Table I. Phosphorescence of Some Phenyl Ketones with n,π^* Lowest Triplets

Ketone	Solvent	E_T,[a] kcal	τ_{short}, msec	τ_{long}, msec[b]
PhCOPh	MC[c]	68.6	5.6	None
	EtOH	69.5	6.2	None
$PhCO(CH_2)_3CH_3$	2-MP[d]	74.5	6.4	(2) 27
	EtOH	74.3	34	(6) 260
	EPT[e]	74.4	27	(17) 74
$PhCOCMe_2(CH_2)_2CH_3$	EPT	72.5	5.5	None
$PhCOCMe_3$	MC	72.0	4.4	None
	EtOH	72.6	7.3	None
$PhCOCH_3$[f]	MC	73.5	4	None
	EtOH	74.0	8.0	(3) 200
1-Indanone[g,h]	3-MP[i]	75.1	1.5	None,[g] 130[h]
	EPA	75.8	2.2	(30) 200[h]
2,2-di-Me-1-indanone[g]	3-MP	74.0	1.7	None
	EPA	74.6	1.9	None
1-Tetralone[g]	3-MP	72.4	2.9	None
	EPA	72.9	3.8	None
p-F-$PhCO(CH_2)_3CH_3$	IP[j]	72.5	39	(19) 130
p-Cl-$PhCO(CH_2)_3CH_3$	IP	70.5	4.7	(7) 75
	EtOH	72.2	40	(50) 100

[a] 0–0 band. [b] Number in parentheses equals percentage of total emission (at 0–0 band). [c] Methylcyclohexane. [d] 2-Methylpentane. [e] 5:5:2 ether–isopentane–triethylamine. [f] Reference 3. [g] Reference 17. [h] Reference 1. [i] 3-Methylpentane. [j] Isopentane.

scheme, where $X_{n,\pi}$ is the fraction of triplets in the $^3n,\pi^*$ state at equilibrium.

$$\begin{array}{ll} & \underline{10\%\,^3n,\pi^*} \xrightarrow{\sim 200\ sec^{-1}} \sim 80\%\ n,\pi^*\ \text{emission} \\ \Delta E \approx & \uparrow\downarrow \\ 350\ \text{cal} & \underline{90\%\,^3\pi,\pi^*} \xrightarrow{\sim 5\ sec^{-1}} \sim 20\%\ \pi,\pi^*\ \text{emission} \end{array}$$

$$1/\tau = X_{n,\pi}k_{n,\pi} + (1 - X_{n,\pi})k_{\pi,\pi} \quad (1)$$

$$\ln\left(\frac{1 - X_{n,\pi}}{X_{n,\pi}}\right) = \frac{\Delta E}{RT} \quad (2)$$

Independent evidence for this assignment is provided (1) by the heavy-atom effect on the lowest energy $S \rightarrow T^*$ absorption;[2] (2) by the n,π^* polarization of the highest energy (supposed 0–0) phosphorescence band;[6] and (3) by the overall n,π^*-like appearance of the phosphorescence spectrum.[2,6] We also note that Lamola has recently observed such an equilibrium mixture of n,π^* and π,π^* triplets in the phosphorescence of a compound containing two separate, nonconjugated chromophores with similar triplet excitation energies.[20]

If the shorter lived component from the halo ketones and from valerophenone in ethanol represents an equilibrium mixture of n,π^* and π,π^* triplets, we must ask then what the longer lived component can be, not only in these ketones but in all cases. We tend to agree with Lim[17] that the long-lived emission does not come directly from the π,π^* triplet. Not only is it awkward to postulate that some of the π,π^* triplets equilibrate with the n,π^* triplet while others do not, it is very difficult to rationalize the lower energy state affording the minor emission component. However, the lack of long-lived phosphorescence from the ketones with no enolizable α hydrogens does not in itself provide unequivocal evidence that the long-lived emission, where observed, involves an enolate ion.

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Dimethyl substitution at the α position lowers the triplet n $\rightarrow \pi^*$ transition energy by 1–2 kcal but does not affect λ_{max} for the $^1A \rightarrow {}^1L_a$ transition, so that the triplet $\pi \rightarrow \pi^*$ transition energy presumably remains constant at 75–76 kcal.[3] Moreover, our unpublished results with pyridyl ketones agree with those of Yang with trifluoromethylphenyl ketones:[12] neither produces any long-lived emission in hydrocarbon glasses. In both kinds of ketones, the $^3n,\pi^*$ state is stabilized relative to the $^3\pi,\pi^*$ state. Consequently, the amount of long-lived emission correlates better with the $^3n,\pi^*$–$^3\pi,\pi^*$ energy separation than it does with the enolizability of the α protons. The observation of a long-lived component, even when the $^3n,\pi^*$ state is lowest, then seems to be diagnostic of the proximity of a $^3\pi,\pi^*$ state, as originally suggested by Yang and Murov.[1]

In summary, a comparison of our results with those of others suggests that the shorter lived phosphorescence component from phenyl alkyl ketones arises from an equilibrium mixture of $^3n,\pi^*$ and $^3\pi,\pi^*$ states. The longer lived component may well involve nonequilibrium loss of an α proton because of its increased importance in basic solvents and because of the reported photoaldol condensation of 1-indanone in isopropyl alcohol.[21] However, its dependence on the $^3n,\pi^*$–$^3\pi,\pi^*$ energy separation, which suggests a $^3\pi,\pi^*$ precursor, is in direct conflict with the results of Lim's polarization measurements,[17] which suggest a $^3n,\pi^*$ precursor.

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(21) F. Bergmann and Y. Hirshberg, *ibid.*, 65, 1429 (1943), report that, in isopropyl alcohol, 1-indanone is not photoreduced but condenses instead. In contrast, cyclopentanone is photoreduced by isopropyl alcohol.[22]

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(23) Alfred P. Sloan Fellow, 1968–1970; address correspondence to this author.

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Cyclopropane Assistance in Neopentyl Solvolysis[1]

Sir:

The effectiveness of neighboring group participation by cyclopropane in solvolytic reactions has been investigated recently by several groups.[2] In contrast to the

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) (a) G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968); (b) W. G. Dauben and J. L. Chitwood, *J. Amer. Chem. Soc.*, 90, 3835 (1968); (c) R. M. Coates and J. L. Kirkpatrick, *ibid.*, 90, 4162 (1968); (d) H. Tanida, *Accounts Chem. Res.*, 1, 239 (1968); (e) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, 90, 4468 (1968); (f) Y. E. Rhodes and T. Takino, *ibid.*, 90, 4469 (1968);

observation that a β-cyclopropyl group in the 7-norbornyl system enhances the rate of solvolysis by a factor of 10^{14},[3] rate and product analyses of 2-cyclopropylethyl brosylate solvolyses indicate that cyclopropyl participation in simple acyclic systems may be only weakly competitive with solvent assistance.[2f] The absence of inductive rate retardation[4] (observed in ethanolysis and acetolysis) in formolysis of 2-cyclopropylethyl brosylate[2f] and the small rate enhancement on methyl substitution[2e] indicate weak participation by cyclopropane. To overcome the apparent predominance of the k_s process overshadowing potential cyclopropane participation, we have determined the rates and products of solvolysis of the corresponding neopentyl system, 2-cyclopropyl-2-methylpropyl brosylate (**1**),[5] in which solvent assistance to ionization is sterically hindered. Since primary neopentyl systems are considered to solvolyze with participation of the available neighboring alkyl groups[6] (k_Δ process) cyclopropane participation should be reflected in rate differences and the structures of rearranged products.

The alcohol, 1-OH, was prepared by the Simmons–Smith reaction of 2,2-dimethyl-3-buten-1-ol, prepared from acetoacetic ester.[7] The brosylate ester was prepared by standard procedures and purified by crystallization from ether–pentane: mp 29–30°. Acetolysis rates were determined titrimetrically in the presence of excess sodium acetate using crystal violet as the indicator. The rate data are given in Table I and compared to other substituted neopentyl acetolyses.

Table I. Relative Rates of Acetolysis of Substituted Neopentyl Systems, R–C(CH_3)$_2$–CH_2–OBs, at 75°

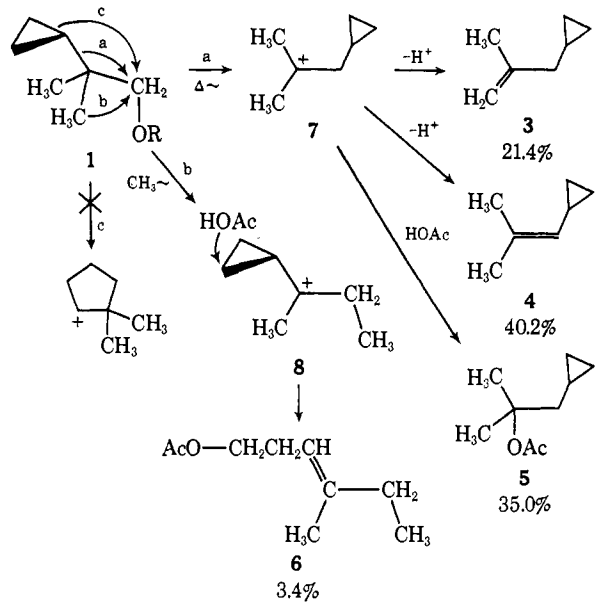
R	k_{rel}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
CH_3[a]	0.026	31.2	1.1
C_2H_5[a]	0.048	30.3	−0.3
i-C_3H_7[a]	0.130	27.9	−4.8
Cyclopropyl[b]	1.00	26.6	−4.5
Vinyl[c]	4.8	24.5	−7.5
Phenyl[d]	5.1	25.5	−4.6

[a] Reference 8. [b] This work: $k \times 10^5$ sec^{-1} (T, °C): 1.32 (74.60), 7.33 (89.67), 19.6 (100.00). [c] Reference 7. [d] Reference 9.

The acetolysis rate of the cyclopropyl compound (**1**) is 39 times greater than that of neopentyl brosylate and eight times greater than that of 3-methyl-2,2-dimethylbutyl brosylate[8] (**2**), an isopropyl analog chosen as a steric model and as a model for relief of strain at the neopentyl quaternary carbon. The relative rate changes parallel changes in the enthalpy of activation indicating stabilization of the transition state for **1** of about 4 kcal/mol relative to neopentyl brosylate. Since cyclopropyl is slightly smaller than isopropyl,[10] rate enhancement of a factor of eight for cyclopropyl relative to isopropyl cannot be explained by relief of strain at the neopentyl carbon.[8]

The acetolysis products (ten half-lives at 75°) were separated and collected by preparative glpc and characterized as shown in Chart I. The structures of **3**, **4**,[11]

Chart I



and **5** are unequivocally identified by their nmr and ir spectra. The structure of **6** is tentatively established by nmr but remains to be compared with an authentic sample. Any cyclopentyl product which might be anticipated by ring opening of the cyclopropyl group, as observed in 2-cyclopropylethyl solvolyses,[12,2f] was not detected and if present must be less than 0.5%.

Products **3**, **4**, and **5** (96.6% of the total) are derived from one intermediate, **7**, the result of apparent cyclopropane migration as shown in Chart I. The minor remaining product, **6**, appears to be derived from methyl migration followed by ring opening of **8** as shown. The migratory aptitude of cyclopropyl relative to methyl is 56 (96.6/(3.4/2)) on the basis of the product ratios and the statistical factor for methyl. The migratory aptitudes of alkyl groups are smaller than for methyl and decrease as the branching at the migrating carbon is increased.[13]

The charge density at the migrating carbon is also a factor which determines relative migratory ability. Electron-withdrawing substituents in para-substituted benzylneopentyl systems reduce the migratory aptitude

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of benzyl groups.[14] In situations in which phenyl is geometrically restricted from assuming an orientation favorable for phenonium ion formation, phenyl has a lower migratory aptitude than alkyl groups,[15] whereas phenyl migrates almost to the exclusion of alkyl migration when a phenonium ion can be achieved.[9] This is the result not of an inductive effect but of the hybridization of the bonding orbitals of the migrating carbon (sp^2, higher s character than alkyl, and more tightly bound), which must be used in migration of phenyl in cases in which phenonium ion formation is precluded. Since the bulk and hybridization of cyclopropane should decrease its migratory aptitude relative to methyl the nearly exclusive cyclopropyl migration observed in this system, **1**, indicates that the transition state for cyclopropyl migration is stabilized relative to the transition state for methyl and isopropyl migration, whereas in other systems migration of *sec*-alkyl is preferred over cyclopropyl.[2j,k]

The relative stabilities of the tertiary carbonium ions formed by migration of cyclopropyl *vs.* methyl must be a minor factor in determining the migratory aptitudes as the preferential cyclopropyl migration observed leads to the less stable tertiary cation, as is also observed in the solvolysis of neophyl systems.[9] This suggests that stabilization of the transition state by delocalization of the positive charge developing at the quaternary neopentyl carbon is small compared to the stabilization gained by cyclopropyl or phenyl migration. These data support a mechanism for solvolysis in which ionization is assisted by cyclopropane participation which at the same time facilitates cyclopropane migration. On this basis partial rate factors for cyclopropyl (k_p^{Δ}), methyl ($k_p^{CH_3}$), and isopropyl ($k_p^{i\text{-}Pr}$) may be calculated from the rate and product data (Table II). Comparison

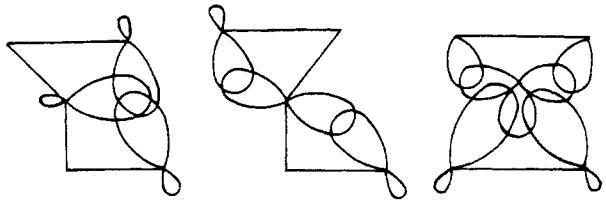
Table II. Partial Rate Factors for Migration of Alkyl Groups in Neopentyl Solvolyses at 75°

R	$k_{obsd} \times 10^7$ sec^{-1}	$k_p^{CH_3}$	k_p^{Δ}	$k_p^{i\text{-}Pr}$
CH_3[a]	3.44	1.15		
Cyclopropyl, **1**[b]	134	2.28	129	
Isopropyl, **2**	17.4	8.26		0.87

[a] Reference 8. [b] This work. [c] Calculated from data of Fritz,[13] 95% methyl migration, 5% isopropyl migration.

of partial rate factors for cyclopropyl *vs.* isopropyl reveals enhancement of the cyclopropane-assisted solvolysis as a facter of 148.

The type of orbital interaction between the cyclopropyl group and the reactive site in the transition state for ionization presents an intriguing quandary. There are no π-bonding centers in cyclopropane available for interaction as in phenyl or vinyl and stabilization of the transition state must result from delocalization of σ bonds of the ring which are high in p character. This might be pictured as cyclopropane ring–edge interaction, **10** (most probable for participation in 2-cyclopropylethyl), of the homocyclopropenyl type[16] and similar to cyclopropane protonation.[17] However no cyclopentyl products or other rearranged products were obtained as might be anticipated from this type of interaction. A



10 11 12

second type of interaction similar to that proposed by Freeman and Balls,[18] **11**, also would not lead directly to the products observed. The simplest explanation, a simple Wagner–Meerwein rearrangement, does not account for the rate enhancement and preferential migration of cyclopropane. Modification of this transition state to include delocalization of both of the cyclopropane ring bonds, such as in **12**,[19] or rearrangement of an initially formed **10** or **11** to the tertiary carbonium ion **7** would account for the observed products and rates in the neopentyl case. Mechanistic economy, however, would be best served by a common transition state for the 2-cyclopropylethyl and cyclopropylneopentyl systems. The question of transition state and intermediate structures for the reactions of these simple cyclopropylethyl systems is being explored further.

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Identification of Pentacyanomonoaquochromate(III)[1]

Sir:

Schaap and coworkers[2–4] have described the preparation, isolation, and absorption spectra of a series of chromium(III) complexes of the form $Cr(CN)_n(H_2O)_{6-n}^{3-n}$. It was reported that the pentacyano complex ($n = 5$) undergoes rapid aquation to the tetracyano complex ($n = 4$) and is therefore difficult to isolate. In this communication we wish to report experimental evidence that the complex identified by Schaap and coworkers as the tetracyano complex is in fact the pentacyano complex.

We have recently investigated the kinetics of the chromium(II)-catalyzed aquation of hexacyanochromate(III) at 25°. The media for these studies were various combinations of NaCN, NaOH, and $NaClO_4$ (ionic strength = 1.0 *M*). When the concentrations of

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