide[8] was prepared from the chloride by reaction with sodium iodide in acetone. The 1-(4-methoxybenzyl)-4-carbomethoxypyridinium iodide was prepared

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[5] R. W. Taft, in "Steric Effects in Organic Chemistry," J. Wiley and Sons Inc., New York, N. Y., 1956, Chap. 13.

[6] E. M. Kosower and J. A. Skorcz, "Proceedings of the Fourth European Molecular Spectroscopy Symposium, Bologna, Italy," September, 1959, Pergamon Press, London, 1962.

[7] F. Gerson and E. Heilbronner, *Helv. Chim. Acta*, **42**, 1877 (1959).

[8] M. Gellrich, personal communication.

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.

[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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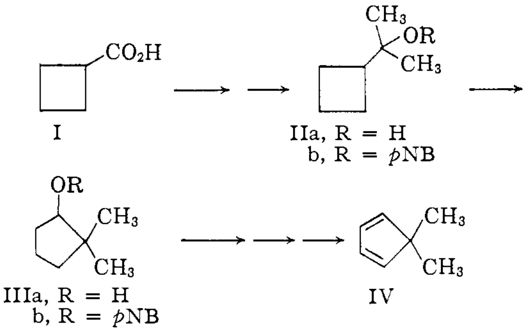
Dimethylcyclobutylcarbinyl *p*-nitrobenzoate was solvolyzed in 60 and 70% aqueous acetone at 100.0° and the driving force for ring expansion calculated to be 2.0 kcal./mole. The driving forces of other three- and four-membered ring expansions are calculated and compared. A linear relation exists between 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.



*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.