Organic and Biological Chemistry

Modes of Carbonium Ion Stabilization.[1]
## Evidence from Charge-Transfer Spectra

Walter Hanstein, Harvey J. Berwin, and T. G. Traylor

*Contribution from The Department of Chemistry, Revelle College,
University of California, San Diego, La Jolla, California.
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Abstract: The charge-transfer frequencies of the complexes of a series of monosubstituted benzenes, ϕY, with either tetracyanoethylene or dichloromaleic anhydride have been determined and correlated with σ_p^+. Substituents Y which accelerate the rate of reaction $Y-CR_2-X \rightarrow Y-C^+R_2 + X^-$ by inductive or delocalization effects (Y = CH_3O-, CH_3CONH-, CH_3, C_2H_5O-, R_2N-) also stabilize the radical cation $Y-C_6H_5^+\cdot$, and lower the charge-transfer frequency. However substituents which accelerate this reaction by internal nucleophilic displacement (Y = $CH_3CONHCH_2-$, $C_2H_5OCH_2-$, $BrCH_2-$) do not lower the charge-transfer frequency (relative to Y = CH_3). Groups which provide cation stabilization in both processes are classified as providing "vertical" stabilization and those which provide stabilization only in the solvolysis of YCR_2X are classified as providing "nonvertical" stabilization. Using these correlations it is shown that the substituents Y = $RHgCH_2-$, R_3PbCH_2-, cyclopropyl, and 1-[2.1.1]bicyclohexyl stabilize carbonium ions by "vertical" processes. Migration within these substituents apparently does not occur in the rate-limiting formation of the carbonium ion.

Considerable interest has centered around the modes of carbonium ion stabilization which lead to large variations in the rate of reaction 1 when changes are made in the nature of the group G, located as shown in


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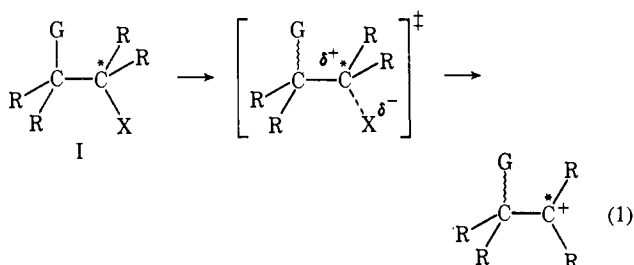
I.[2-5] There is almost universal agreement concerning the mechanism of the acceleration which results when G is a known nucleophilic group such as G = $-O^-$, $-SR$, $-NR_2$, $-C(=O)O^-$, $-NHC(=O)R$, etc.[2] As the C*–X bond ionizes the nucleophilic group moves closer to C+ and forms a partial σ bond with this carbon. We have
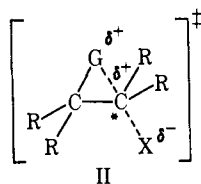
called this effect "internal nucleophilic displacement"[6a] here abbreviated ND_I.[6b]

There is no such agreement concerning the mechanism of the accelerated reaction which occurs when G is
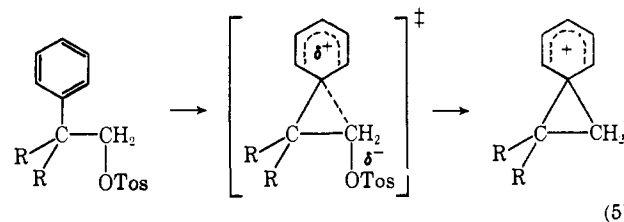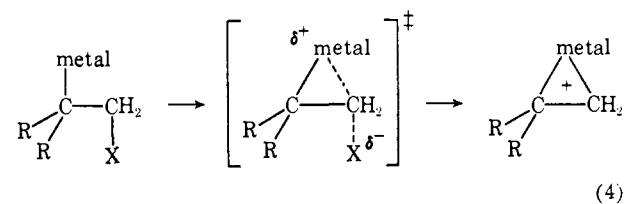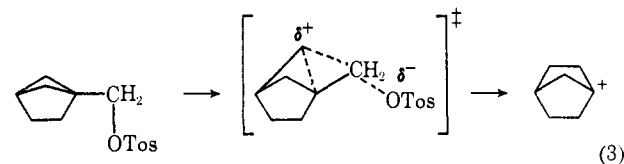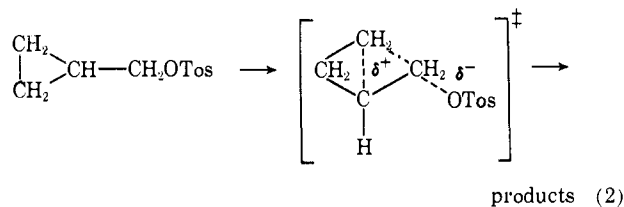
$$ \text{products} \quad (2) $$

$$ (3) $$

$$ (4) $$

$$ (5) $$

(2) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(4) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(5) (a) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, pp 7–147; (b) p 101; (c) p 113; (d) p 56.

(6) (a) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (b) we use ND_I rather than the older term "neighboring group participation" because the latter is often used to specify all possible kinds of cation stabilization by the group, G, including $\sigma-\pi$ conjugation; (c) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967).

an aryl, vinyl, or aliphatic group, or a metallic group containing, e.g., Fe, Hg, Sn, Ge, or Si.[3,4,6-9]

Typical interpretations of accelerated solvolysis reactions in terms of nuclear movement are shown in eq 2,[10] 3,[11] 4,[13] and 5.[7]

Although the formulation shown in eq 3 has not been challenged until now, alternative interpretations have been previously presented for the other cases. For example, as alternatives to the mechanisms shown in eq 2 and 4 the following equations involving $\sigma-\pi$ conjugation of either a C–C bond[5c,12] or a C–metal bond[6a,c] have been proposed.

$$Y{-}CR_2X \xrightarrow{k_8} \left[Y{-}\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}{\cdots}X^{\delta-} \right]^{\ddagger} \longrightarrow Y{-}C{\overset{R}{\underset{R}{\big\langle}}} \quad (8)$$
III
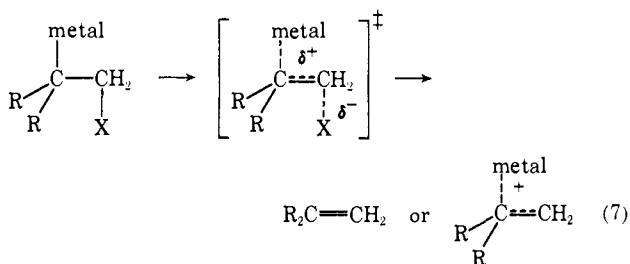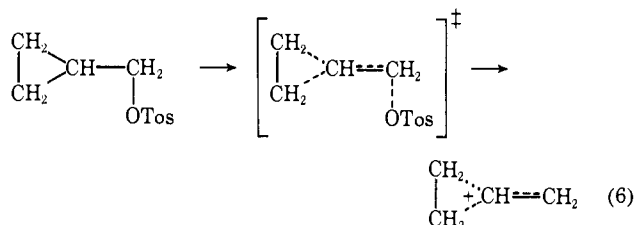
Such conjugation does not require either changes in the C–C bond length or the C–metal bond length or any movement of the stabilizing group toward the positive center.[14]

One way of deciding whether a group acts to stabilize a positive charge by ND_I or by $\sigma-\pi$ conjugation is to study the effect of that group in a vertical, i.e., Franck–Condon[16] process. Such processes occur too rapidly to allow nuclear movements. Therefore the energy of a vertical process cannot be lowered by ND_I but can be lowered by all kinds of conjugation.

We report here the selection of a vertical process which places positive charge on carbon. We have studied the effect of various substituents on the energy of the vertical process in order to probe the nature of electron donation by these substituents.

Results

We are interested in the following reactions, each of which place positive charge on carbon.

The Vertical Process. One vertical process related to the carbonium ion forming reactions shown above is the gas-phase removal of an electron. It is well known that many of the same groups, Y, which accelerate the solvolysis of III also lower the ionization potentials of the related free radicals and olefins.[18,19]

$$Y{-}\overset{R}{\underset{R}{\dot{C}}}{\big\langle} \xrightarrow[\text{IP}_{11}]{-e^-} Y{-}\overset{R}{\underset{R}{\overset{+}{C}}}{\big\langle} \quad (11)$$

$$\overset{Y}{\underset{R}{\big\rangle}}C{=}C{\overset{R}{\underset{R}{\big\langle}}} \xrightarrow[\text{IP}_{12}]{-e^-} \overset{Y}{\underset{R}{\big\rangle}}\overset{+}{C}{-}\dot{C}{\overset{R}{\underset{R}{\big\langle}}} \quad (12)$$
V

Similarly Y groups which accelerate the rates of reactions 9 and 10 also lower the ionization potential.
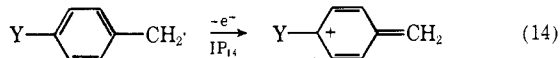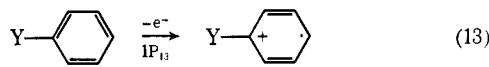
For our purpose it is especially interesting that these ionization potentials (eq 12, 13, and 14) correlate with σ^+ (i.e., with rates of reaction 9).[17] These quantitative

$$IP_{11} \cong -45\sigma^+ + \text{constant} \quad (15)^{20}$$

$$IP_{13} = -17.4\sigma^+ + \text{constant} \quad (16)^{19}$$

$$IP_{14} = -19\sigma^+ + \text{constant} \quad (17)^{21}$$

correlations suggest that ionization potentials can be used to distinguish stabilization involving ND_I from other types of stabilization.

We have chosen to study another vertical process, namely the charge transfer[22-24] between the donors IV

(7) (a) D. J. Cram, J. Amer. Chem. Soc., **86**, 3767 (1964); (b) D. J. Cram and J. A. Thompson, ibid., **89**, 6766 (1967).

(8) H. C. Brown and C. J. Kim, ibid., **90**, 2082 (1968).

(9) A. Diaz, I. Lazdins, and S. Winstein, ibid., **90**, 6546 (1968), and references quoted therein.

(10) K. L. Servis and J. D. Roberts, ibid., **87**, 1331 (1965).

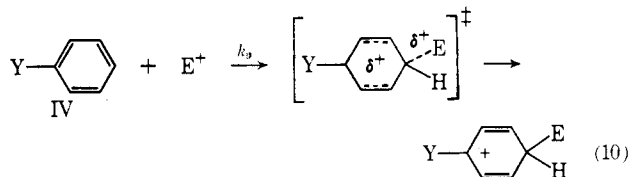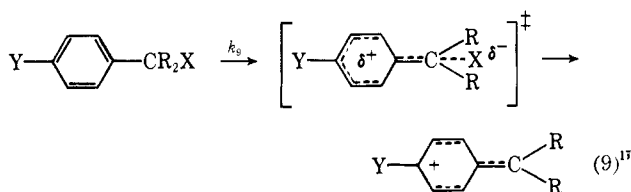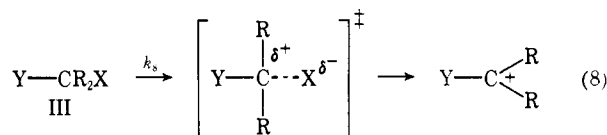(11) K. B. Wiberg and B. R. Lowry, ibid., **85**, 3190 (1963). See ref 12 for a summary of other studies.

(12) C. D. Gutsche and D. Redmore, Advan. Alicyclic Chem., Suppl., **1**, 6 (1968).
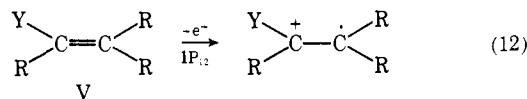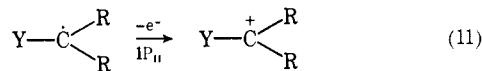
(13) W. Kitching, Organometal. Rev., **3**, 35 (1968).

(14) The term "$\sigma-\pi$ conjugation," synonymous with "hyperconjugation" is usually formulated as a true delocalization and is therefore subject to the Born–Oppenheimer approximation.[15]

(15) (a) R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Amer. Chem. Soc., **63**, 41 (1941); (b) M. J. S. Dewar, "Hyperconjugation," The Ronald Press, New York, N. Y., 1962, p 23.

(16) H. H. Jaffee and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 139.

(17) (a) H. C. Brown and Y. Okamoto, J. Amer. Chem. Soc., **80**, 4979 (1958); (b) L. M. Stock and H. C. Brown, Advan. Phys. Org. Chem., **1**, 35 (1963).

(18) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957; see also ref 11 for more recent references.
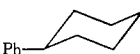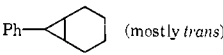
(19) (a) A. Streitwieser, Jr., Progr. Phys. Org. Chem., **1**, 1 (1963). This correlation does not include any potential neighboring groups as substituents; (b) p 28.

(20) R. W. Taft, R. H. Martin, and F. W. Lampe, J. Amer. Chem. Soc., **87**, 2490 (1965).

(21) A. G. Harrison, P. Kenarle, and F. P. Lossing, ibid., **83**, 777 (1961).

(22) S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matson, ibid., **75**, 2900 (1953).

Table I. Frequencies for Charge-Transfer Absorptions in Complexes of Tetracyanoethylene (TCNE) or Dichloromaleic Anhydride (DCMA) with Substituted Benzenes[c]

No.	π base	λ_{max}, mμ (TCNE)[a]	ν_{TCNE}, cm^{-1}	ν_{DCMA}[a]
1	PhH	387	25,800[b]	
2	Ph-t-Bu	415	24,100	
3	Ph-i-Pr	415	24,130	
4	Ph-Et	412	24,200	
5	Ph-Me	411	24,300[b]	33,560
6	PhNHCOCH$_3$	480	20,800	
7	PhOCH$_3$	507	19,700[b]	28,600
8	PhCH$_2$Cl	380	26,300	
9	PhCH$_2$Br	382	26,200	
10	PhCH$_2$OCH$_2$Ph	396	25,300	
11	PhCH$_2$CN	360	27,800	
12	PhCH$_2$Ph	410	24,400	
13	Ph$_3$CH	405	24,700	
14	PhCH$_2$SiMe$_3$	486	20,100	29,940
15	PhCH$_2$HgCH$_2$Ph	635	15,780	24,940
16	Ph⟨⟩	413	24,200	
17	PhOH	481	20,800	
18	PhCH=CH$_2$	480	20,800	
19	PhNMe$_2$	520	19,200	21,230
20	PhOPh	495	20,200	
21	Ph-Ph	498	20,100[b]	
22	PhCH$_2$CO$_2$Et	381	26,200	
23	PhCH$_2$NHCOCH$_3$	410	24,400	
24	PhCH$_2$SnMe$_3$			26,700
25	PhCH$_2$CH$_2$PbPh$_3$	396	25,200	
26	PhCH$_2$CHHgCHCH$_2$Ph (with CH$_3$ CH$_3$)	415	24,100	
27	Ph—⟨⟩ (mostly *trans*)	500	20,000	
28	Ph—◁	470	21,300	
29	PhCH$_2$PbPh$_3$	615	16,300	25,840

[a] The second, higher energy bands which are discernible in some cases are not reported here. They will be discussed in future publications. [b] Similar values were reported in ref 25a. [c] Solvent CH$_2$-Cl$_2$; temperature 25°.

or V and two standard acceptors, tetracyanoethylene (TCNE)[25] and dichloromaleic anhydride (DCMA). The easily measurable absorption frequencies of the charge-transfer complexes[23] are known to be directly related to the ionization potentials[22] of the respective donors. Equation 18, showing the absorption process, indicates that some positive charge is placed on the carbon α to the Y substituent.

$$\left[\text{Y—⟨⟩ acceptor} \right]_{complex} \xrightarrow{h\nu} \left[\text{Y—⟨+⟩ acceptor}^- \right]_{complex} \quad (18)$$
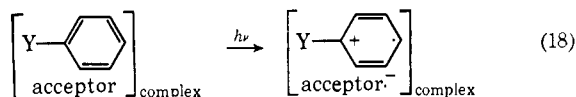
(23) (a) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964; (b) E. Kosower, *Progr. Phys. Org. Chem.*, 1, 81 (1963); (c) G. Briegleb, "Elektronen-Donator Acceptor-Komplexe," Springer-Verlag, Berlin, Germany, 1961.

(24) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, 79, 4839 (1957), have concluded that geometry of charge-transfer complexes (*i.e.*, steric effects) do not greatly affect the frequency of the CT absorption. We are also assuming that neither donor nor acceptor is distorted in the complex.

(25) (a) R. E. Merrifield and W. D. Phillips, *ibid.*, 80, 2778 (1958); (b) E. M. Voight and C. Reid, *ibid.*, 86, 3930 (1964).
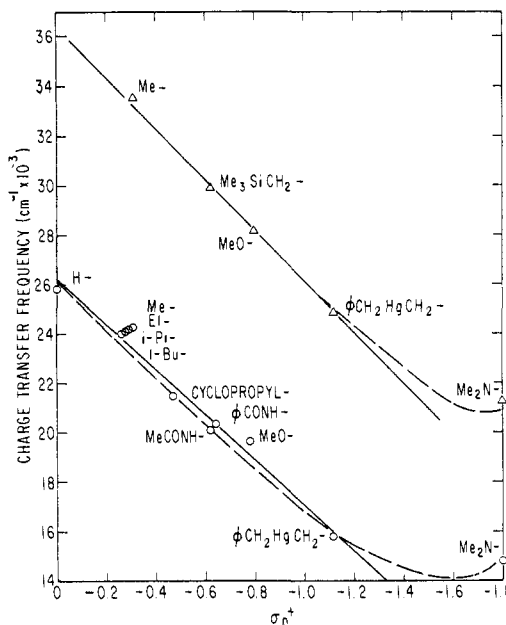
Figure 1. Plots of charge-transfer frequencies of YC$_6$H$_5$-acceptor complexes against σ_p^+ of Y. Identity of Y is shown adjacent to each point: △, acceptor–dichloromaleic anhydride; ○, acceptor–tetracyanoethylene; —, best linear correlations; ---, correlation including ground-state bonding using equations discussed in ref 23a,b.

Table I lists the charge-transfer frequencies of a variety of monosubstituted benzenes complexed with TCNE or with DCMA.

Plots of the charge-transfer frequencies with both acceptors against σ_p^+ for the groups, Y, which stabilize positively charged carbon by inductive or resonance effects are shown in Figure 1. It can be seen that the frequencies correlate satisfactorily, although not perfectly, with σ_p^+.[26] The best lines for each plot determine eq 19 and 20.

$$\nu_{TCNE} = (9300\sigma^+ + 26,200) \pm 500 \text{ cm}^{-1} \quad (19)$$

$$\nu_{DCMA} = (10,400\sigma^+ + 36,400) \pm 600 \text{ cm}^{-1} \quad (20)$$

Limitations of Hammett Relationships for Charge-Transfer Frequencies. We have plotted the frequencies of charge-transfer absorptions against σ_{para}^+ for monosubstituted benzenes. The validity of such a plot depends on the assumption that the orbital from which the electron is removed by charge transfer has the same symmetry as the orbital which participates in *para* attack of reaction 10. This assumption fails in the following instances.

(1) When Y is an electron-withdrawing substituent.[27a,b] Energy levels of the highest filled orbitals of monosubstituted benzenes, shown below, illustrate why this is so. Although *para* electrophilic attack always involves ψ_3 regardless of the nature of Y, the electron will be removed from ψ_3 by charge transfer only when Y is an electron-donating substituent.[27a]

(26) D. N. Kravtsov and B. A. Faingor, *Izv. Akad. Nauk SSSR*, 289 (1968), have reported a correlation between σ^+ and frequencies of charge transfer between *sym*-trinitrobenzene and *para*-substituted dimethylanilines.

(27) (a) Actually C$_6$H$_5$CN and C$_6$H$_5$CF$_3$ give charge-transfer frequencies which are only 1400 cm^{-1} less than those predicted from eq 19. (b) This does not apply to the dimethylanilines of Kravtsov and Faingor[26] and they did treat electron-withdrawing substituents. However, their ρ slope is much lower than ours making their method less sensitive.

electron-donating Y   electron-withdrawing Y^{27b}
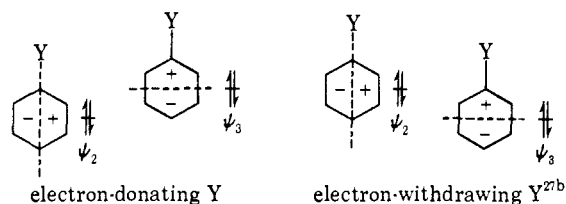
(2) When the ionization potential of an aliphatic analog R–Y is equal to or lower than that of benzene. The ionization of Y–Ph is then likely to involve an electron from Y itself or from the Y–C σ bond. In either case the π electrons (*i.e.*, ψ_2 and ψ_3) of the benzene ring may not be strongly involved in the ionization. Substituents which must be excluded for this reason are Y = C_6H_5O-, α-naphthyl, p-anisyl, CH_3S-, I–, etc.

In summary, the ionization potentials or charge-transfer frequencies may be treated by a Hammett equation when Y causes only a small perturbation on the benzene ring. In other words the substituent must not severely alter the symmetry of the π orbitals.

Although charge-transfer frequencies are much easier to measure than are the ionization potentials themselves, they sometimes are not accurate measures of the ionization potentials. Then the charge-transfer frequencies are not useful for our purposes. The only situation in which this inaccuracy occurs is when there is strong bonding between the donor and acceptor in the ground state.[23,24] The excitation process then removes an electron from this bond rather than from the "free" donor. Fortunately, the only aromatic donors which bond to TCNE or DCMA in this way are alkylanilines and other C_6H_5Y in which σ_Y^+ is more negative than -1.4.[23] We have accordingly restricted our study to substituents having values of σ_Y^+ between 0 and -1.4.

The similarity of the slopes in Figure 1 for the two different acceptors and the proportionality of ν to ionization potentials[23] indicate that the treatment is reasonably accurate within the limitations stated above. Furthermore, when the units of eq 19 are converted to kcal/mole the slope becomes -19. This slope com-

$$\nu_{PhH} - \nu_{PhY} = \Delta\Delta F_{H\to Y} = -19\sigma^+ RT \quad (21)$$

pares to -19.1 for ionization potentials of benzyl radicals,[21] -6 for solvolyses of benzyl halides,[6a] -17.4 for ionization potentials of substituted benzenes,[19] and $+13.4$ for charge-transfer spectra in substituted N-ethylpyridinium iodides.[5d] The charge-transfer energies appear to be very sensitive to substituent effects.

Discussion

Vertical and Nonvertical Stabilization. We conceive two limiting types of transition-state stabilization by groups attached to positively charged carbon (see eq 1). We shall say that the substituent Y provides "vertical stabilization" if Y does not change its geometry or its distance from the positively charged carbon as the transition state is approached. Groups which should fall into this category are those known to act by resonance or inductive effects such as Y = CH_3O-, CH_3- CONH–, $(CH_3)_2N-$, CH_3-, CH_3CH_2-, etc. The reason for this may be seen in the carbon–oxygen overlap integrals calculated at single and double bond distances for the cation $CH_3O^+CH_2$.[28,29] The overlap integrals,

which are closely related to bond strengths, differ by only about thirty per cent and indicate that most of the stabilization of Y–C$^+H_2$ by Y = CH_3O may be achieved without change in the O–CH_2 bond length.

We shall say there is "nonvertical stabilization" if the substituent Y changes its geometry or its distance from the reaction site as the transition state is approached. Substituents which can be placed in this category are the known nucleophilic groups such as Y = $^-OCH_2-$, $C_2H_5SCH_2-$, $^-O_2CCH_2-$, $CH_3CONHCH_2-$, etc. Considerations of overlap integrals between these groups and the reaction site reveal almost negligible interaction. This indicates that ND_I stabilization requires some movement of the nucleophilic group.
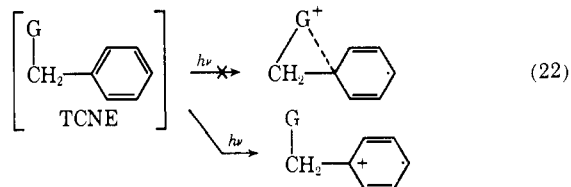
In cases where G of I is a metal (*e.g.*, eq 4) or has no unshared pairs (*e.g.*, eq 2 and 3) or when the internal nucleophile is constrained to be close to the reaction site as in VI,[9] the stabilization could be vertical or nonver-

VI
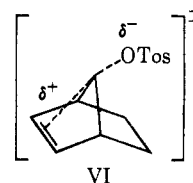
tical. In these cases no *a priori* decisions can be made with confidence and we must devise tests for vertical stabilization to make such decisions.

Tests for Vertical Stabilization. We are unable to conceive a method of directly testing reactions to see whether a group, Y, actually does accelerate solvolysis by vertical stabilization. However, we can determine whether such a group is *capable* of vertical stabilization by determining its effect on a known vertical process as we have described. If the group displays vertical stabilization in one process we then infer that it probably displays the vertical stabilization to a similar extent in another process which places positive charge in the same position[30a] (*e.g.*, compare reaction 8 with reaction 11).

Our results show that ND_I groups do not display any of their stabilizing influences on vertical processes (charge-transfer spectra).[30b] In contrast, substituents

$$\left[\begin{array}{c} G \\ | \\ CH_2- \end{array} \bigcirc \right] \xrightarrow[]{h\nu} \nrightarrow \begin{array}{c} G^+ \\ / \\ CH_2- \end{array} \bigcirc \qquad (22)$$
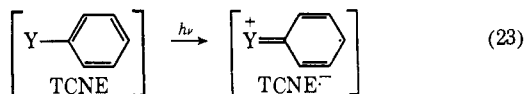
which accelerate solvolyses by resonance or inductive effects have large effects on charge-transfer spectra (Figure 1).

(28) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 15; (b) p 105; (c) p 50.
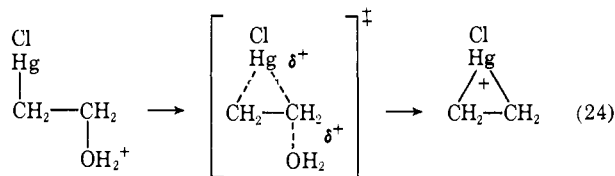
(29) S. Ehrenson, *Progr. Phys. Org. Chem.*, 2, 195 (1964).

(30) (a) This conclusion may not be entirely justified because some unknown cause may be responsible for the apparent correlation. In any case the large effect of Y upon charge-transfer spectra must be explained without invoking the nuclear movements which are usually postulated for some of the substituents discussed here. (b) We have previously concluded that neighboring (ND₁) groups do not accelerate solvolysis of benzyl chloride because p-$C_2H_5SCH_2C_6H_4CH_2Cl$ solvolyzes at about the same rate as benzyl chloride.[6a] (c) We have noted[6a] that strongly electron-donating groups show σ^+ behavior even in reaction 8. That is $^1/_{2.1} \log (k_Y/k_H)_8 \cong \log (k_Y/k_H)_9 = \rho\sigma^+$. ND₁ groups were excluded.

$$\left[Y\!\!-\!\!\!\bigcirc \atop TCNE \right] \xrightarrow{h\nu} \left[\overset{+}{Y}\!\!=\!\!\!\bigcirc \atop TCNE^{-} \right] \qquad (23)$$
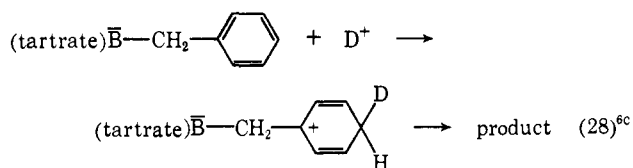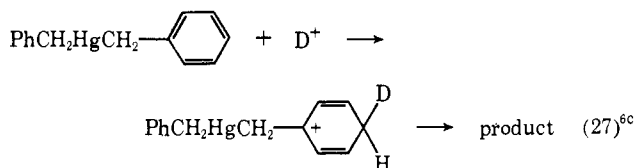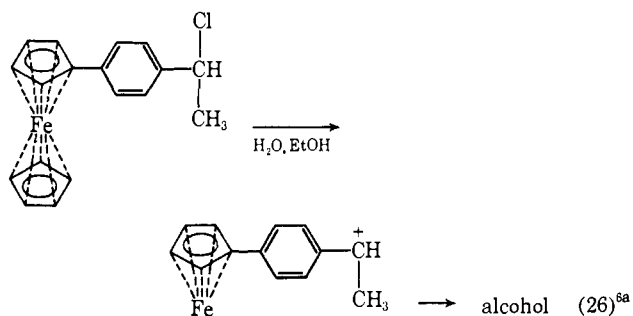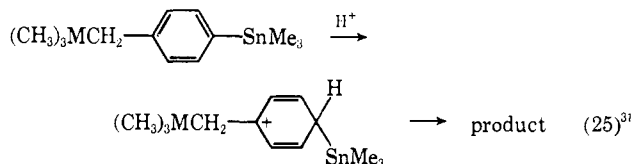
The capability of Y in stabilizing positively charged transition states is measured by the well-known linear free-energy (Hammett) relationships based on eq 8,[30c] 9, or 10. The Hammett relationships for charge-transfer spectra (eq 19 and 20) are used to measure the capability of Y in stabilizing the charge-transfer excited states. If σ_Y^+ obtained from reactions is the same as that obtained from charge-transfer spectra, then we conclude that ND_I does not occur in the reactions.

Carbon–Metal σ–π Conjugation. There are many instances in which apparent carbonium ion formation is accelerated by a neighboring carbon–metal bond (Y = CH_2MR_n in eq 8). These reactions are usually formulated[13] as internal displacement processes illustrated

$$\begin{array}{c} Cl \\ | \\ Hg \\ | \\ CH_2\!-\!CH_2 \\ | \\ OH_2^+ \end{array} \longrightarrow \left[\begin{array}{c} Cl \\ | \\ Hg \;\; \delta^+ \\ \diagup \;\;\diagdown \\ CH_2\!-\!CH_2 \\ \diagdown \;\; \delta^+ \\ OH_2 \end{array} \right]^+ \longrightarrow \begin{array}{c} Cl \\ | \\ Hg \\ \diagup^+\!\diagdown \\ CH_2\!-\!CH_2 \end{array} \quad (24)$$

by eq 24. Recently several such metal groups have been shown to have strong electron-donating power in the *para* position of a benzene ring.

$$(CH_3)_3MCH_2\!-\!\!\bigcirc\!\!-\!SnMe_3 \xrightarrow{H^+}$$

$$(CH_3)_3MCH_2\!-\!\!\overset{H}{\underset{SnMe_3}{\bigcirc^+}} \longrightarrow \text{product} \quad (25)^{31}$$

(structure ferrocene-CH(CH_3)Cl) $\xrightarrow{H_2O,\,EtOH}$

(structure ferrocene-CH$^+$CH_3) $\longrightarrow$ alcohol $(26)^{6a}$

$$PhCH_2HgCH_2\!-\!\!\bigcirc + D^+ \longrightarrow$$

$$PhCH_2HgCH_2\!-\!\!\overset{D}{\underset{H}{\bigcirc^+}} \longrightarrow \text{product} \quad (27)^{6c}$$

$$(tartrate)\bar{B}\!-\!CH_2\!-\!\!\bigcirc + D^+ \longrightarrow$$

$$(tartrate)\bar{B}\!-\!CH_2\!-\!\!\overset{D}{\underset{H}{\bigcirc^+}} \longrightarrow \text{product} \quad (28)^{6c}$$
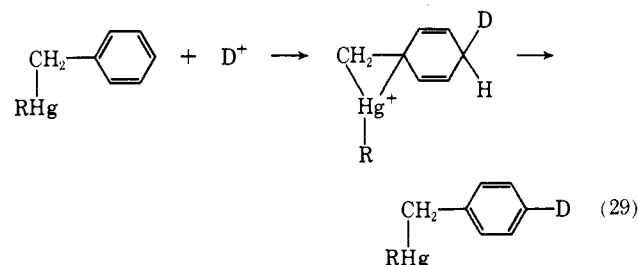
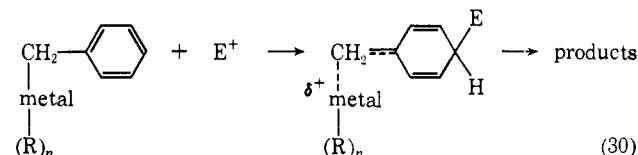Cais[32] has suggested that acceleration of reaction 26 results from nucleophilic participation by the iron atom

(31) C. Eaborn, *J. Chem. Soc.* 4858 (1956).
(32) M. Cais, *Organometal. Rev.*, 1, 435 (1966).

and, by analogy to reaction 24, reaction 27 could have been formulated as follows. We have suggested[6a,b]

$$CH_2\!-\!\!\bigcirc + D^+ \longrightarrow CH_2\!-\!\!\overset{D}{\underset{\overset{|}{\underset{R}{Hg^+}}}{\bigcirc\!\!\diagdown\!H}} \longrightarrow$$

$$CH_2\!-\!\!\bigcirc\!\!-\!D \quad (29)$$
$$\quad\quad\quad | \atop RHg$$

that the major driving force for *all* these processes is carbon–metal σ–π conjugation[33] (a vertical process) like Mulliken's[15a,b] C–H hyperconjugation.

$$CH_2\!-\!\!\bigcirc + E^+ \longrightarrow CH_2\!\!=\!\!\overset{E}{\underset{\overset{\delta^+}{\underset{(R)_n}{metal}}}{\bigcirc\!\!\diagdown\!H}} \longrightarrow \text{products}$$
$$\quad | \atop metal \atop | \atop (R)_n \qquad\qquad\qquad\qquad\qquad (30)$$

We can now determine whether the cation stabilizations provided by Y = –CH_2–metal in reactions such as 25, 27, and 28 are detectable in our vertical process and imply whether they are vertical (eq 30) or nonvertical (eq 29) stabilizations in the reactions in question. Comparison of the σ_p^+ values of certain metallic groups on the benzene ring as determined by charge-transfer spectra with σ_p^+ values obtained from reactions 25 and 27 is presented in Table II. We see that the ability of

Table II. Values of σ_p^+ for Various Groups Y on Benzenes as Determined by Reaction Rates and by Charge-Transfer Spectra

Group Y	σ^+ (from reactions)	σ^+ (from CT)
H–	0	−0.03
CH_3O–	−0.778[c]	−0.74[a] (−0.75[b])
CH_3CONH–	−0.58[h]	−0.60[a]
(CH_3)_3SiCH_2–	−0.61[d,i]	−0.66[a] (−0.63[b])
(CH_3)_3SnCH_2–	−0.76[e]	−0.9[b]
CH_3CH_2–	−0.295[c]	−0.25[b]
Ph_3PbCH_2–		−1.08[a]
Ph_3PbCH_2CH_2–	∼(−0.3)[g]	−0.22[a]
PhCH_2HgCH_2–	−1.11[f]	−1.12[a,b]
PhCH_2CHHgCHCH_2–∼(−0.3)[g]		−0.25[a]
$\quad$ CH_3 CH_3		

[a] From eq 19. [b] From eq 20. [c] Reference 17. [d] Calculated from data in ref 34. [e] Calculated from data in R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., New York, N. Y., 1965, p 287. [f] Reference 6c. [g] Assumed to be about like ethyl based upon slight differences in CT of alkylbenzenes. [h] Reference 6a. [i] R. W. Taft, E. Price, E. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 85, 3146 (1963), reported σ_R° of (CH_3)_3SiCH_2 to be about like that of a methyl group as determined by ^{19}F chemical shifts. However, the reported σ_R° does not agree with that determined from reactions;[35] R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 556.

(33) (a) A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, 59, 707 (1948); (b) C. Eaborn[31] suggested the possibility of C–Si σ–π conjugation in ArCH_2SiMe_3, but the Me_3SiCH_2–group has more recently been treated as an inductive group.[34-36]
(34) R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometal. Chem.*, 2, 154 (1964).
(35) D. R. M. Walton, *ibid.*, 3, 438 (1965).
(36) (a) H. Bock and H. Alt, *Angew. Chem. Intern. Ed. Engl.*, 6, 942 (1967); (b) H. Bock, H. Alt, and H. Seidl, *J. Amer. Chem. Soc.*, 91, 355 (1969).

these metallic groups to donate electrons in nonvertical processes is mirrored exactly in a vertical process.

It now remains to determine whether the observed vertical stabilization is due to an inductive effect as has been suggested[34-36] or to conjugative effect.[6a,33] We can distinguish these effects by "insulating" the R_3MCH_2- (e.g., Ph_3PbCH_2-) from the ring with another CH_2 group. Insertion of a methylene group between a substituent and the benzene ring ($YCH_2C_6H_5$) destroys the conjugative effect of Y. If the effect on Y–Ph for Y = Ph_3PbCH_2- were conjugative and the inductive effect of Ph_3Pb were about like that of an alkyl group then the σ^+ of Ph_3PbCH_2- should be like those of other alkyls, ~-0.25 on the charge-transfer plot, Figure 1. On the other hand, the same change from Y–Ph to Y–CH_2Ph should merely reduce an inductive effect by a factor of 2.8. The σ^+ of Ph_3PbCH_2- is -0.83 greater in that of CH_3-. This exaltation should drop to $-0.83/2.8 = -0.3$ greater than CH_3- or a total of -0.55 for $Ph_3PbCH_2CH_2-$. We observe that σ^+ values of both $Ph_3PbCH_2CH_2-$ and $Ph-CH_2CHHgCHCH_2-$

$$\overset{|}{CH_3} \quad \overset{|}{CH_3}$$
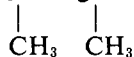
are about -0.25 and conclude that the large electron-donating effects of Y = R_nMCH_2- (in charge transfer) are conjugative.

The charge–transfer process can therefore be formulated as in eq 31 in which no change in geometry occurs.


(31)
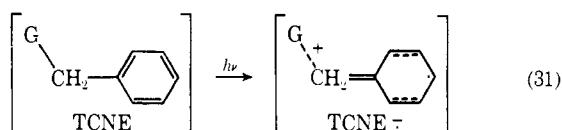
By analogy, we conclude that reactions 25, 27, and 28 should also be formulated as $\sigma-\pi$ conjugation (reaction 30). The extensive implications of carbon–metal $\sigma-\pi$ conjugation in organometallic chemistry and the stereochemical and other structural properties of this conjugative effect will be discussed fully in subsequent papers.
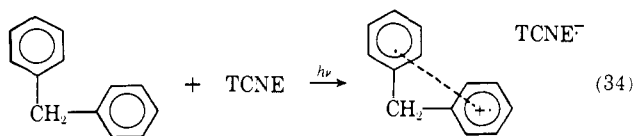
Phenyl Participation. Both the proposals that a



(32)
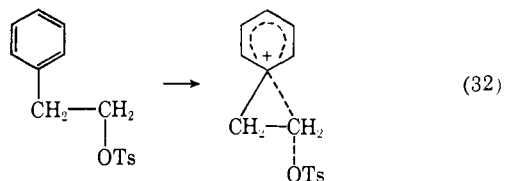
phenyl group migrates (eq 32) and does not migrate (eq

(33)
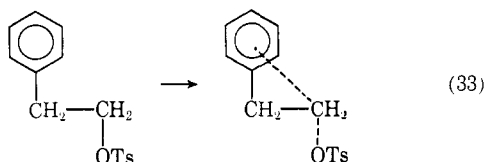
33) during solvolyses of various β-phenethyl tosylates have been defended recently.[7-9] Equation 33 corresponds to a vertical stabilization and should therefore be related to a π-cloud stabilization of the benzene cation.[5b]

(34)

We are unable to detect vertical stabilization in the TCNE complex of diphenylmethane or triphenylmethane.

However, Cram and Bauer[37] have studied the charge-transfer spectra of VII and VIII and have shown that as

VII

VIII
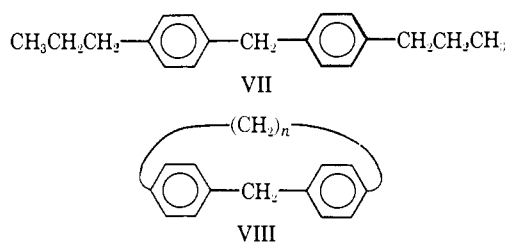
n decreases, bringing the phenyl rings closer, the charge-transfer frequency decreases.[38,39] This indicates that the π-cloud interaction shown in reactions 33 and 34 is possible when the two phenyl rings are forced into close proximity. In an open system, such an interaction would appear to require some movement of the phenyl rings. We therefore tentatively suggest that the acceleration provided by the phenyl group in the solvolysis of 2-phenethyl tosylate is nonvertical.[40,41]

Delocalization of Strained σ Bonds. (C–C Hyperconjugation). The solvolyses of carbon compounds having a strained ring attached to the site of substitution are greatly accelerated when compared to unstrained systems as shown by a few examples in Table III.

Table III[a]

Structure	Relative rate constants
	(1)
	>500
	8
	7×10^6 [b]
	200[c]

[a] Abstracted from ref 2. [b] W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 1014 (1968). [c] K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963).

There has been disagreement as to the nature of this acceleration; the possibilities of carbon migration at the transition state and of simple delocalization have been proposed. It is now generally agreed that the cyclopropyl group stabilizes the transition state without

products (35)
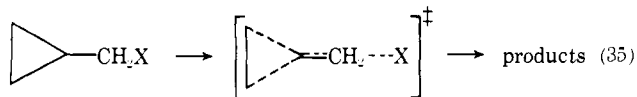
(37) D. J. Cram and R. H. Bauer, *J. Amer. Chem. Soc.*, 81, 5971 (1959).
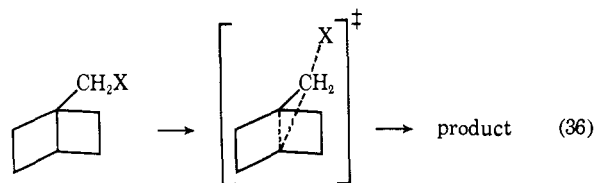
(38) Part of this change in charge-transfer frequency may arise from the strain introduced in the benzene rings.

(39) E. M. Layton, Jr., *J. Mol. Spectrosc.*, 5, 181 (1960).

(40) The use of charge-transfer spectra to test for vertical stabilizations giving large accelerations (>10³ acceleration in reaction 8) is quite definitive. However, our conclusions concerning the small effect of a β-phenyl group are admittedly suggestive rather than conclusive. See ref 5b for clarification of this point.

(41) See ref 39 for uv data which can be interpreted similarly.

migration whereas migration is generally assumed[42,43] for the bicyclic systems of Table III.

$$\text{(structure with } CH_2X \text{)} \rightarrow \left[\text{(bicyclic structure with } CH_2 \text{ and } X) \right]^{\ddagger} \rightarrow \text{product} \quad (36)$$

Because eq 35 represents a vertical stabilization and eq 36 (or 3) a nonvertical one, we are able to decide between these two kinds of formulations by using the charge-transfer criterion. For example, the rate of solvolysis of p-cyclopropylcumyl chloride reveals a σ_p^+ value of -0.46.[44] The charge-transfer spectrum with TCNE (Table I) gives a σ_p^+ of -0.52. This corroborates the vertical nature of the electron supply by the cyclopropyl group.[45] The observation that the 7-norcaryl group has a charge transfer $\sigma^+ = -0.68$ agrees with the observed effect of alkyl substitutions on the rates of solvolysis of cyclopropylcarbinyl compounds.[46]

A study of the charge-transfer spectra of other phenyl-substituted strained systems is in progress. Preliminary observations comparing the charge-transfer frequencies of the complex of TCNE with the olefins IX, X, and XI indicate that the 2,1,1-bicyclohexyl group

IX (ν 28,600 cm^{-1})   X (ν 25,200 cm^{-1})   XI (ν 20,900 cm^{-1})
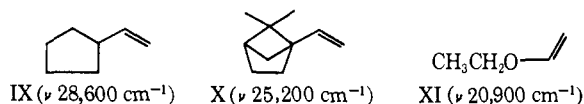
shows vertical stabilization of cations as pictured in XII and XIII. The formulations XII and XIII are sim-

XII   TCNE$^{-\cdot}$ XIII
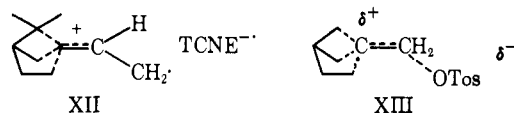
ilar to that for vertical cyclopropyl stabilization and are very different from the ring-expansion formulations illustrated by reaction 36.

Further studies will determine whether it is necessary to invoke ring expansion as a driving force for any of the reactions of Table III. It is our intention to use the correlations provided by ionization potentials and charge-transfer spectra of model unsaturated compounds in order to investigate other reactions for which rate-limiting skeletal changes have been suggested.[3,4]

Nonvertical Nature of the Baker–Nathan Effects. The observations that substituents $Y = -AH_n$ are more electron donating than $Y = -A(CH_3)_n$ in aromatic reactions such as 9 or 10 (Baker–Nathan effect) is often attributed to A–H hyperconjugation. In such reactions σ_p^+ is -0.78 for CH_3O and -0.92 for OH. However we find from charge-transfer spectra that σ_p^+ for CH_3O is -0.75 and σ_p^+ for OH is -0.58. The latter is almost identical with σ_p^+ for OH of -0.60 obtained from gaseous ionization potentials.[19a]

We suggest that the exalted value of σ^+ for OH observed in solution is due to a nonvertical process. Such a process is shown in eq 37 where the solvent rear-

$$(CH_3)_3Si \text{---} \bigcirc \text{---} OH \; + \; H^+ \; \longrightarrow$$

$$(37)^{31}$$
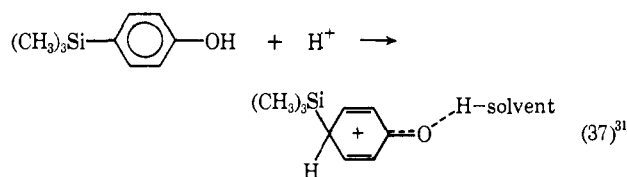
ranges (moves) so as to bond more strongly to the OH as the transition state is approached. A similar suggestion was made by Eaborn.[31]

A second and more common example of the Baker–Nathan effect is the observed series $Y = CH_3- > C_2H_5- > (CH_3)_3C-$ in reactions 10 and 11. As an alternative to the hyperconjugation hypothesis, some authors[47–49] have suggested that the size of the alkyl group affects the solvation energies of both the reactant and the transition state. Both ionization potentials[18,47b] and charge-transfer spectra (Figure 1) give the reverse of the Baker–Nathan order and suggest that some nonvertical solvent effect accounts for the Baker–Nathan order.

Only one example of a large separation in the Baker–Nathan order has been reported.[50] This might be attributed to nonvertical hydrogen bonding[51] similar to that of eq 37, viz.[51a]

Experimental Section

(42) See Table III, footnote b.
(43) See Table III, footnote c.
(44) R. C. Hahn, T. F. Corbin, and H. Schechter, J. Amer. Chem. Soc., 90, 3404 (1968).
(45) E. M. Kosower and M. Ito, Proc. Chem. Soc., 25 (1962), reached somewhat similar although less quantitative conclusions from the uv spectra of cyclopropyl ketones. See ref 5c for a cogent summary of cyclopropyl group effects.
(46) P. R. Schleyer and G. W. Van Dine, J. Amer. Chem. Soc., 88, 2321 (1966).

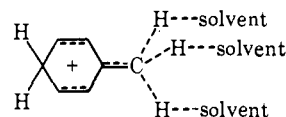(47) (a) W. M. Schubert, J. M. Craven, R. G. Minton, and R. B. Murphy, Tetrahedron, 194 (1959); (b) W. M. Schubert and D. F. Gurka, J. Amer. Chem. Soc., 91, 1443 (1969).
(48) R. A. Clement and J. N. Naghizadeh, ibid., 81, 3154 (1959).
(49) A. Himoe and L. M. Stock, ibid., 91, 1452 (1969).
(50) E. M. Arnett and J. W. Larsen, ibid., 91, 1438 (1969).
(51) V. J. Shiner, Jr. and C. J. Verbanic, ibid., 79, 369, 373 (1957).
(51a) NOTE ADDED IN PROOF. F. R. Jensen and B. Smart, J. Amer. Chem. Soc., 91, 5687 (1969), have applied the method of ref 6a to the strained system, 1-norbornylbenzene, and have reached the same conclusions as those presented here and in ref 6a and 6c.
(52) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1964, p 256.
(53) J. B. Pedley and H. A. Skinner, Trans. Faraday Soc., 55, 544 (1959).
(54) (a) "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Co., Cleveland, Ohio, 1965, p C665; (b) L. C. Willemsens and G. J. M. van der Kerk, "Investigations in the Field of Organolead Chemistry," International Lead Zinc Research Organization, Inc., 1965, p 95.

turnings (0.38 g, 0.016 mol), and 10 ml of anhydrous ether by combining all three components and starting the reaction with a small amount of MeMgI in ether. After refluxing for 1 hr under Ar, the solution was filtered under Ar, added dropwise to a mixture of triphenyllead chloride (Alfa Inorganics) (5.0 g, 0.011 mol), and refluxed under Ar for 2 hr. Hydrolysis with 20% ammonium chloride followed by ether extraction, drying over magnesium sulfate, and evaporation of the solvent yielded pale yellow crystals which were recrystallized from ethanol: yield, 3.3 g (55%) white crystals, mp 114.5–116°. Nmr and ir spectra are consistent with the structure $Ph_3PbCH_2CH_2Ph$.

Anal. Calcd for $C_{26}H_{24}Pb$: C, 57.44; H, 4.45. Found: C, 57.43; H, 4.53.

Anisole (7) (bp 152–153° (760 mm)) and benzyltrimethylsilane (14) (bp 95° (35 mm)) were distilled before use.

Both phenylcyclopropane (bp 86–87° (4 mm), $n^{25}D$ 1.5304, lit.[56a]

bp 174° (760 mm), $n^{20}D$ 1.5316) and 7-phenylnorcarane (bp 141° (14 mm), $n^{25}D$ 1.5452, lit.[57] no properties recorded) were prepared by the pyrazalone method of Kishner.[56b] Both were chromatographed on Matheson Coleman and Bell alumina using methylene chloride immediately before use. Neither decolorized potassium permanganate.

The 1-vinyl-5,5-dimethylbicyclo[2.1.1]hexane (XI) supplied by Professor Hammond[58] was purified by gas–liquid chromatography before use. Vinylcyclopentane (X) and ethyl vinyl ether (XII) were from Aldrich.

(55) E. A. Zollner, *Iowa State Coll. J. Sci.*, **9**, 213 (1934).
(56) (a) D. Davidson and J. Feldman, *J. Amer. Chem. Soc.*, **66**, 488 (1944); (b) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **45**, 949 (1913), [*Chem. Abstr.*, **7**, 3964 (1913)].

(57) G. L. Closs and L. E. Closs, *Tetrahedron Lett.*, 26 (1960).
(58) R. S. H. Liu and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 1892 (1964).

Deoxygenation by Atomic Carbon. II. The Generation of Carbenes from the Reaction of Carbonyl Compounds with Metastable Singlet State Carbon Atoms[1]

Philip S. Skell and James H. Plonka[2]

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received July 18, 1969

Abstract: Carbon atoms produced in a low-intensity carbon arc under high vacuum react with ketones and aldehydes at −196° to produce carbenes and carbon monoxide. The distribution of the intramolecular rearrangement products is the same as from tosyl hydrazone derived carbenes.

The large value of the bond strength of carbon monoxide (256.7 kcal/mol)[3] suggests that the reaction of carbon atoms with oxygen containing compounds to form carbon monoxide should be a thermodynamically favorable process. Atomic carbon produced by nuclear transformation has been reported[4,5] to give carbon monoxide on reaction with oxygen, ethylene oxide, and carbon dioxide.

We have reported[1] that carbon atoms from a low-intensity arc are efficient deoxygenating agents: acetone reacts with carbon atoms on codeposition at a liquid nitrogen cooled surface to produce propylene and carbon monoxide as the major products. This process is calculated to be exothermic by 85–100 kcal/mol on

$$CH_3\overset{O}{\underset{\|}{C}}CH_3 + C \xrightarrow[-196°]{} CH_3\ddot{C}CH_3 + CO$$
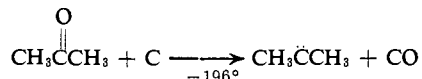
the basis of bond strengths.[1]

Results and Discussion

A. The Deoxygenation Process. Simultaneous deposition at a liquid nitrogen cooled surface of aldehydes

and ketones with carbon vapor results in extensive formation of carbon monoxide and hydrocarbons (olefins and cyclopropanes) characteristic of the corresponding carbene. This process has been named deoxygenation.
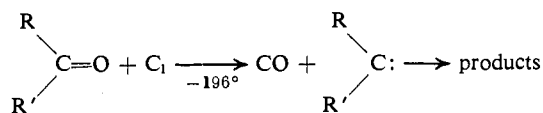
Several quantitative predictions concerning the deoxygenation of ketones and aldehydes can be made.

(1) The amount of carbene-derived products should equal the amount of carbon monoxide produced.

(2) In an experiment employing ^{14}C-enriched carbon vapor, the carbene derived products should be radioinactive, while the carbon monoxide should be radioactive.

(3) If no competitive pathways for carbon monoxide production are operative, it should have a relative molar activity of unity. The observation of such a value would eliminate a photochemical decomposition caused by light emission from the arc.

Table I demonstrates the correspondence of carbon monoxide yields with the yields of carbene derived products for the deoxygenations of acetone and 2-butanone. The observation of such a close correlation

(1) A preliminary communication has appeared: P. S. Skell, J. H. Plonka, and R. R. Engel, *J. Am. Chem. Soc.*, **89**, 1748 (1967).
(2) National Institutes of Health Predoctoral Fellow, 1967–1970.
(3) A. E. Douglass, *J. Phys. Chem.*, **59**, 109 (1955).
(4) C. MacKay and R. Wolfgang, *Radiochim. Acta*, **1**, 42 (1962).
(5) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965).