COMPETITIVE FORMATION OF SECONDARY AND TERTIARY ARYL BROMOCARBONIUM IONS IN BROMINATION

par Jacques-Emile DUBOIS[*], Marie-Françoise RUASSE et Alain ARGILE

(Laboratoire de Chimie Organique Physique de l'Université de PARIS VII,

associé au C N R S , 1, rue Guy de la Brosse, 75005 – PARIS – France)

It has been shown recently[1] that the heats of formation of carbonium ions in solution closely parallel the free energies of reactions which generate the same ions Thus, kinetics are valid methods for obtaining thermodynamic data on ions, particularly for those able to rearrange to more stable species and whose stabilities are difficult to measure directly [2] For comparing stabilities of tertiary and secondary cations, solvolysis, the classical reaction for generating carbonium ions, is unfortunately inconvenient since unassisted ionization frequently competes with solvent or anchimerically assisted processes [3] We report here results which suggest that bromination of dissymmetrically substituted olefins can provide an estimate of the relative ease of formation of secondary and tertiary aryl carbonium ions

It is now well established that bromine addition to an aryl olefin can lead, in a dual-pathway mechanism, to two carbonium ions with neither bromine participation[4] nor solvent assistance in the rate-determining step [5] In this way, a suitably substituted olefin can generate tertiary and secondary carbonium ions by reactions with rate constants k_{tert} and k_{sec} respectively, where k_{sec}/k_{tert} reflects the relative stabilities of the ions II and III since the ground state and the mechanism of formation are strictly identical in the two carbonium ion forming steps We, therefore, measured the rate constants of X and Y- substituted α-methyl
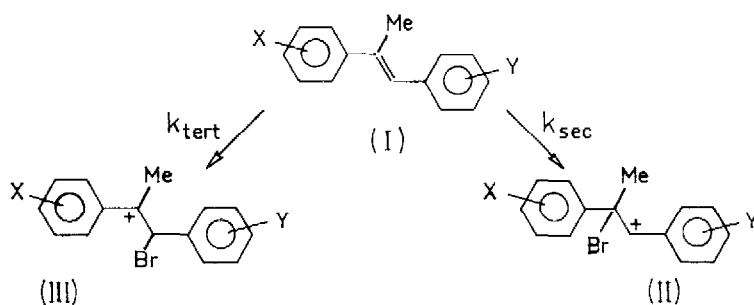
stilbenes, choosing X and Y so that either the tertiary or the secondary pathway predominates

For the tertiary pathway, a partial structure-reactivity relationship for the variation of X was established from compounds (X = p-OH to p-CF$_3$, Y = H) for which the secondary pathway

TABLE   EXPERIMENTAL RATE CONSTANTS FOR BROMINE ADDITION TO α-METHYL STILBENES
IN METHANOL , COMPARISON OF THE TERTIARY AND SECONDARY PATHWAYS

N°	X [a]	Y	k_{exp}	k_{tert} [c]	k_{sec} [d]	Importance of each pathway		$\Delta(\Delta G)^{III}_{II}$ [e]
						tert %	sec %	
1	H	m-CF$_3$	137	f	g	100	0	g
2	H	m-Cl	244	"	"	100	0	"
3	H	p-Cl	391	"	"	100	0	"
4	H	p-F	604	"	"	100	0	"
5	H	H	997	"	"	100	0	"
6	H	p-Me	1850	"	"	100	0	"
7	H	p-OMe	8610	$2\ 66\ 10^3$	$5.95\ 10^3$	30	70	0 5
8	H	p-NMe$_2$	$1\ 75\ 10^7$	$2\ 70\ 10^4$	$1.74\ 10^7$	0	100	3 85
9	p-Cl	p-OMe	3760	$8\ 7\ 10^2$	$2.9\ 10^3$	25	75	0 7
10	m-Cl	p-OMe	1880	$5\ 4\ 10$	$1\ 8\ 10^3$	3	97	2.1
11	m-CF$_3$	p-OMe	905	$1\ 6\ 10$	$8.9\ 10^2$	0	100	2.7

[a] X is the substituent on the ring α to the methyl substituted olefinic carbon atom and Y the
other one   [b] k_{exp} is measured in $M^{-1} mn^{-1}$ at 25° in methanol (0 2M NaBr) with an average error
of 2%, by potentiometry[8] except for compound 8 (couloamperometry)[9] In this medium, k_{exp} is
related to the addition of free bromine and of tribromide ion[6] Previous measurements[7] have show
that the variations of k_{exp} correspond to those of k_{Br_2} only   [c] Calculated from eq.3
[d] Calculated from $k_{sec} = k_{exp} - k_{tert}$ [e] $\Delta(\Delta G)^{III}_{II} = RT\ (\log_e k_{sec} - \log_e k_{tert})$ in kcal mol^{-1}
[f] identical to k_{exp} [g] unknown at present

is of negligible importance[7]

(1) $\log k = -4\ 87\ (\sigma_X + 0\ 77\ \Delta\sigma_X^+) + 3\ 08$

Data in the Table enable us to measure the effect of Y We observe a linear ρσ relationship
for variation of Y, only for the least electron-donating substituents (compounds 1 to 6), as
shown in Fig

(2) $\log k = -1\ 77\ \sigma_Y + 2\ 96$ (R=0.988, s=0.03)

Several factors – the linearity of eq 2, the small value[10] of ρ for Y, and the fact
that its effect is better expressed[11] by σ than by σ$^+$ – lead us to conclude that the tertiary

pathway is followed when Y varies from m-CF$_3$ to p-Me Thus, the general free energy relationship for the tertiary pathway is .

(3) $\log k = -4\ 87\ (\sigma_X + 0\ 77\ \Delta\sigma_X^+) - 1.77\ \sigma_Y + 3\ 0$

The deviations from eq 2 for compounds 7 and 8 can reasonably be attributed[12] to the occurrence of the secondary pathway Taking into account the kinetic relationship derived from the Scheme, $k_{exp} = k_{sec} + k_{tert}$ (4), and calculating k_{tert} from eq 2, we obtain k_{sec} for these
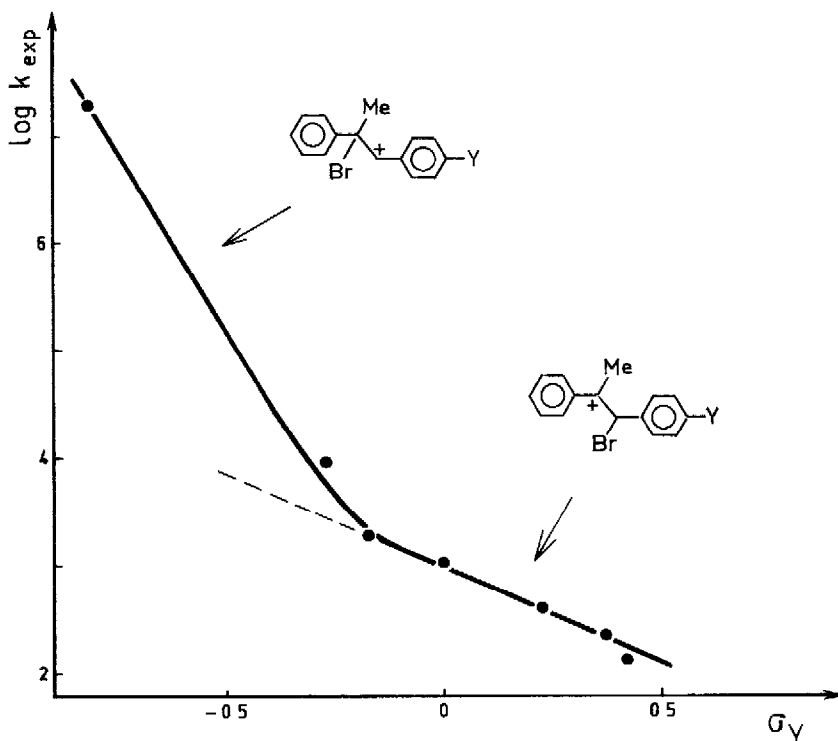
Bromination of Y-substituted α-methyl stilbenes.
The breakdown of the ρσ relationship indicates the change from tertiary to secondary pathway.

compounds In the same way, for compounds where Y = p-OMe and X is variable and less electron-donating than H (compounds n° 9, 10 and 11), we find that k_{sec} calculated by the same method is higher than k_{tert}. Consequently, these compounds must be brominated largely via the secondary pathway (see Table)

Energy differences between transition states leading to the secondary and the tertiary carbonium ions are calculated and given in the Table How does this energy difference between transition states reflect that between the ions ? The answer to this question is supplied by two items of information Firstly, the results of Larsen et al [1] suggest that the structural effects on transition state stability should be closely related to the stabilization of the ion Secondly, solvent and substituent effects on bromination[5] as on limiting solvolysis[14] indicate that transition states closely resemble the intermediates in these reactions Consequently, we can consider that the values in the Table are accurate approximations to the energy differences between the carbonium ions The method proposed to obtain these energy differences is based on the equation 4 and therefore demands the measurement of k_{exp} for compoun which are suspected to react partially or completely by the secondary pathway A reactivity-structure correlation for this pathway, analogous to eq 3 for the tertiary one, would allow the prediction of stability differences whatever the substituents X and Y A partial relationship of this type can be deduced for the α-methyl stilbenes (N° 7, 9, 10, 11) where Y = p-OMe

$$\log k_{sec} = -1.74 \, \sigma_X + 3.80 \quad (R=0.947, \, s=0.06)$$ Further studies are in progress to determine other such relationships of more general validity

1   a) J W Larsen and P A Bouis, J Amer Chem Soc , *97*, 4418 (1975) , b) E M Arnett and J W Larsen, in "Carbonium Ions I", ed by G A Olah and P v.R Schleyer, Wiley-Inter science, 1968, p 441

2   H H Freedman, in "Carbonium Ions IV", ed by G A Olah and P v R Schleyer, Wiley-Inter science, 1973, p 1501

3   H C. Brown and C J Kim, J Amer Chem Soc , *91*, 4286, 4287 (1969) , C J Lancelot and P v R Schleyer, ibid , 4291, 4294, 4296, 7508 (1969)

4   M F Ruasse and J E Dubois, J Org Chem , *37*, 1770 (1972), *38*, 493 (1973)

5   M F Ruasse and J E Dubois, J Amer Chem Soc , *97*, 1977 (1975)

6   E Bienvenue-Goetz and J E Dubois, Bull Soc Chim Fr , 2089,(1968), J E Dubois and X Q Huynh, ibid , 1436, (1968)

7   J E Dubois, M F Ruasse and A Argile, Tetrahedron, *31*, 2921 (1975) In the α-Me stilbenes, the X-substituted ring is not in the plane of the incipient carbonium ion, so that the resonance effects of X are not completely transmitted to the charged carbon atom.

8   R P Bell and E N Ramsden, J Chem Soc , *161*, (1958)

9   J E Dubois, P Alcais and G Barbier, J Electroanal.Chem , *8*, 359, (1964)

10 In the tertiary pathway, the effects of Y are transmitted to the incipient ion by the bromomethylene group, whereas X is directly on the ring conjugated with the developing charge, so that the ρ_β (for Y) should be less than ρ_α (for X)

11 The ring bearing Y is not directly conjugated with the charge With σ, the correlation coefficient is 0 988, with σ^+ it is 0 961 Moreover the p-F compound is less reactive than the unsubstituted one indicating that σ is more appropriate than σ^+

12 An other reason for deviation could be the occurrence of a bromonium ion intermediate The p-anisyl group effect on the stereochemistry is however in contradiction with this hypothesis [13] Studies in progress on the regiochemistry for these compounds agree with the carbonium ion scheme

13 R C Fahey and H J Schneider, J Amer Chem.Soc , *90*, 4429 (1968)

14 D J Raber, R C Bingham, J M Harris, J L Fry and P.v R Schleyer, J Amer Chem.Soc , *92*, 5977 (1970)