in conductance were monitored by a conductance amplifier, constructed by using metal-film resistors to provide more stable readings when ambient temperatures varied overnight during long kinetic runs. The amplifier was connected to a SOLARTRON 7151 computing multimeter, which collected and stored readings at set times. Extensive use of ultrasonics was made prior to all of the kinetic runs to try to ensure that molecular aggregates were broken up.

The kinetic run by high-performance liquid chromatography (reversed phase) was carried out by direct analysis of reaction solutions using the equipment and the method described earlier,[17] in which the disappearance of starting material and appearance of product were monitored simultaneously. The chromatography column (15 cm × $^1/_4$ in.) was packed with 5-$\mu$m SPHERISORB ODS2, and results were obtained by eluting with 90% (v/v) methanol/water (flow rate 1 mL/min, $\lambda$ = 263 nm, volume of sample injected 15.0 $\mu$L).

**Products.** The diode-array system was an LKB rapid spectral detector Model 2140 (with the LKB 2140-202 Wavescan software package for the IBM PC), connected to the LDC HPLC system described earlier.[48] Some solutions were studied at a single wavelength ($\lambda$ = 263 nm) directly after conductometric rate measurements ($<10^{-3}$ M) had been completed, but for others, separate measurements in sealed ampules were made (ca. $2 \times 10^{-3}$ M).

**Calculations.** MINDO/3[23a] and MM2[27] calculations were carried out by standard methods.

**Acknowledgment.** We are grateful to G. Llewellyn for technical assistance with the kinetic studies, to D. S. Jones for improving the temperature stability of the conductance amplifier, to M. S. Garley for providing computer control for the 7151 computing multimeter, and to M. Bremer (Erlangen) for the MINDO/3 calculations. We also thank SERC for financial support for HPLC equipment (T.W.B.) and the British Council for a Senior Fellowship (H.M.). The work at Erlangen and Lübeck was supported by the Fonds der Chemischen Industrie.

**Registry No.** **6** (X = OTs), 15587-83-4; **6** (X = OH), 15231-50-2; **6** (ketone), 4541-35-9; **11a**, 79816-89-0; **11b**, 114583-33-4; **12**, 6651-34-9; **13** (X = OTs), 114583-27-6; **13** (X = OH), 114583-32-3; **13** (ketone), 114583-39-0; **14**, 114583-34-5; **15**, 114583-35-6; **16** (X = OTs), 114583-28-7; **16** (X = OH), 114583-36-7; **16** (ketone), 114583-40-3; **17**, 114583-37-8; **18** (X = OTs), 114583-29-8; **18** (X = OH), 114583-38-9; **18** (ketone), 81396-36-3; **19**, 65378-75-8; **20**, 114583-30-1; **21**, 4249-12-1; **22**, 4087-50-7; **23**, 103647-19-4.

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# Gas-Phase Basicity of Olefinic $C_5$ and $C_6$ Carbonyl Compounds

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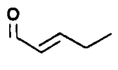
*Received November 5, 1987*

Determination of gas-phase basicity of olefinic $C_5$ aldehydes or acids and $C_6$ ketones is made from the measurement of proton transfer equilibrium constants in ion cyclotron resonance experiments. The values, lying between 800 and 850 kJ mol$^{-1}$, are compared with those obtained for lower homologues. The $\alpha,\beta$-unsaturated effect of substitution on the basicity of the carbonyl group is briefly discussed. It is generally observed that the gas-phase basicity of an acid is lower than that of the corresponding aldehyde.

The knowledge of gas-phase basicity (GB) and proton affinity (PA) leads to the determination of heats of formation of protonated species and allows the understanding of structural effects upon reactivity in the absence of solvent. From these points of view, polyfunctional molecules such as conjugated aldehydes, ketones, or acids constitute an interesting subject of investigation in view of their extensive use in organic synthesis. If there is now little doubt that for such molecules the thermodynamically most favorable protonation site is the oxygen of the carbonyl group, the quantitative estimate of the effect of alkyl or hydroxyl substitution upon protonation thermochemistry is poorly documented.[1-4] The present study deals with the gas-phase protonation of aldehydes, ketones, and acids **1**–**9** bearing $\alpha,\beta$-unsaturated $C_4H_7$ alkyl chains.

The determination of the GB of **1**–**9** is made from the measurement of proton transfer equilibrium constants in ion cyclotron resonance (ICR) experiments. The PA values and the $\Delta H_f°$ of the corresponding $C_5H_9O^+$, $C_6H_4O^+$, and $C_5H_9O_2^+$ ions which are deduced are compared with those of lower homologues in order to draw conclusions as to the effects of substitution on the stability of the protonated species.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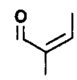
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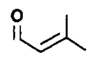
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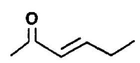
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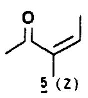
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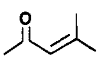
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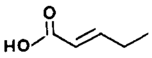
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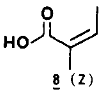
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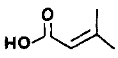
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[†] DCMR—Ecole Polytechnique.

[‡] EPFL—Institut de Chimie Physique.

(1) Vajda, J. H.; Harrison, A. G. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 293–306.

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0022-3263/88/1953-3498$01.50/0 © 1988 American Chemical Society

**Table I. Experimental Free Energy Change, $\Delta G_1°$, during the Reaction $M + BH^+ \rightleftarrows MH^+ + B$ (B = Reference Base) and Related Gas-Phase Basicity GB**

| M | B | GB(B)[a] | $\Delta G_1°$ | GB(M)[b] |
|---|---|---|---|---|
| **1** (*E*) | allyl ethyl ether | 812[c] | 3.3 | |
| | 3-pentanone | 815[d] | −0.4 | 815 |
| | propyl acetate | 813 | 1.3 | |
| **2** (*Z*) | di-*n*-propyl ether | 818 | 2.1 | |
| | 3-hexanone | 819[d] | 0.8 | 819 |
| | 4-methylcyclohexanone | 820[d] | −1.7 | |
| **3** | 2-methylbenzofuran | 829[e] | −2.1 | |
| | di-*n*-pentyl ether | 826 | 2.1 | 828 |
| | cyclooctanone | 826[d] | 2.5 | |
| **4** (*E*) | 3,4-dimethylfuran | 839[f] | −4.6 | |
| | 2,5-dimethylfuran | 838 | −4.6 | 834 |
| | 2,4-pentanedione | 837 | −2.1 | |
| **5** (*Z*) | 2,4-pentanedione | 837 | 0.0 | |
| | 2,5-dimethylfuran | 838[f] | −2.1 | 837 |
| | 2,3-dihydropyran | 837[g] | 0.4 | |
| **6** | 2-fluoropyridine | 854 | −6.3 | 847 |
| | 4-cyanopyridine | 849 | −1.7 | |
| **7** (*E*) | methyl acetate | 797 | 2.5 | |
| | tetrahydrofuran | 805 | −3.8 | 800 |
| | diethyl ether | 808 | −7.5 | |
| **8** (*Z*) | cyclopentanone | 805[d] | −2.5 | 802 |
| | tetrahydrofuran | 805 | −3.3 | |
| **9** | tetrahydropyran | 807 | −2.5 | |
| | diethyl ether | 808 | −2.1 | |
| | cyclopentanone | 805[d] | −2.9 | 804 |
| | 2-butanone | 806[d] | −3.8 | |

[a] In kJ $mol^{-1}$. Values from ref 10 unless otherwise indicated; based on $GB(NH_3)$ = 822 kJ $mol^{-1}$. [b] In kJ $mol^{-1}$. ±0.8 kJ $mol^{-1}$, deviation on the experimental determination of $\Delta G_1°$. [c] Bouchoux, G.; Djazi, F.; Hoppilliard, Y.; Houriet, R.; Rolli, E. *Org. Mass Spectrom.* **1986**, *21*, 209–213. [d] Bouchoux, G.; Houriet, R. *Tetrahedron Lett.* **1984**, *25*, 5755–5758. [e] Houriet, R.; Audier, H. E., unpublished result. [f] Houriet, R.; Rolli, E.; Bouchoux, G.; Hoppilliard, Y. *Helv. Chim. Acta* **1985**, *68*, 2037–2045. [g] Bouchoux, G.; Hanna, I.; Houriet, R.; Rolli, E. *Can. J. Chem.* **1986**, *64*, 1345–1347.

**Table II. Proton Affinities and Heats of Formation for 1–9**[a]

| M | PA(M) | $\Delta H_f°_{298}(M)$ | $\Delta H_f°_{298}(MH^+)$ |
|---|---|---|---|
| **1** | 849 | −128 | 553 |
| **2** | 853 | −140 | 537 |
| **3** | 862 | −143 | 525 |
| **4** | 868 | −182 | 480 |
| **5** | 871 | −194 | 465 |
| **6** | 881 | −197 | 452 |
| **7** | 834 | −383 | 313 |
| **8** | 836 | −395 | 299 |
| **9** | 838 | −398 | 294 |

[a] In kJ $mol^{-1}$.

**Table III. Auxiliary GB, PA, and $\Delta H_f°$ Values**[a]

| M | GB(M) | PA(M) | $\Delta H_f°_{298}(M)$[d] | $\Delta H_f°_{298}(MH^+)$ |
|---|---|---|---|---|
| **10** | 782[b] | 815[b] | −74 (−69[g]) | 640 |
| **11** | 788[b] | 821[b] | −107 | 602 |
| **12** | 807[b] | 840[b] | −108 (−101[h]) | 583 |
| **13** | 809[b] | 842[b] | −129 | 559 |
| **14** | 819[c] | 851[c] | −161 | 518[e] |
| **15** | 834[c] | 867[c] | −162 | 501[e] |
| **16** | (790)[f] | (820)[f] | −330 | (380)[f] |
| **17** | 793[c] | 825[c] | −362 | 343[e] |
| **18** | 801[c] | 833[c] | −363 | 334[e] |

[a] In kJ $mol^{-1}$. [b] Adapted from ref 1 by Lias, Liebman, and Levin[7] and adjusted to $GB(NH_3)$ = 822 kJ $mol^{-1}$. [c] Reference 2. [d] Estimated by using Benson's procedure.[6] [e] Note the slight difference in $\Delta H_f°(MH^+)$ with respect to ref 2 and due to the new $\Delta H_f°(M)$ estimated here with the second edition of ref 6. [f] $\Delta H_f°((\mathbf{16}\text{-H})^+$ = 380 kJ $mol^{-1}$, extrapolated value, see text. [g] Estimated by using the incremental method of Pedley et al.[12] [h] Experimental Values.[12]

## Results and Discussion

A number of proton transfer reactions (1), in which B is a reference base, were carried out in the ICR cell under conditions similar to those described previously.[5]

$$M + BH^+ \rightleftarrows MH^+ + B \qquad (1)$$

The associated equilibrium constant $K_{eq}$

$$K_{eq} = \frac{[MH^+][B]}{[BH^+][M]}$$

is evaluated by measurement of the signal associated with $MH^+$ and $BH^+$ ions. The ratio of concentration [B]/[M] was determined by the pressure measurements from an ionization gauge corrected for relative ionization cross sections.[5] The change in free energy $\Delta G_1° = -RT \ln K_{eq}$ yields the gas-phase basicity of M as GB(M) = GB(B) − $\Delta G_1°$. All measurements were made at ambient temperature ($T$ = 313 K). The basicity data are reported in Table I.

The corresponding proton affinity values, PA, may be deduced from the relationship

$$PA(M) = GB(M) - T\Delta S_2$$

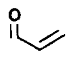
where the $T\Delta S_2$ term associated with reaction 2 may be

$$MH^+ \rightarrow M + H^+ \qquad (2)$$

simply approximated by considering only the translational entropy for the free proton, i.e., $T\Delta S_2 \simeq -34$ kJ $mol^{-1}$ at 313 K. This approximation is justified here by the fact that the considered molecules M are large enough so that the sum of translational and vibrational entropy contributions is nearly equal for M and for $MH^+$ and are thus cancelling in $\Delta S_2$. Similarly, no change in the number of rotational degrees of freedom is expected upon protonation if occurring on the carbonyl group.[2] Consequently, all the PA values quoted in Table II were obtained by PA(M) = GB(M) + 34 kJ $mol^{-1}$.

The heats of formation of neutral **1–9** (Table II) were estimated by the group increment method of Benson;[6] a CO–($C_d$, C) value of −134 kJ $mol^{-1}$ was adopted.[2] Finally, the combination of PA(M), $\Delta H_f°(M)$, and $\Delta H_f°(H^+)$ = 1530 kJ $mol^{-1}$ leads to the heats of formation of the $MH^+$ cations presented in the last column of Table II.

In order to broaden the scope of the discussion on the basicity of **1–9**, we also consider the results reported for the lower homologues **10–18**. The relevant thermochemical data, taken from the literature, are reported in Table III.



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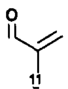

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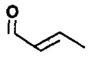

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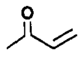

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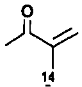

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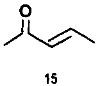

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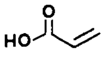

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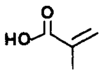

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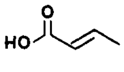

**18**

The effect of substitution on the heat of formation of odd- and even-electron cations has been shown by Holmes and co-workers to obey a law of the type

$$\Delta H_f°(\text{cation}) = \alpha - \beta \log n \qquad (3)$$

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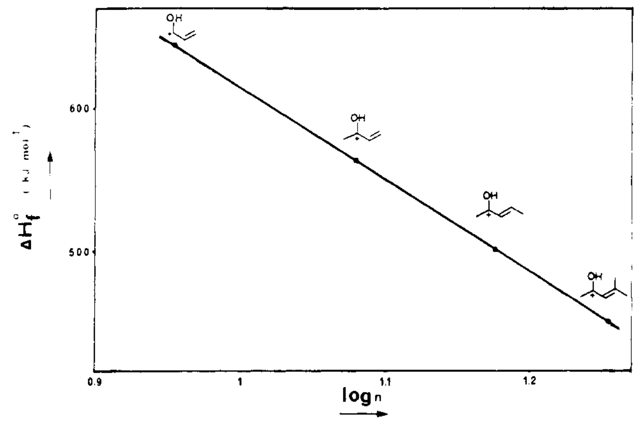
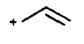


**Figure 1.** Incidence of successive substitution of a $CH_3$ group on a positive center: $\Delta H_f^\circ$(ion) as a function of log $n$ ($n$ = total number of atoms).

where $n$ is the total number of atoms in the cation.[8,9] For example, linear correlation between $\Delta H_f^\circ$ and log $n$ were found for **19**–**21**, illustrating the effect of methyl substitution on the positive center of allylic cations.[8]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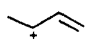
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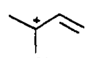
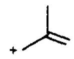

**21**

Several protonated molecules taken from **1**–**18** were thought to behave similarly if protonation occurred on the oxygen of the carbonyl group. Accordingly, the incidence of successive replacement of a hydrogen atom by a OH group on the positive center of allylic cations **19**–**21** but also **22** and **23** is considered.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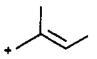

**23**

Excellent linear correlations were found for the five series **19**, (**10** + H)$^+$, (**16** + H)$^+$; **20**, (**12** + H)$^+$, (**18** + H)$^+$; **21**, (**3** + H)$^+$, (**9** + H)$^+$; **22**, (**11** + H)$^+$, (**17** + H)$^+$; and **23**, (**2** + H)$^+$, (**8** + H)$^+$ by using eq 3 and $\Delta H_f^\circ$ values of 941, 854, 774, 883, and 795 kJ mol$^{-1}$ for **19**, **20**, **21**, **22**, and **23** respectively.[10]

These clear correlations confirm that the protonated structures consist of substituted carbenium ions formed by protonation of the carbonyl group. Furthermore, an estimate of $\Delta H_f^\circ{}_{298}$ ((**16** + H)$^+$) = 380 kJ mol$^{-1}$ may be extrapolated. This is in agreement with the upper limit of 410 kJ mol$^{-1}$ estimated by Baer and co-workers.[11] in a photoionization study of butanoic acid.

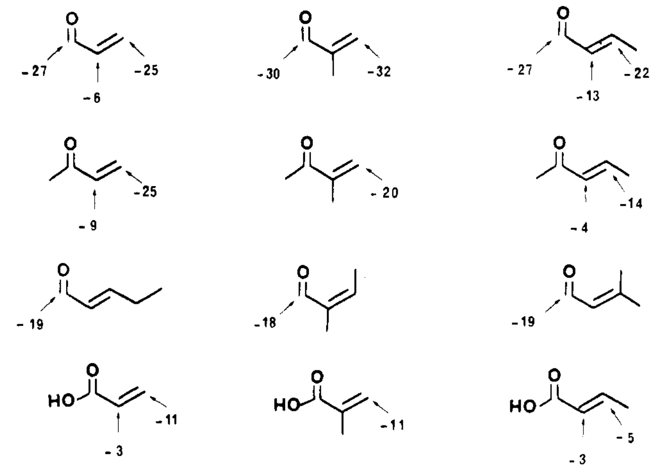
The effect of methyl substitution on the stabilization of hydroxyvinylcarbenium cations is illustrated by the correlation found for the series (**10** + H)$^+$, (**13** + H)$^+$, (**15** + H)$^+$, and (**6** + H)$^+$ as indicated in Figure 1.

In the previous sections, we discussed the influence of structure on the thermodynamical stability of the ions, i.e., of the protonation products of conjugated aldehydes, ketones, and carboxylic acids. We want now to focus on the reactivity properties of these latter neutrals molecules by considering the influence of substitution on their proton affinity. For this purpose we consider the isodesmic reaction 4, where $M_{CH_3}$ and $M_H$ are the methyl-substituted

$$M_{CH_3} + (M_H + H)^+ \rightarrow M_H + (M_{CH_3} + H)^+ \qquad (4)$$

and unsubstituted molecules M taken from the set **1**–**18**. The corresponding enthalpy variation, $\Delta H_4^\circ$, is simply the difference PA($M_H$) − PA($M_{CH_3}$), which may be evaluated from Tables I, II, and III. The corresponding data are summarized in Chart I.

### Chart I[a]



[a] $\Delta H_4^\circ$ in kJ mol$^{-1}$ (see text for the definition).

The first observation is that the effect of methyl substitution is to increase the basicity of all carbonyl compounds ($\Delta H_4^\circ < 0$), the tendency being emphasized in aldehydes whereas it remains smaller in carboxylic acids. The second point is that the effect is largest for methyl substitution on carbons C(1) and C(3) as expected from consideration of the two limiting resonance forms A and B of the oxygen protonated species.

A B

The methyl substitution at C(1) is accompanied by a $\Delta H_4^\circ$ lying between −18 and −30 kJ mol$^{-1}$. This difference is the net result of an enthalpy gain of 54 kJ mol$^{-1}$ when passing from a methyl ketone ($M_{CH_3}$) to an aldehyde ($M_H$) (reaction 4) and an enthalpy loss of 79 ± 7 kJ mol$^{-1}$ when passing from ($M_H$ + H)$^+$ to ($M_{CH_3}$ + H)$^+$.

The methyl substitution in the C(2) position leads to small $\Delta H_4^\circ$ values (−3 to −17 kJ mol$^{-1}$). This lack of stabilizing effect of the methyl group on the protonated species is in keeping with the absence of an appreciable positive charge in the C(2) carbon of the substituted allylic cations.

The increase in proton affinity brought by a methyl substitution in position C(3) is comparable to that observed for C(1) substitution. Its efficiency is identical in the case of aldehydes and ketones because in these cases $\Delta H_4^\circ$ is close to 24 ± 8 kJ mol$^{-1}$. However, the first substitution is more efficient (compare −25 kJ mol$^{-1}$ for the couple **13**/**15** and only −14 kJ mol$^{-1}$ for the couple **15**/**6**). In the case of acids, the incidence of a methyl substitution in C(3) is drastically reduced ($\Delta H_4^\circ$ = −5 to −11 kJ mol$^{-1}$). One may note that the stabilizing influence of an ethyl vs a

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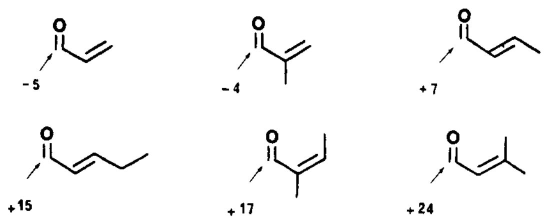
**Chart II**[a]



[a] $\Delta H_5°$ in kJ $mol^{-1}$ (see text for the definition).

methyl group is significantly increased in the aldehyde series whereas it does not show up in either ketones or carboxylic acids.

The role of a hydroxyl group substitution in C(1) may be similarly discussed. The enthalpy variation associated with reaction 5 is equal to $\Delta H_5° = PA(M_H) - PA(M_{OH})$.

$$M_{OH} + (M_H + H)^+ \rightarrow M_H + (M_{OH} + H)^+ \qquad (5)$$

Examination of the data contained in Chart II reveals a contrasting behavior.

In an intuitive picture, the π-donating effect of the hydroxyl group is expected to increase the basicity of the carbonyl oxygen. An increase in proton affinity is indeed observed when passing from aldehyde to acid for the first two couples **10**/**16** and **11**/**17** ($\Delta H_5°$ = −5 and −4 kJ $mol^{-1}$ respectively). However, in all other cases, the proton affinity of the acid is found to be lower than that of the corresponding aldehyde by an amount as large as 15–24 kJ $mol^{-1}$.

This lowering in PA upon going from an aldehyde to the analogous acid parallels the behavior of conjugated aromatic compounds as exemplified by the proton affinity values of benzaldehyde (838 kJ $mol^{-1}$) and benzoic acid (829 kJ $mol^{-1}$).[7]

## Conclusion

A complete set of α,β-unsaturated carbonyl compounds has been examined, and the results allow the following conclusions: a good correlation of $\Delta H_f°(MH^+)$ with the logarithm of the number of atoms is observed, pointing to protonation on the oxygen of the carbonyl group; the effect of methyl substitution upon gas-phase basicities is to increase significantly the latter when situated on position C(1) or C(3); the gas-phase basicity of an α,β-unsaturated acid is generally lower than that of the corresponding aldehyde.

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# Competitive Singlet–Singlet Energy Transfer and Electron Transfer Activation of Aryl Azides: Application to Photo-Cross-Linking Experiments

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*Received December 1, 1987*

Direct irradiation of 4-[(dimethylamino)carbonyl]phenyl azide (DAA) in an inert solvent with UV light causes ring expansion to an intermediate dehydroazepine and eventual isolation of 4,4′-azobis[[(dimethylamino)carbonyl]benzene] (AZB). The dehydroazepine can be trapped with nucleophilic reagents to give substituted 3*H*-azepines. The photochemistry of DAA takes a different course when it is sensitized by pyrene, 1-acetamidopyrene (**5**), or 9-acetamidoacridine (**2**). Under these conditions, single-electron transfer occurs in competition with energy transfer as evidenced by detection of radical ions in laser transient absorption spectroscopy and by formation of 4-[(dimethylamino)carbonyl]aniline (DAH) as a major product. Energy transfer and electron transfer compete also when the sensitizer and the aryl azide are linked together by a flexible chain of methylene groups. These results have particular significance for the application of such compounds to photolabeling experiments.

The photochemistry of aryl azides ($ArN_3$) plays an important role in biochemistry and biology. Irradiation of these reagents with UV light leads to loss of nitrogen and formation of highly reactive intermediates. The intermediates may form bonds rapidly at the site of their generation to give products that can be used to identify the targeted macromolecules. These transformations form the central part of several procedures generically identified as photolabeling experiments.[4] It was previously believed that the key reactive intermediates in these photolabeling experiments were arylnitrenes (ArN). However, recent work in our laboratories has confirmed earlier speculation that dehydroazepines, from ring expansion of singlet nitrenes or the excited azides themselves, are probably the intermediates involved in the bond-forming step.[5,6]

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