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(12) One of the two "acetates" proposed by Morgan[3] was found by ^{13}C NMR to be an exceptionally low-field quaternary methyl (^1H NMR 2.06 ppm).

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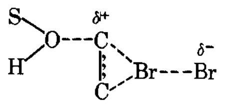
Role of the Solvent in Bromine Additions to Olefins. Solvent Independence of the Charge Distribution in Transition States and Intermediates

Sir:

Solvent dependence of stereoselectivity in aryl olefin bromination[1] has been attributed to competition between bromine bridging and *nucleophilic* solvation in the carbonium ion intermediate **1**: the more the positive charge is solvated, the less the importance of bromine assistance. Specific solvation would favor the carbonium over the bromonium ion intermediate and would lead to low stereoselectivity. However, solvation of the 1-pentene bromination transition state **2**, known to be bromonium ion-like,[2] is essentially *electrophilic*.[3] Insofar as the intermediate closely resembles the transition state,[3] these observations appear contradictory. The contradiction would be resolved if the solvation of carbonium ion intermediate[4] were substantially different from that of bridged bromonium ions. We now report results on the bromination of styrene (I) and *trans*-stilbene (II), which negate this hypothesis.



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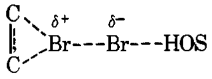

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Rate constants of the molecular bromine addition to olefins I and II in solvents whose Y^5 varies over 5 units are shown in Table I and compared with those of 1-pentene.

Solvent effects on 1-pentene, styrene, and stilbene bromination are remarkably similar.

$$\log k_{\text{sty}} = 0.83 \log k_{1\text{-pe}} - 1.73 \quad (R = 0.997,\ s = 0.004) \tag{1}$$

$$\log k_{\text{stil}} = 1.02 \log k_{1\text{-pe}} + 0.91 \quad (R = 0.999,\ s = 0.005) \tag{2}$$

For 1-pentene, Winstein's equation[5] in its simplest form applies[3]

$$\log (k/k_0) = 1.16\text{Y} \tag{3}$$

From eq 1-3, m values of 0.96 and 1.20 were obtained for styrene and stilbene, respectively. Solvent effects on 1-bromoadamantane solvolysis, where nucleophilic solvation is impossible, are correlated[6] by Y with m = 1.20. This value corresponds to a transition state where the leaving group is a bromide ion, as in bromination. We can, therefore, conclude that nucleophilic solvation is insignificant in bromination of 1-pentene and stilbene which have similar m values (1.16 and 1.20, respectively). Although the m value for styrene is smaller (0.96), this decrease cannot be attributed to nucleophilic solvent assistance since this generally leads to much smaller values,[6] e.g., for isopropyl bromide solvolysis, m = 0.43.

Table I. Solvent Effects on the Bromination of Styrene, *trans*-Stilbene, and 1-Pentene

		k_{Br_2}[a] l. mol^{-1} sec^{-1}		
Solvent	Y[b]	Stilbene	Styrene	1-Pentene
H_2O	3.4	$7.8\ 10^5$ [d]	$1.1\ 10^7$ [g]	$2.5\ 10^7$ [h]
M-50[c]	1.97		$2.3\ 10^6$	$9.15\ 10^5$ [h]
CF_3CH_2OH	1.04	$1.7\ 10^3$		$6.85\ 10^4$ [h]
CH_3OH	−1.09	$1.1\ 10$[e]	$1.16\ 10^3$ [g]	$3.80\ 10^2$ [h]
CH_3COOH	−1.64	$1.8\ 10^{-2}$ [f]	8.4[f]	1.13

[a] Rate constants are measured at 25° by electrometric and spectrophotometric methods described previously, ref 2, 3, and 17. [b] Reference 5 and 6. [c] 50% (volume) aqueous methanol. [d] Reference 16. [e] Reference 17. [f] Reference 19. [g] Reference 18. [h] Reference 3.

Thus no nucleophilic assistance can be detected regardless of whether the transition state is carbonium or bromonium ion-like. Nevertheless, the solvent operates in two ways: firstly, through a medium effect on the magnitude of the charge separation between cationic and anionic parts of the transition state and secondly by electrophilic solvation demonstrated, at least for methanol, by the solvent isotope effect,[3] k_H/k_D = 1.40. Since specific solvation of the cationic part does not exist, the solvent cannot influence significantly the distribution of the positive charge between the olefinic carbon atoms and the bromine.

On the other hand, we have shown elsewhere[4] that the charge distribution depends on substituent character. There is, therefore, a distinct separation between the factors which determine charge magnitude (solvent) and charge distribution (substituents). This view agrees with Schleyer's observations[7] in the β-aryl ethyl ester solvolysis where the importance of neighboring phenyl assistance depends not on the solvent but only on the ring substituents.

Consistent with the concept of a transition state with only the anionic part solvated is the fact that substituent effects on the bromination of alkenes are closely similar, regardless of the solvent.[8] However, recently,[9] Olah et al. claim that substituent effects are enhanced on going from Freon 113 at −35° to methanol at 25°.

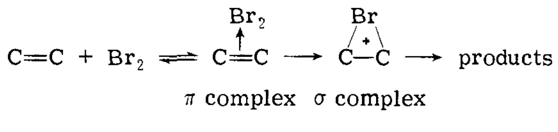
$$\log k \text{ (Freon 113, } -35°) = 0.69 \log k \text{ (MeOH, } 25°) + \text{Cte } (R = 0.969)\cdot$$

This result is surprising since we have shown[3] that structural effects are very similar in methanol and Freon 112.

$$\log k \text{ (Freon 112, } 25°) = 1.10 \log k \text{ (MeOH, } 25°) - 5.99 \ (R = 0.965)$$

$$\log k \text{ (Freon 112, } 25°) = 1.45 \log k \text{ (Freon 113, } -35°) + \text{Cte } (R = 0.956)$$

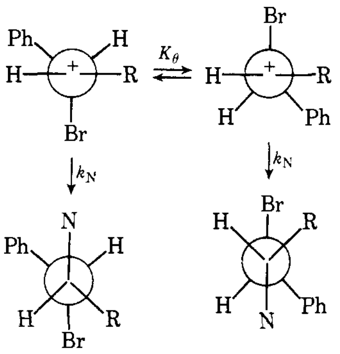
Now, $\rho = f(1/T)$; i.e., substituent effects should decrease with rise in temperature, and it is inconceivable that the change in solvent from Freon 113 to Freon 112[10] should modify the mechanism enough to invert the normal trend of ρ with temperature. According to Olah's interpretation, the transition state would be less charged, further from the σ



$$\mathrm{C{=}C} + \mathrm{Br_2} \rightleftharpoons \underset{\pi\ \text{complex}}{\overset{\mathrm{Br_2}\atop\uparrow}{\mathrm{C{=}C}}} \longrightarrow \underset{\sigma\ \text{complex}}{\overset{\mathrm{Br}^{+}}{\mathrm{C{-}C}}} \longrightarrow \text{products}$$

intermediate and closer to the π complex in Freon 113 at −35° than in methanol at +25°, but he reckons without the Freon 112 results. Since it is generally accepted that π complex stability is rather insensitive to solvent,[11] this interpretation implies that the σ complex would be more stable in Freon 113 than in methanol, a rather unlikely event! Thus, Olah's results are contradictory not only with ours but also with the Hammond postulate.[12] A possible source of error in his work in Freon 113 could be the choice of a competitive kinetic method; our data were obtained by direct measurement. It has been found[13,14] that the competitive methods frequently lead to a compression of the reactivity span which would, of course, give rise to the reported low value of ρ. It would seem, therefore, unwise to invoke for bromination in Freon 113 at −35° any fundamentally new mechanism.

Since we find that *solvent changes cannot lead to significant variation in bromine bridging* as specific nucleophilic solvation is absent, the problem of solvent dependence of stereoselectivity must be resolved in other terms. In so far as our results have eliminated the conventional interpretation of this problem, a reexamination of the role of the solvent in determining stereochemistry is now necessary, knowing that the solvent intervenes only in the last step: nucleophilic trapping of the intermediate. Thus the influence of solvent probably lies in the competition between conformer equilibration K_θ and nucleophilic attack k_{N} according to the scheme postulated by Collins[15] in order to account for the stereoselective reactions of carbonium ions.



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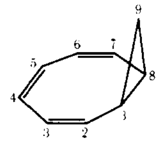
On the Walk Rearrangement of Bicyclo[4.1.0]hepta-2,4-diene and of Bicyclo[2.1.0]pent-2-ene. A Semiempirical MO Study

Sir:

The 1,7-sigmatropic rearrangement of **1** and the 1,5-sigmatropic rearrangement of **2** proceed with inversion of configuration at the migrating carbon atom.[1] The 1,3-sigmatropic rearrangement of **3** is yet unknown.[2] Therefore **1** follows a path which is in accordance with orbital symmetry considerations[3] and **2** a path which is in accordance with the Berson–Salem hypothesis[4] (Table I).

Following simple arguments concerning ring strain,[5] the three-membered ring of **1** should be more stable than that of **3** and should be about as stable as in **2**. The same conclusions should also hold for an aromatic transition state,[6] favoring a stability order **4** > **5** > **6** for pericyclic bonding; in other words the less strained "forbidden concerted" transition state (with no pericyclic bonding) should compete in the reverse order **9** > **8** > **7**.



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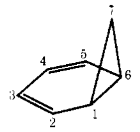

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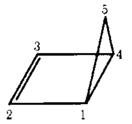

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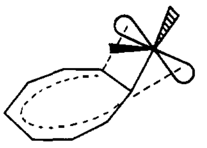

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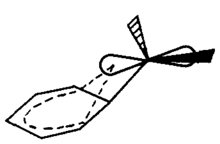

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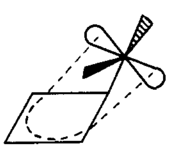

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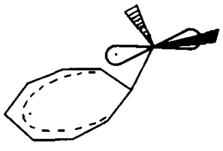

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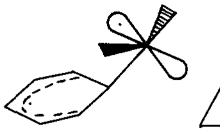

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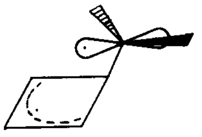

9

We wish to report optimized semiempirical MINDO/2 calculations[7] on the transition states **5**, **8** and **6**, **9** in the sigmatropic rearrangements of **2** and **3**, including configuration interaction[8] for proper bond dissociation. Due to computational expenses a study of the transition states in the thermal rearrangement of **1** was out of range. For the evaluation of the energy hypersurface as given in Figure 1, we proceeded in the following order: (a) assumption of the migrating carbon as a midpoint on the reaction coordinate, this implies a plane of symmetry through the migrating carbon atom and bisecting the polyene unit (C_s symmetry); (b) determination of the conformation lowest in energy by optimizing bond lengths and bond angles, for the minimiza-