Steric Crowding in Organic Chemistry. IV. Ultraviolet Absorption Spectra of Crowded Olefins

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The ultraviolet absorption spectra of a group of crowded olefins have been determined for both cyclohexane solutions (182 nm and above) and the vapor state (183 nm and above). Marked shifts in the π–π^* absorption maximum to higher wavelengths were observed in 1,1-disubstituted olefins, cis-1,2-disubstituted olefins, and trisubstituted olefins. Neopentyl substituents caused the largest shifts. *cis*-1,2-Di-*tert*-butylethylene (in solution) is the only olefin which shows a maximum at higher wavelength for the cis relative to the trans isomer. An efficient Wittig synthesis of crowded 1,1-disubstituted ethylenes was developed.

The ultraviolet spectra of isolated olefinic double bonds have been investigated recently in several laboratories.[2–5] Together with previous work,[6] these studies have established that simple unstrained olefins have characteristic absorption maxima at 174–178 nm for monosubstituted olefins, 174–184.5 nm for *cis*-1,2-disubstituted olefins (the higher wavelength is characteristic of fatty acid esters, lower molecular weight hydrocarbons absorb at 174–182 nm) with the trans isomers typically 3–4 nm higher, 186–189 nm for 1,1-disubstituted olefins, 177–191 nm for trisubstituted olefins, and 187–191 nm for tetrasubstituted olefins.

The observed maxima are assigned to the π-bonding to π-antibonding ($\pi \rightarrow \pi^*$) transition which produces the intense N → V band.[7,8] Other absorption, of much lower intensity and apparently due to Ryberg transitions, occurs in some cases on the long-wavelength portion of the N → V band.[8–12] Recent reports give a detailed interpretation of the spectra of simple olefins.[8,11–13]

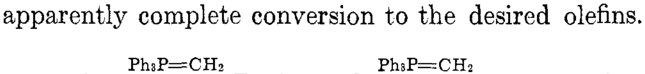
Polyolefins with homoconjugated double bonds, such as 1,4-pentadiene[6] and linoleic acid,[2] display the effects of delocalization of the double bonds with absorption maxima at higher wavelengths, and molar absorptivities 40% less than dienes with isolated double bonds. Cyclopropyl substituents also shift the absorption to higher wavelengths.[4]

The effect of angle strain on the ultraviolet absorption spectra of cyclic olefins has been examined in a variety of systems, including small-ring hydrocarbons,[14,15] steroids and terpenoids,[16] bicyclo[3.3.1]non-1-ene,[17] and highly strained olefins derived from natural products.[18]

Conjugated 1,3-dienes with bulky substitution on the double bond have also been examined and found to be twisted out of conjugation, giving a shift in the electronic spectrum to lower wavelength.[19] However, there has been no systematic investigation of the effects of bulky substitution on the ultraviolet absorption of noncyclic olefins; so to complement our previous studies on vibrational spectra of such compounds[20] we have examined the electronic absorption spectra of olefins **1–16** above 182 nm. The results are presented in Table I, together with selected data for reference.

Results and Discussion

All of the compounds utilized had been reported previously, but a modified general route to the pure 1,1-disubstituted olefins was also developed. This route was used for 2-ethyl-3,3-dimethyl-1-butene (**5**) and 2-isopropyl-3,3-dimethyl-1-butene (**6**) and involved the Wittig reaction in dimethyl sulfoxide at elevated temperatures. The procedure of Corey[21] involves generation of the methylsulfinyl carbanion from DMSO and NaH, and then formation of the phosphorane by addition of the phosphonium halide. The phosphorane reacts rapidly with most ketones at room temperature under these conditions, but we found that these conditions failed with ethyl *tert*-butyl ketone. However, use of longer reaction times and elevated temperatures gave apparently complete conversion to the desired olefins.



$$\text{no reaction} \xleftarrow[\text{DMSO, 25°}]{Ph_3P{=}CH_2} \text{Et-}t\text{-BuC{=}O} \xrightarrow[\text{DMSO, 80°}]{Ph_3P{=}CH_2} \text{Et-}t\text{-BuC{=}CH}_2$$

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Higher temperatures were unsuccessful with di-*tert*-butyl ketone, even at 150°, at which point the decomposition of the solvent becomes excessive.

Pyrolysis[20] or solvolysis[22] of the corresponding tertiary *p*-nitrobenzoates was used to prepare the trisubstituted olefins **14–16**.

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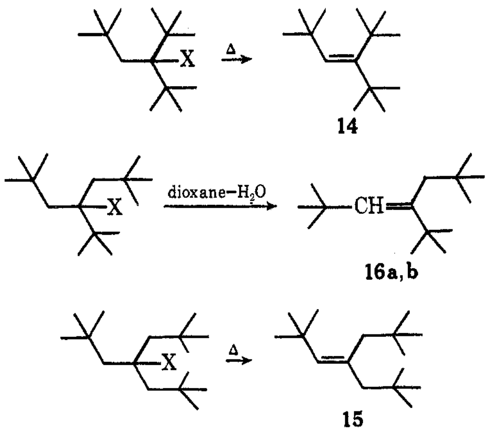
TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF OLEFINS[a]

1,1 Disubstituted	λ_{max}, nm (ϵ_{max})	1,2 Disubstituted	λ_{max}, nm (ϵ_{max})	Trisubstituted	λ_{max}, nm (ϵ_{max})
Me$_2$C=CH$_2$	188.2 (11,300)[b,c]	MeCH=CHMe		MeCH=CMe$_2$	177.5 (11,000)[b,f]
		trans	178.0 (13,000)[b]		
MeEtC=CH$_2$ (1)	186.0 (8,800) 188.3 (9,700)[b]	cis	174.0 (16,000)[b]	MeCH=CMe-*t*-Bu (trans) (**12**)	186.5 (11,750) 184.0[d]
Me-*i*-PrC=CH$_2$ (**2**)	186.5 (10,800) 187.0[d]	*t*-BuCH=CHMe (cis) (**9**)	184.5 (11,150) 183.0[d]	*t*-BuCH=CMe$_2$ (**13**)	192.0 (10,050) 193.5[d]
Me-*t*-BuC=CH$_2$ (**3**)	186.0 (10,850) 187.0[d]	*t*-BuCH=CH-*t*-Bu		*t*-BuCH=C-*t*-Bu$_2$ (**14**)	194.5 (13,300) 191.0[d]
MeNpC=CH$_2$ (**4**)	191.0 (8,600) 190.5[d]	cis (**10**)	185.5 (12,550) 183.0[d]	*t*-BuCH=CNp$_2$ (**15**)	200.0 (9,650)[g]
Et-*t*-BuC=CH$_2$ (**5**)	186.0 (10,850) 188.0[d]	trans (**11**)	184.5 (15,050) 184.0[d]	*t*-BuCH=C-*t*-BuNp (**16**)	197.5 (10,500) 198[d]
i-Pr-*t*-BuC=CH$_2$ (**6**)	188.5 (12,100) 187.5[d]	*cis*-2-octene	181.5 (13,450)[e]		
t-Bu$_2$C=CH$_2$ (**7**)	189.0 (11,650) 189.0[d]	*trans*-2-octene	184.0 (10,450)[e]		
Np$_2$C=CH$_2$ (**8**)	196.5 (7,900) 197.5[d]				

[a] Unless otherwise indicated results are for this work and were measured for cyclohexane solutions. Np = neopentyl. [b] Reference 6 (vapor). [c] We find 187.0 in cyclohexane solution and 184.0 and 188.0 (equal intensity) in the vapor. [d] Vapor spectrum. [e] Reference 2. [f] We observe a maximum at 187.0 (10,000), and ref 9 gives 188.7 (5800). Our vapor spectrum shows maxima at 183.0 > 185.5 > 191.5. [g] The vapor spectrum shows a series of maxima at 183.5, 185.5, 190.0, 197.0, 203.0, and 207.5, with the highest intensities at 183.5 and 185.5 nm.



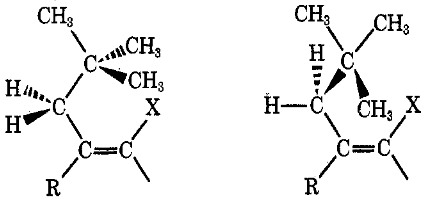
X = *p*-nitrobenzoate

Inspection of molecular models suggests that the *tert*-butyl substituted olefins **6** and **7** suffer intramolecular steric crowding between the groups. This crowding apparently results in distortion of the double bond that is reflected in the spectra, which show augmentation of ϵ and a 2–3-nm bathochromic shift in λ_{max} relative to the unstrained **1**–**3** (this shift corresponds to 1.6–2.4 kcal/mol). The neopentyl-substituted compounds **4** and **8** show pronounced bathochromic shifts in λ_{max} of 5 and 10.5 nm, respectively. The models suggest that in neopentylethylenes the neopentyl group is significantly repulsed by any other substituent larger than hydrogen on the same olefinic carbon, so that the conformations shown in Chart I may tend to be favored, with the methyl groups close to the double bond.[23] Bond stretching and twisting may also occur, but the extent of these deformations cannot be specified.

The possible proximity of the methyl group and the π cloud suggests two sources of the bathochromic shifts in these compounds. There may be orbital interactions between the methyl groups and the π electrons of the double bond which change the energy levels of the ground and excited electronic states resulting in a net lowering of the energy of the transition. Alternatively, a nonbonding repulsion could distort the double bond and change the energy levels.

CHART I

CONFORMATIONS OF 1-ALKYL-1-NEOPENTYLETHYLENES



The 1,2-disubstituted ethylenes have generally lower wavelength absorption maxima and higher molar absorptivity than the 1,1-disubstituted compounds, with the trans compounds usually absorbing at longer wavelength than the cis isomers. This behavior has been analyzed in terms of the dipole moments of the molecules: olefins with dipole moments in the direction of the bond, such as 1,1-disubstituted compounds, absorb at longer wavelength, whereas if there is a component of the dipole moment perpendicular to the bond, as in cis-1,2-disubstituted olefins, the excitation energy is increased.[10]

cis-1-Methyl-2-*tert*-butylethylene (**9**) absorbs 3 nm higher than *cis*-2-octene, and *cis*-1,2-di-*tert*-butylethylene absorbs 1 nm higher (in solution) than the trans isomer. This is the only example of higher wavelength absorption of a cis relative to a trans isomer, but this effect is partly due to solvation effects, as the cis isomer does absorb at lower wavelength in the vapor.

The cause of the difference between the trisubstituted olefins **12** and **13** is not obvious on steric grounds. It is interesting, however, that Heathcock and Poulter[4a] observed the equivalent difference between the corresponding isopropyl derivatives, and classified it as a

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[23] For a review of the properties of the neopentyl substituent see M. Montagné, *Bull. Soc. Chim. Fr.*, 347 (1970).

"special *gem*-dimethyl" effect. The model of tri-*tert*-butylethylene (**14**) indicates a highly crowded double bond with a strong twisting force, but the increase in λ_{max} is modest. The trisubstituted olefins with neo-

t-BuCH=CMe$_2$
13, λ_{max} 192.0 (ϵ 10,050)

i-PrCH=CMe$_2$
λ_{max} 191.0 (ϵ 10,200)

MeCH=CMe-*t*-Bu
(trans) **12**, λ_{max} 186.5 (ϵ 11,750)

MeCH=CMe-*i*-Pr
(trans), λ_{max} 186.5 (ϵ 10,000)

pentyl substituents (**15** and **16a**) show rather larger shifts, consistent with the behavior of the 1,1-disubstituted neopentylethylenes.

The patterns of behavior in the ultraviolet absorption are rather different from those of the vibrational spectra,[20] where the *tert*-butyl derivatives have much larger frequency shifts than the corresponding neopentyl derivatives; for example, **4**, **8**, and **15** absorb at 1640, 1635.5, and 1636 cm^{-1}, respectively, whereas **3**, **7**, and **14** absorb at 1638.5, 1615.5, and 1583 cm^{-1}, respectively.

Spectral information has recently become available on some highly distorted polycyclic olefins. Bicyclo[3.3.1]non-1-ene has a near-normal vibrational absorption (1620–1625 cm^{-1})[17] but a low-energy electronic absorption [206–207 nm (ϵ 7500–7000)].[17] A tetrasubstituted olefinic alcohol derived from katonic acid has Raman and ultraviolet absorptions at 1690 cm^{-1} and 224 nm (ϵ 5200), respectively.[18] Molecular models, and an X-ray crystallographic study in the latter case,[18] show these double bonds to be substantially deformed.

The geometries of the acyclic compounds considered in this report have not been experimentally determined, but two calculations have appeared[24,25] of the geometry of *cis*-1,2-di-*tert*-butylethylene (**10**). These agree on a value of 136° for the C=C–C angle of this compound. Neither of these calculations considered out-of-plane bond twisting, and only one[24] included bond stretching. The complete analysis of the properties of these crowded olefins in terms of their structures will require more experimental information on the molecular geometries and a more thorough theoretical evaluation of the relative contributions of in-plane bond bending, out-of-plane bond twisting, and bond stretching.

Experimental Section[26]

Elemental analyses were performed by the Bernhardt Mikroanalytisches Laboratorium, Elbach über Engleskirchen, Germany. Nmr spectra were measured on a Varian A-60 instrument with tetramethylsilane as an internal standard. Raman spectra were measured with a Cary 81 instrument equipped with a He-Ne laser source. Gas chromatography (glpc) was performed with a Varian Aerograph 90P-3 instrument and the columns and temperatures specified.

Source of Samples.—Compounds **1–4**, **8**, **9**, and **11–13** were obtained 98–99% pure from Chemical Samples Co., Columbus, Ohio. *cis*-1,2-Di-*tert*-butylethylene (**10**) was obtained by the selective hydrogenation[27] of di-*tert*-butylacetylene (Chemical Samples Co.) and was purified by glpc (10 ft × $^3/_8$ in., DEGS on Chromosorb P, 110°, 75 ml/min He). Compounds **14–16** were prepared by pyrolysis or solvolysis of the corresponding *p*-nitrobenzoate esters[22] by the procedure reported previously.[20] 1,1-Di-*tert*-butylethylene (**7**) was prepared by the published procedure,[28] and compounds **5** and **6** were prepared by a modification of the Wittig reaction in DMSO[21] at elevated temperature.

Tri-*tert*-butylethylene (**14**)[20] was collected by glpc (10 ft × $^3/_8$ in., 30% SE-52 on Chromosorb W column, 160°, 75 ml/min He): uv max (cyclohexane) 194.5 nm (ϵ 13,300); Raman (neat) 1583 cm^{-1} (C=C); nmr (CCl$_4$) δ 1.07, 1.09, and 1.22 (each s, 9, *t*-Bu) and 5.22 (s, 1, vinyl H); mass spectrum (70 eV) *m/e* 196 (molecular ion).

Anal. Calcd for C$_{14}$H$_{28}$ (196.38): C, 85.63; H, 14.37. Found: C, 85.79; H, 14.41.

1,1-Dineopentyl-2-*tert*-butylethylene (**15**)[22] was prepared by pyrolysis of trineopentylcarbinyl *p*-nitrobenzoate (7.70 g, 0.0196 mol) in a 100-ml round-bottom flask up to 220° (0.1 Torr). There was collected in a Dry Ice trap 3.1 g (0.0138 mol, 71%) of **15** pure by glpc: uv max (cyclohexane) 200.0 nm (ϵ 9650); Raman (neat) 1636 cm^{-1} (C=C); nmr (CCl$_4$) δ 0.88, 0.99, and 1.12 (each s, 9, *t*-Bu), 1.90 and 2.18 (each s, 2, –CH$_2$-*t*-Bu), and 5.05 (s, 1, vinyl H).

Anal. Calcd for C$_{16}$H$_{32}$ (224.33): C, 85.63; H, 14.37. Found: C, 85.55; H, 14.46.

1,2-Di-*tert*-butyl-1-neopentylethylene (**16**)[22] was prepared by solvolysis as previously reported[22] and separated by glpc (20 ft × $^3/_8$ in. 30% FFAP on Chromosorb W column, 133°, 75 ml/min He) to give the cis and trans isomers. These were not differentiated but are designated as **16a** and **16b**. The compound of retention time 33 min, **16a**, constituted 87% of the total: uv max (cyclohexane) 197.5 nm (ϵ 10,500); Raman (neat) 1625 cm^{-1} (C=C); nmr (CCl$_4$) δ 1.00, 1.09, and 1.10 (each s, 9, *t*-Bu), 2.20 CH$_2$-*t*-Bu), and 5.31 (s, 1, vinyl H).

Anal. Calcd for C$_{15}$H$_{30}$ (210.41): C, 85.63; H, 14.37. Found: C, 86.04; H, 13.90.

The compound of retention time 47 min, **16b**, was 3% of the total: Raman (neat) 1622 cm^{-1} (C=C); nmr (CCl$_4$) δ 0.90, 0.97, and 1.07 (each s, 9, *t*-Bu), 1.95 (s, 2 H, CH$_2$-*t*-Bu), and 4.90 (s, 1, vinyl H). 2,3,5,5-Tetramethyl-3-neopentyl-1-hexene[22] had a retention time of 56 min and constituted 8% of the total.

2-Ethyl-3,3-dimethyl-1-butene (**5**) was obtained by treating 10.0 g (0.0880 mol) of ethyl *tert*-butyl ketone (Chemical Samples Co.) with the Wittig reagent (prepared by the published procedure)[21] obtained from 38.0 g (0.103 mol) of methyltriphenylphosphonium bromide and 0.100 mol of NaH at 80° for 24 hr. The product was distilled at 75° (pot) (40 mm) to give 7.24 g of liquid which by nmr and glpc analysis contained about 50% benzene. Separation by glpc (10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb W, 105°, 120 ml/min He) gave pure **5**: nmr (CCl$_4$) δ 1.01 (t, 3, J = 7 Hz, CH$_2$CH$_3$), 1.05 (s, 9, *t*-Bu), 2.03 (quartet, 2, J = 7 Hz, CH$_2$CH$_3$), and 4.60 and 4.78 (each singlet with fine structure, 1, C=CH$_2$).

2-Isopropyl-3,3-dimethyl-1-butene (**6**) was prepared and purified as above to give **6**: nmr (CCl$_4$) δ 1.00 (d, 6, J = 7 Hz, CHMe$_2$), 1.05 (s, 9, *t*-Bu), 2.35 (m, 1, CHMe$_2$), 4.65 (s, 1, vinyl H trans to *t*-Bu), and 4.73 (m, 1, J = 1 Hz, vinyl H *trans* to *i*-Pr).

Spectroscopy.—For determination of ultraviolet absorption spectra, an extended-range Beckman Model DK-2 spectrophotometer was employed as previously described.[2] Sample and reference cells were fused quartz and had path lengths of 0.01099 and 0.01004 cm (for solution spectra, useful to 182.0 nm) and 2.0 cm (for vapor spectra, useful to 183.0 nm). Solutions were prepared with Phillips Spectro Grade cyclohexane. Olefin samples, typically 4–6 mg, were weighed in sections of disposable 50-μl pipets on a Cahn electrobalance; the pipet section was weighed, partially filled with sample, reweighed, transferred to a 5-ml or 10-ml volumetric flask, and crushed under cyclohexane. Weighings of samples **1** and **2** may be inaccurate owing to their high volatility. Spectra of sample vapor in a nitrogen atmosphere were obtained by flushing the 2-cm cells with nitrogen, then allowing a small drop of sample to vaporize in the cell.

The CPK Atomic Models (Ealing Corporation) were used to construct molecular models.

Registry No.—**2**, 563-78-0; **3**, 594-56-9; **4**, 107-39-1; **5**, 18231-53-3; **6**, 20442-64-2; **7**, 5857-68-1; **8**, 141-

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[26] Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

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[28] M. S. Newman, A. Arkell, and T. Funkunaga, *ibid.*, **82**, 2498 (1960).

70-8; **9,** 762-63-0; **10,** 692-47-7; **11,** 692-48-8; **12,** 598-96-9; **13,** 107-40-4; **14,** 28923-90-2; **15,** 34235-29-5; **16,** 34235-30-8; $Me_2C{=}CH_2$, 115-11-7; $MeCH{=}CMe_2$, 513-35-9; cyclohexane, 110-82-7.

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Micellar Effects upon the Reaction of the Tri-*p*-anisyl Carbonium Ion with Nucleophiles[1]

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Anionic micelles of sodium lauryl sulfate (NaLS) strongly catalyze the acid heterolysis of tri-*p*-anisylmethanol but do not affect the rate of attack of water upon the carbonium ion. Cationic micelles of cetyltrimethylammonium bromide (CTABr) and nonionic micelles of Igepal strongly inhibit the acid heterolysis but also do not affect the rate of attack of water upon the carbonium ion. Micelles of NaLS strongly inhibit the attack of hydroxide or azide ions upon the carbonium ion, and micelles of CTABr and Igepal weakly catalyze these reactions. Igepal decreases acidity as measured by H_0' and H_R.

One of the first kinetic studies of micellar catalysis and inhibition was that carried out by Duynstee and Grunwald on the alkaline fading of stable triphenylmethyl dye cations, *e.g.*, crystal violet.[2] Attack of the hydroxide ion upon the carbonium ion was inhibited by anionic and catalyzed by cationic micelles. These kinetic effects are readily explicable in terms of electrostatic interactions between the micelles and the initial and transition states.[3]

The equilibrium constant for carbonium ion formation from tri-*p*-anisylmethanol (ROH) in dilute acid is markedly increased by anionic micelles of sodium lauryl sulfate (NaLS) and decreased by cationic micelles of cetyltrimethylammonium bromide (CTABr),[8] and it was of interest to examine the forward and back reactions.

We have recently examined the kinetic salt effects upon the reaction of the tri-*p*-anisyl carbonium ion with water and related them to salt effects upon the H_R scale.[9,10] Our aim in the present work was to examine micellar effects upon the reactions shown in eq 1.

$$R^+ + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ROH + H^+ \qquad (1)$$

This investigation cannot be carried out using the triphenylmethyl dye cations because they are stable in water and hydroxylic solvents in the absence of added nucleophiles.[2,11] We were also interested in examining micellar effects upon the reactions of the relatively reactive tri-*p*-anisyl carbonium ion with hydroxide and azide ion for comparison with results obtained using the stable dyestuff cations in which the positive charge is delocalized into the amino-substituted aryl groups.[2]

Only ionic surfactants were used in the original work on micellar effects on acidity functions.[8] We have now extended these measurements to the uncharged micelles of Igepal, which is a nonylphenyl polyethylene oxide (mol wt 1403) and also measured the effects of Igepal upon the rates of nucleophilic attack upon the tri-*p*-anisyl carbonium ion.

Experimental Section

Materials.—The purification of the ionic surfactants has been described.[8] Igepal was kindly supplied by GAF Corp. and was used without purification. The carbonium ion was introduced as a solution of tri-*p*-anisylmethyl chloride (Aldrich) in dilute HCl. All solutions were made up using distilled deionized water, and were degassed before use.[9]

Kinetics.—The reactions with water were followed at 25.0° using a Durrum-Gibson stopped flow apparatus. A solution of the carbonium ion, R^+, in dilute HCl in one drive syringe was rapidly mixed with excess NaOAc in the other drive syringe.[9] The first-order rate constant, k_ψ, for attack of water upon R^+ was found to be 12.4 sec^{-1}, in good agreement with our earlier results.[9]

For experiments with hydroxide ion a slight excess of NaOH was used in one drive syringe, and for experiments with azide ion the acid was neutralized by a slight excess of hydroxide ion.[9]

Indicator Measurements.—The ionizations of tri-*p*-anisylmethanol and *p*-nitroaniline in Igepal were measured following general methods.[8,12]

Results

Indicator Measurements.—The ability of nonionic micelles of Igepal to reduce $-H_0'$ and $-H_R$ (Tables I and II) suggests that the base rather than the anilinium or carbonium ion is taken up by the micelles which protect it from the hydronium ion; and nonpolar organic solvents (except at high concentration) decrease acidity functions, in part by stabilizing the organic base.[11] Igepal has a terminal hydroxyl group which could react with the carbonium ion and thereby further reduce $-H_R$, but this reaction is probably not important because the rate of attack of water upon the carbonium ion is unaffected by Igepal (and the ionic micelles). How-

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[1] Support of this work by the National Science Foundation is gratefully acknowledged.

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