Alkoxycarbenium Ions. Relative Thermodynamic Stabilities in Solution

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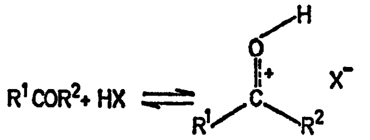
Summary The relative stabilities of several methoxycarbenium ions have been determined directly *via* a stepwise equilibration method.

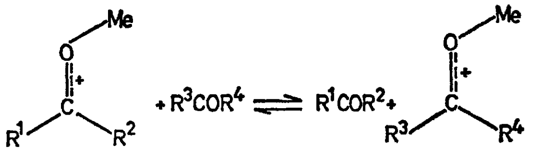
Considerable doubt exists concerning the basicity of carbonyl compounds, *i.e.*, concerning the relative stabilities of hydroxycarbenium ions (**1**) formed by protonation of carbonyl bases [see equation (1)].[1] In an effort to examine the effect of structure on stabilities of carbocations of this type, we have developed an unambiguous method in homogeneous solution for the direct determination of the relative stabilities of alkoxycarbenium ions (**2**), which should serve as good models for the corresponding hydroxycarbenium ions (**1**).



(1)

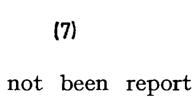
(1)

Stable alkoxycarbenium ion salts† were prepared by methylation of the corresponding carbonyl compounds with trimethyloxonium tetrafluoroborate in methylene chloride solution.[2] The isolated methoxycarbenium salts exhibit sharp, characteristic, well separated ^{1}H n.m.r. resonances which can be used to monitor the course of the equilibration reactions with carbonyl bases in liquid sulphur dioxide as shown in equation (2). These equilibrations take place readily at room temperature within 1—2 weeks without significant decomposition. It is noteworthy that reversible methyl (alkyl) transfers between alkoxycarbenium ions and carbonyl bases in homogeneous solution have not been reported previously.[3] Equilibrium constants for these exchanges were calculated from the relative concentrations of each species in solution using standard ^{1}H n.m.r. integration techniques since the transmethylation reaction is slow on the n.m.r. time scale. The results of

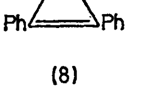


(2)

(2)



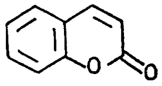
(3) R = H
(4) R = Me



(5)

$(p\text{-}MeOC_6H_4)_2CO$

(6)



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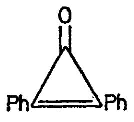

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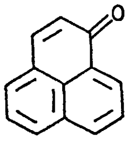

(9)

Table

Equilibration data for alkoxycarbenium ion–carbonyl pairs.[a]

Entry	Equilibration pair	*K*
1.	(**3**) + (**6**)	1·2 ± 0·05
2.	(**4**) + (**6**)	0·17 ± 0·01
3.	(**4**) + (**7**)	0·14 ± 0·01
4.	(**4**) + (**8**)	44[b]
5.	(**5**) + (**9**)	<0·05[b]

[a] All equilibrations were run in liquid SO_2 at 25°. [b] Results of single runs only.

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† All new compounds gave satisfactory elemental analyses and their spectroscopic properties were in accord with the assigned structures.

several such equilibrations are shown in the Table. In general, each equilibrium was approached from both directions and the results of duplicate experiments were averaged to obtain the tabulated results. The internal consistency of these results can be evaluated from entries 1, 2, 3, *i.e.*, $K_2/K_3 = K_1$.

With regard to the use of alkoxycarbenium ions (**2**) as models for the corresponding hydroxycarbenium ions (**1**), it is interesting to note that in each case the equilibrium position favours formation of the alkoxycarbenium ion corresponding to the most basic carbonyl compound on the proton basicity scale. Thus, the basicities of these carbonyl compounds using available pK_a estimates fall in the order 2,6-dimethyl-γ-pyrone ($pK_a = 0{\cdot}4$[4]) > perinaphthenone ($pK_a = -1{\cdot}4$[5]) > diphenylcyclopropenone ($pK_a = -2{\cdot}5$[6]) > 4,4′-dimethoxybenzophenone ($pK_a = -4{\cdot}4$[7]) > coumarin ($pK_a = -4{\cdot}8$[1]). It will be interesting to extend this general equilibration method to a wide variety of carbonyl compounds and to define the scope of the correspondence between proton basicities and alkoxycarbenium ion stabilities.‡

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‡ Comparison of the u.v.–visible and ^{1}H n.m.r. spectra of alkoxycarbenium ions with the corresponding hydroxycarbenium ions provide further support for the analogy between these carbocations. Complete spectral characterizations for these ions will be presented elsewhere.

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