same manner as **10G** above to yield the desired product **10H:** mp 48 °C; NMR ($CDCl_3$) δ 1.5 (t, 3, J_{HH} = 11.3 Hz, $-CH_2CH_3$), 2.6 (s, 3, $-CH_3$), 4.15 (q, 2, J_{HH} = 11.3 Hz, $-CH_2CH_3$), 6.5 (s, 1, 3-aromatic proton), 7.2–8.3 (m, 4, aromatic).

2-Methyl-4-methoxyquinoline (10I). The oil obtained from treating compound **8I** by the general procedure was sublimed three times to give colorless crystals, 0.23 g (30% yield) of **10I.** A 53% yield of Ph_3PO, mp 150–153 °C, was found; **10I** had mp 63–65 °C (lit.[17] mp 58–59 °C).

2-Methyl-4-phenylquinoline (10J). The oil obtained from treating compound **8J** by the general procedure was sublimed at 80 °C under vacuum. The material left after sublimation was impure Ph_3PO in 90% yield. The sublimate weighed 0.55 g (64% yield), slightly yellow needles, **10J,** mp 96.5–98 °C (lit.[18] mp 97–98 °C).

2-Methylindeno[1,2,3-*de*]quinoline (10L). The oil obtained from treating compound **8L** by the general procedure was purified in the same manner as **10G** to yield the desired product **10L:** mp 135 °C dec; NMR ($CDCl_3$) δ 2.8 (s, 3, $-CH_3$), 7.2–8.0 (m, 8, aromatic).

4-Amino-2-methylquinoline (10M). The oil obtained from treating compound **8M** by the general procedure was dissolved in CH_2Cl_2 and dripped slowly into hexane. The resulting precipitate was collected and recrystallized in benzene–hexane to yield 0.29 g (31% yield) of **10M,** mp 167–169 °C (lit.[19] mp 167–169 °C).

Registry No.—**1,** 2091-46-5; **2,** 54599-99-4; **4,** 60661-63-4; **5,** 60661-64-5; **7,** 60661-65-6; **8F,** 60661-66-7; **8G,** 60661-67-8; **8H,** 60661-68-9; **8I,** 60661-69-0; **8J,** 60661-70-3; **8K,** 60661-71-4; **8L,** 60661-72-5; **8M,** 60661-73-6; **8N,** 60661-74-7; **8O,** 60661-75-8; **8P,** 54774-75-3; **8Q,** 60661-76-9; **8R,** 54774-76-4; **8S,** 60661-77-0; **8T,** 60661-78-1; **8U,** 60661-79-2; **8V,** 60661-80-5; **9A** (keto form), 60661-81-6; **9B,** 60661-82-7; **9C,** 60661-83-8; **9D,** 54774-78-6; **9E,** 60661-84-9; **10G,** 60661-85-0; **10H,** 46272-56-4; **10I,** 31835-53-7; **10J,** 1721-92-2; **10L,** 60661-86-1; **10M,** 6628-04-2; triphenylphosphine, 603-35-0; propargyl bromide, 106-96-7; methanol, 67-56-1; CH_3OD. 1455-13-6; prop-1-ynyltriphenylphosphonium bromide, 54599-98-3; benzoic acid hydrazide, 613-94-5; 2,4-dinitrophenylhydrazine, 119-26-6; 4-nitrophinylhydrazine, 100-16-3; phenylhydrazine, 100-63-0; 2-nitrobenzenamine, 88-74-4; 2-aminobenzoic acid, 118-92-3; 1-amino-9,10-anthracenedione, 82-45-1; ethyl 2-aminobenzoate, 87-25-2; methyl 2-aminobenzoate, 134-20-3; (2-aminophenyl)phenylmethanone, 2835-77-0; 2-aminobenzamide, 88-68-6; 1-amino-9*H*-fluoren-9-one, 6344-62-3; 2-aminobenzonitrile, 1885-29-6; 4-aminobenzoic acid, 150-13-0; 1-(4-aminophenyl)ethanone, 99-92-3; benzenamine, 62-53-3; 2-methoxybenzenamine, 90-04-0; methyl glycinate, 616-34-2; 1,2-benzenediamine, 95-54-5; 2-aminophenol, 95-55-6; 2-amino-4-methylphenol, 95-84-1; 2-amino-4-nitrophenol, 99-57-0; triphenylphosphine oxide, 791-28-6; **9A** (enol form), 61484-35-3.

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The Effect of the Base Strength upon the Structure of the Transition State in E2 Reactions. Kinetics of Eliminations from 2-Arylethyltrimethylammonium Bromides Promoted by Sodium Phenoxide and Sodium *m*-Nitrophenoxide in *N,N*-Dimethylformamide

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Received June 28, 1976

Values of the Hammett constant, ρ, and deuterium kinetic isotope effect (k_H/k_D) have been determined for the eliminations from 2-arylethyltrimethylammonium bromides promoted by sodium phenoxide and sodium *m*-nitrophenoxide in *N,N*-dimethylformamide. These values indicate that the transition state of the reaction with sodium phenoxide has a carbanion character higher than that of the reaction with sodium *m*-nitrophenoxide. The phenomenon is mainly due to a significant decrease of C_α–leaving group bond stretching at the transition state of the reaction with the stronger base since the degree of C_β–H bond rupture in the reaction with sodium phenoxide is smaller than in the reaction with sodium *m*-nitrophenoxide. These results are compared with those obtained in the elimination from 2-arylethyl bromides and discussed in the light of recent theories concerning the effect of structural changes in the reactants on the transition state of E2 reactions.

The study of the effect of structural changes in the reactants on the structure of the transition state of E2 reactions is of great importance from both theoretical and practical points of view. Recently, on the basis of theoretical treatments, it has been shown that both parallel and perpendicular modes of vibration of the transition state can be affected by structural changes in the reactants.[1,2] The effects on the parallel modes (parallel effects) result in modifications of the structure of the transition state in agreement with the Hammond postulate;[3] those on the perpendicular modes (perpendicular effects) result in modifications in the opposite direction. As a further development of the theory, it has been also suggested that the relative weight of perpendicular and parallel effects can closely depend on the location of the transition state in the reaction

Table I. Kinetic Data for the Elimination Reactions of p-Y-$C_6H_4CZ_2CH_2N^+(CH_3)_3Br^-$ with Phenoxides in DMF at 55.7 °C

Registry no.	Y	Z	Sodium phenoxide[a]	Sodium m-nitrophenoxide
6068-85-5	H	H	$1.23 \pm 0.01 \times 10^{-3}$	$4.15 \pm 0.02 \times 10^{-5}$
1012-70-0	H	D	$4.35 \pm 0.15 \times 10^{-4}$ [b]	$1.85 \pm 0.11 \times 10^{-5}$ [b]
19836-63-6	CH_3	H	$3.26 \pm 0.02 \times 10^{-4}$	$1.31 \pm 0.01 \times 10^{-5}$
6948-08-9	OCH_3	H	$6.95 \pm 0.38 \times 10^{-5}$	$2.94 \pm 0.16 \times 10^{-6}$
60582-50-5	Br	H	$1.12 \pm 0.08 \times 10^{-2}$	$2.90 \pm 0.03 \times 10^{-4}$

[a] In the presence of $NaClO_4$ (0.46 N). [b] Corrected for the presence of the undeuterated compound.

Table II. Hammett Correlations and Kinetic Isotope Effects in Elimination Reactions of 2-Arylethyltrimethylammonium Bromides Promoted by Phenoxides in DMF at 55.7 °C

Nucleophile	ρ	k_H/k_D
Sodium phenoxide	4.25[a]	2.83 ± 0.12
Sodium m-nitrophenoxide	3.81[b]	2.26 ± 0.14

[a] $r = 0.994$; $S = 0.125$. [b] $r = 0.991$; $S = 0.137$.

potential energy diagram.[4-6a] An important consequence appears to be that systems with an E1cB-like or an E1-like transition state are expected to display a sensitivity to variations in the structure of reactants significantly different from that of systems characterized by a "central" transition state. In this way it has been possible to rationalize some apparent discrepancies concerning leaving group effects and substituent effects at C_β in elimination reactions involving transition states with different degrees of carbanion character.

Recently, we have clearly shown that in the eliminations from 2-arylethyl bromides promoted by phenoxides in N,N-dimethylformamide (DMF) a change to a stronger base leads to a more carbanionic transition state.[7] This result is in agreement with theoretical predictions[2,6a] since the reaction should take place by way of a transition state in the central-E1cB region where perpendicular and parallel effects are expected to be of comparable importance. However, according to the theory a completely different result (less carbanion character with the stronger base) should be expected for a reaction utilizing an E1cB-like transition state, a clear predominance of parallel effects being predicted in this case.[6] With the aim of obtaining information on this point we have investigated the effect of base strength on the elimination reactions of 2-arylethyltrimethylammonium salts.

Results and Discussion

Kinetics of the reactions of para-substituted 2-phenylethyltrimethylammonium bromides (substituents: Br, H, CH_3, OCH_3) and 2-phenylethyl-2,2-d_2-trimethylammonium bromide with sodium phenoxide and sodium m-nitrophenoxide have been carried out in DMF at 55.7 °C by spectrophotometric analysis of styrene or para-substituted styrene. Aliquots of the reaction mixture were withdrawn, the olefin extracted by n-heptane, and the optical density of the solution measured after appropriate dilution. The spectrophotometric yield in olefin was larger than 95% in each case.

The concentration of substrate was ca. 2×10^{-3} M; that of nucleophile, 0.03–0.06 M with sodium phenoxide and 0.36 M with sodium m-nitrophenoxide. In the experiments with sodium phenoxide, $NaClO_4$ (0.46 M) was also present in order to keep constant the salt concentration during the reaction. Good first-order plots were obtained and, in the presence of $NaClO_4$, the second-order rate constant was independent of the phenoxide concentration.

The kinetic results, collected in Table I, satisfactorily correlate with the Hammett equation. The ρ values (reported in Table II together with the values of the deuterium kinetic isotope effect, k_H/k_D) are among the more positive ever recorded for an E2 reaction[8] (even larger that the ρ values reported for the eliminations from the same substrates promoted by EtONa and t-BuOK in the corresponding alcohols[9]) and clearly indicate a transition state of high carbanion character for both eliminations. Likewise, also the very low k_H/k_D values observed are in agreement with an activated complex in which the transfer of the proton to the base is almost complete.

The comparison between the ρ values shows that the reaction with sodium phenoxide ($pK_a \simeq 18$)[10] has a transition state with a higher carbanion character than that of the reaction with sodium m-nitrophenoxide ($pK_a = 15.4$);[10] it follows that, also in eliminations characterized by an E1cB-like transition state, a change to a stronger base produces a significant increase in the carbanion character of the transition state. This result parallels that observed in the reaction of 2-phenylethyl bromides where the ρ value was found to rise from 1.84 to 2.64 for a ca. 4×10^5-fold increase in the nucleophile basicity.[7] As in the reactions of bromo derivatives,[7,11] the result obtained in eliminations from ammonium salts is due mainly to a decreased degree of C_α–leaving group bond breaking in the transition state of the reaction with the stronger base and not to an increase in the extent of C_β–H bond breaking. In fact, since the proton transfer is well past the midpoint, the larger k_H/k_D value found with sodium phenoxide indicates a smaller degree of rupture of this bond as the base strength increases.

In conclusion, a change of the nucleophile basicity has an effect on the transition state structure of E2 reactions which does not seem to depend upon the character of the transition state in a substantial way. A more "reactant-like" transition state appears to be the general outcome for reactions occurring by way of either a central or E1cB-like transition state. Since this result is caused, to a large extent, by a decrease of C_α–leaving group bond stretching at the transition state, an increase in the carbanion character is also observed.

However, when the effect on the degree of C_β–H bond breaking is considered, E1cB-like and central transition states appear to display a different sensitivity to changes in nucleophile basicity. Accordingly, in going to a stronger base the extent of C_β–H bond breaking decreases in the reaction of 2-arylethyltrimethylammonium ions, whereas it remains practically unchanged in the reaction of 2-arylethyl bromides.[10] The result for the E1cB-like transition state is in agreement with the Hammond postulate (less proton transfer with the stronger base) and therefore supports the suggestion[5] that parallel effects can be somewhat more important than the perpendicular ones in E1cB-like transition states, even if this is not sufficient to produce a less carbanionic transition state as the nucleophile basicity is increased.

The effects caused by changes in the intrinsic basicity of the nucleophile on the transition state structure of E2 reactions can also be compared with those caused by changes in the medium basicity (brought about by modifications in base association and/or solvation), even though in this latter case the interpretation of the data can often be made uncertain by the concomitant change in the nature of the solvent. Interestingly, results similar to those of the present work have been obtained in the eliminations from 2-arylethyldimethylsulfonium bromides promoted by NaOH in H_2O–Me_2SO,[12,13] where an increase in the Me_2SO concentration was found to determine a rise in the ρ value and a concomitant decrease in the extent of C–H and C–S bond breaking in the transition state. Likewise, a more carbanionic transition state was observed in the syn-elimination reactions of 2-arylcyclopentyl tosylates as the base–solvent system was changed from *t*-BuOK–*t*-BuOH to crown ether complexed *t*-BuOK in *t*-BuOH.[14] It does not seem possible, however, to generalize these results since in the reactions of 2-arylethyl bromides the structure of the transition state appears not be affected to a significant extent by modifications in the medium basicity.[15,16] A similar situation also obtains in the elimination from 1-arylethyltrimethylammonium salts promoted by ethoxide ions in EtOH–Me_2SO mixture.[17]

Finally we wish to note the fact that the ρ value for the eliminations from 2-arylethyltrimethylammonium salts decreases as the base–solvent system is changed from EtONa–EtOH to *t*-BuOK–*t*-BuOH.[9] In the light of present results it does not seem possible to attribute this decrease to a base-strength effect.

However, when the base–solvent system is changed from EtONa–EtOH to *i*-PrOK–*i*-PrOH an increase in the ρ value is observed for the eliminations from both 2-arylethyltrimethylammonium salts and the corresponding sulfonium salts.[18] For the latter compounds the increase is very large and has been attributed to a decrease in C_α–S bond breaking in the more basic medium greater than the decrease in C_β–H bond rupture.

Experimental Section

Materials. 2-Arylethyltrimethylammonium bromides were prepared by reaction in methanol of the corresponding 2-arylethyl bromides[15] with an aqueous solution (33%) of trimethylamine. The mixture was allowed to stand at room temperature until separation of the solid product, which was recrystallized from ethanol–ether. Their properties were as follows.

2-Phenylethyltrimethylammonium bromide, mp 238–239 °C (lit.[9] 238–239 °C).

2-Phenylethyl-*2,2-d*$_2$-trimethylammonium bromide, mp 238.5–239 °C (lit.[9] 238–239 °C). Mass spectra showed 86% of deuteration.

2-(*p*-Tolyl)ethyltrimethylammonium bromide, mp 198–199 °C (lit.[9] 200.5–201 °C).

2-(*p*-Anisyl)ethyltrimethylammonium bromide, mp 216.5–218 °C (lit.[9] 217.7–218.2 °C).

2-(*p*-Bromophenyl)ethyltrimethylammonium bromide, mp 258.5–259.5 °C.

Sodium phenoxide was prepared by reaction of phenol with equimolecular amounts of NaOH in water. Water was removed at reduced pressure and the residue recrystallized from dry acetone. Before use, the phenoxide was kept at 100 °C and 1 mm for 90 min.

Sodium *m*-nitrophenoxide was prepared from *m*-nitrophenol and sodium methoxide in methanol. Methanol was removed at reduced pressure, and the residue recrystallized from ethanol-benzene and dried for 3 h at 100 °C and 1 mm.

Sodium perchlorate was a commercial product (B.D.H.), used without further purification.

Kinetic Studies. Known amounts of quaternary ammonium salt, of the nucleophile, and, in the case of the reaction with sodium phenoxide, of $NaClO_4$ were placed into a volumetric flask (20 ml). DMF (a commercial product, Carlo Erba RPE) was added and, after dissolution of all materials, the solution was diluted to the calibration mark. After shaking, the flask was placed in a thermostated bath and allowed to come to thermal equilibrium. Aliquots (2 ml) were taken periodically and poured into a separatory funnel containing *n*-heptane (8 ml), water (50 ml), and 6 N HNO_3 (1 ml). After rapid mixing the organic layer was separated and the aqueous phase further extracted with *n*-heptane (2 × 7 ml). The combined organic layers were washed twice with water and diluted to 25 ml in a volumetric flask. The optical density of the resulting solution was determined at the following wavelengths (nm): 249, styrene; 252, *p*-methylstyrene; 258, *p*-methoxystyrene; and 255, *p*-bromostyrene. Blank experiments have shown complete recovery of the olefin with this procedure.

Acknowledgment. Thanks are due to the Italian National Council of Research (C. N. R.) for financial support.

Registry No.—Sodium phenoxide, 139-02-6; sodium *m*-nitrophenoxide, 3019-85-0.

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