Table II. 1-(3-Bromo-2,5,6-trimethylphenyl)propyne (1) Coupled ^{13}C NMR Coupling Constants (Hz) and Chemical Shifts

atom	^{13}C δ	*J* H3	*J* H7	*J* H10	*J* H11	*J* H12
1	77.7 (q)	4.4				
2	94.1 (q)	10.6				
3	4.4 (q)	131.4				
4	125.3 (br m)[a]					
5	136.5 (qv)		6.4	6.4		
6	121.2 (qv)		5.0	5.4		
7	132.2 (dq)		163.1		5.1	
8	135.1 (qv)				5.4	5.4
9	137.7 (br m)[a]					
10	21.3 (q)			128.0		
11	19.7 (qd)		5.0		126.8	
12	17.5 (q)					126.9

[a] Unresolved.

of the solvent followed by column chromatography afforded **1** (10.65 g, 90%), which crystallized from ethanol, mp 63–63.5 °C: IR 2230 cm^{-1} ($C\equiv C$ stretch); ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 1 H,4-H), 2.50 (s, 3 H,2-CH_3), 2.32 (s, 3 H, 6-CH_3), 2.20 (s, 3 H, acetylenic CH_3), 2.16 (s, 3 H, 5-CH_3). For INADEQUATE, see Table I, and the coupled ^{13}C coupling constants and chemical shifts are given in Table II. Mass spectrum, *m/e* 236/238. Anal. Calcd for $C_{12}H_{13}Br$: C, 60.78; H, 5.53; Br, 33.69. Found: C, 60.88, H, 5.55; Br, 33.63.

1-(2,3,6-Trimethylphenyl)propyne (3). A solution of *n*-BuLi in hexane (8.1 mL of 1.50 M, 12 mmol) was added dropwise to a stirred solution of 1-(3-bromo-2,5,6-trimethylphenyl)propyne (**1**) (1.43 g, 6 mmol) in dry ether (100 mL) at −70 °C under nitrogen. After being stirred for 4 h at 5 °C, the reaction mixture was hydrolyzed with (200 mL) of water. The organic phase was separated, and the aqueous phase was extracted three times with ether (3 × 50 mL). The combined ethereal phase was washed three times with H_2O (3 × 100 mL) and dried over ($MgSO_4$). Removal of the solvent followed by column chromatography afforded the dehalogenated product **3** as an oil (700 mg, 74%): IR 2220 cm^{-1} ($C\equiv C$ stretch); 1H NMR ($CDCl_3$) δ 6.97 (d, 1 H, 5-H, *J* = 7.9 Hz), 6.93 (d, 1 H, 4-H, *J* = 7.9 Hz), 2.40 (s, 3 H, 6-CH_3), 2.39 (s, 3 H, 2-CH_3), 2.24 (s, 3 H, 3-CH_3), 2.16 (s, 3 H, acetylenic CH_3); mass spectrum, *m/e* 158. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.03; H, 8.91.

3,5-Dibromo-2,4-diethyl-7,7a-dimethyl-3a,7a-dihydrobenzo[*b*]thiophene 1,1-Dioxide (6). A solution of 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide[1] (2.37 g, 10 mmol) in *t*-BuOH (20 mL) was refluxed for 100 h. After removal of the solvent, the residue was dissolved in MeOH (10 mL), and H_2O (100 mL) was added. After standing for 15 h at −20 °C, the product was collected over a glass filter (0.5 g, 25%, mp 142–146 °C): ^{1}H NMR ($CDCl_3$) δ 6.08 (q, 1 H, 6-H, *J* = 1.5 Hz), 3.66 (s, 1 H, 3a-H), 2.73 (sxt, 1 H, 4-CH_2, *J* = 13.8, 7.5 Hz), 2.57 (q, 2 H, 2-CH_2, *J* = 7.6 Hz), 2.33 (sxt, 1 H, 4-CH_2, *J* = 13.8, 7.5 Hz), 1.99 (d, 3 H, 7-CH_3, *J* = 1.5 Hz), 1.52 (s, 3 H, 7a-CH_3), 1.23 (t, 3 H, 2-CH_3, *J* = 7.6 Hz), 1.64 (t, 3 H, 4-CH_3, *J* = 7.5 Hz); mass spectrum, *m/e* 410/412. Anal. Calcd for $C_{14}H_{18}Br_2O_2S$: C, 41.00; H, 4.42. Found: C, 40.86; H, 4.36.

1-(3-Bromo-5,6-dimethyl-2-ethylphenyl)-1-butyne (7). A solution of 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide[1] (2.37 g, 10 mmol) in *t*-BuOH (20 mL) was refluxed for 160 h. Removal of the solvent followed by column chromatography (Al_2O_3 neutral, pentane) afforded **7** as an oil (1.25 g, 94%): IR 2230 cm^{-1} ($C\equiv C$ stretch); ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 1 H, 4-H), 2.97 (q, 2 H, 2-CH_2, *J* = 7.5 Hz), 2.51 (q, 2 H, acetylenic CH_2, *J* = 7.5 Hz), 2.32 (s, 3 H, 5-CH_3), 2.20 (s, 3 H, 6-CH_3), 1.28 (t, 3 H, acetylenic CH_3, *J* = 7.5 Hz), 1.17 (3 H, 2-CH_3, *J* = 7.5 Hz); mass spectrum, *m/e* 264/266. Anal. Calcd for $C_{14}H_{17}Br$: C, 63.41; H, 6.46; Br, 30.13. Found: C, 63.50; H, 6.44; Br, 30.13.

1-(3-Bromo-5,6-diethyl-2-methylphenyl)propyne (8). A solution of 3-bromo-5-ethyl-2-methylthiophene 1,1-dioxide[5] (4.00 g, 17 mmol) in *t*-BuOH (30 mL) was refluxed for 240 h. Removal of the solvent followed by column chromatography afforded **8** as an oil (1.85 g, 83%): IR 2230 cm^{-1} ($C\equiv C$ stretch); ^{1}H NMR ($CDCl_3$) δ 7.27 (s, 1 H, 4-H), 2.80 (q, 2 H, 6-CH_2, *J* = 7.5 Hz), 2.59 (q, 2 H, 5-CH_2, *J* = 7.6 Hz), 2.50 (s, 3 H, 2-CH_3), 2.15 (s, 3 H, acetylenic CH_3), 1.19 (t, 3 H, 5-CH_3, *J* = 7.6 Hz), 1.16 (t, 3 H, 6-CH_3, *J* = 7.5 Hz); mass spectrum, *m/e* 264/266. Anal. Calcd for $C_{14}H_{17}Br$: C, 63.41; H, 6.46; Br, 30.13. Found: C, 63.29; H, 6.45; Br, 30.23.

1-(3-Chloro-2,5,6-trimethylphenyl)propyne (9). A solution of 3-chloro-2,5-dimethylthiophene 1,1-dioxide[8] (1.79 g, 10 mmol) in *t*-BuOH (20 mL) was refluxed for 5 days (120 h). Removal of the solvent followed by column chromatography afforded **9** (0.72 g, 75%), which crystallized from ethanol, mp 49–51 °C: IR 2240 cm^{-1} ($C\equiv C$ stretch); ^{1}H NMR ($CDCl_3$) δ 7.06 (s, 1 H, 4-H), 2.47 (s, 3 H, 2-CH_3), 2.34 (s, 3 H, 6-CH_3), 2.21 (s, 3 H, 5-CH_3), 2.16 (s, 3 H, acetylenic CH_3); mass spectrum, *m/e* 192/194. Anal. Calcd for $C_{12}H_{13}Cl$: C, 74.80; H, 6.80; Cl, 18.40. Found: C, 74.74; H, 6.78; Cl, 18.38.

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Registry No. **1**, 114532-51-3; **3**, 114532-52-4; **6**, 114532-53-5; **7**, 114532-54-6; **8**, 114532-55-7; **9**, 114532-56-8; 3-bromo-2,5-dimethylthiophene 1,1-dioxide, 83173-98-2; 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide, 114532-57-9; 3-bromo-5-ethyl-2-methylthiophene 1,1-dioxide, 83173-99-3; 3-chloro-2,5-dimethylthiophene 1,1-dioxide, 70061-41-5.

Supplementary Material Available: Tables of coupled ^{13}C coupling constants and chemical shifts for compounds **3**, **7**, **8**, and **9** (4 pages). Ordering information is given on any current masthead page.

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(8) Usieli, V.; Gronowitz, S.; Andersson, I. *J. Organomet. Chem.* **1979**, *165*, 357. The yield was increased to 70% by using the method of: Tillborg, W. J. M.; Smael, P.; Visser, J. P.; Kouvenhoven, C. G.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 85.

The Critical Hydrophobic Interaction Concentration for Aqueous Tetra-*n*-butylammonium Bromide

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In the course of our studies of medium effects on organic reactions in highly aqueous binary mixtures,[1] we recently defined the "critical hydrophobic interaction concentration" (chic)[2] for a hydrophobic cosolvent in aqueous solution. This is the concentration where the hydrophobic hydration shells of the cosolvent start to overlap appreciably, leading to cooperative association to small clusters. On the basis of kinetic[2] and spectroscopic[3] evidence, the chic for *t*-BuOH is 1.4 ± 0.3 m at 25 °C, in reasonable accord with Grunwald's isodelphic/lyodelphic analysis[4] of the solution thermodynamics of *t*-BuOH–H_2O. Since one may view the chic as an extension to small hydrophobic solutes of the concept of the critical micelle concentration (cmc)[5] for surfactant molecules, an endeavor was made to obtain evidence for a chic for *n*-Bu_4NBr. This

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(2) Haak, J. R.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1986**, *108*, 1705.

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(4) Grunwald, E. *J. Am. Chem. Soc.* **1984**, *106*, 5414.

(5) For a discussion of the cmc concept, see: Lindman, B.; Wennerström, H. *Top. Curr. Chem.* **1980**, *87*, 1.

(6) For a brief review of the unconventional hydration properties of tetraalkylammonium salts, see: Franks, F. In *Water. A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 2., Chapter 1.

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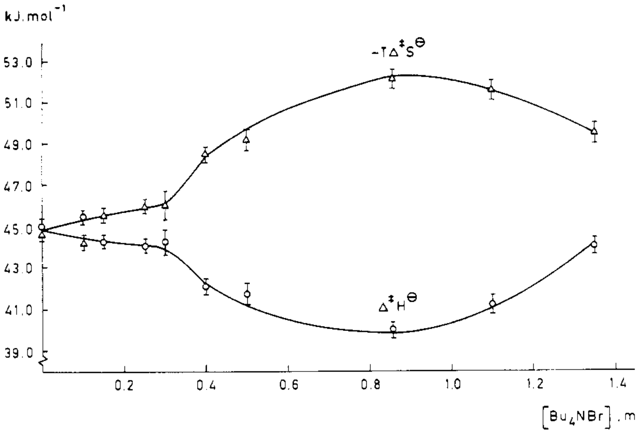


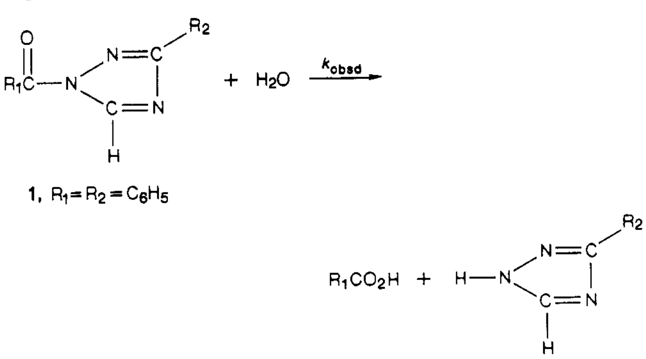
Figure 1. Plots of $\Delta^{\ddagger}H^{\ominus}$ and $-T\Delta^{\ddagger}S^{\ominus}$ vs [n-Bu_4NBr] for the neutral hydrolysis of 1 at 25 °C.

Table I. Pseudo-First-Order Rate Constants and Isobaric Activation Parameters for the Neutral Hydrolysis of 1 in Aqueous Electrolyte Solutions at 25 °C

electrolyte	conc, mol·kg^{-1}	$10^5 k_{obsd}$, s^{-1}	$\Delta^{\ddagger}H^{\ominus}$, kJ·mol^{-1}	$\Delta^{\ddagger}S^{\ominus}$, J·mol^{-1} K^{-1}
		127.4	45.0 ± 0.3	−149 ± 1
n-Bu_4NBr	0.10	119.6	45.5 ± 0.2	−148 ± 1
n-Bu_4NBr	0.15	115.3	44.2 ± 0.2	−153 ± 1
n-Bu_4NBr	0.25	103.5	44.0 ± 0.2	−154 ± 1
n-Bu_4NBr	0.30	97.5	44.2 ± 0.6	−154 ± 1
n-Bu_4NBr	0.40	85.3	42.1 ± 0.1	−163 ± 1
n-Bu_4NBr	0.50	73.8	41.7 ± 0.5	−165 ± 2
n-Bu_4NBr	0.86	45.4	40.0 ± 0.3	−175 ± 1
n-Bu_4NBr	1.10	33.4	41.2 ± 0.4	−173 ± 1
n-Bu_4NBr	1.35	26.5	44.0 ± 0.3	−166 ± 1
n-Bu_4NBr	1.80	17.4	45.0 ± 0.3	−166 ± 1
Me_4NBr	2.00	80.5	50.2 ± 0.2	−135 ± 1
CTAB	3×10^{-4}	123.5	46.8 ± 0.1	−144 ± 1
CTAB	5×10^{-4}	124.1	47.1 ± 0.3	−143 ± 1
CTAB	7.5×10^{-4}	124.7	46.8 ± 0.3	−144 ± 1
CTAB	11×10^{-4}	87.1	59.1 ± 0.4	−105 ± 1
CTAB	13×10^{-4}	68.0	59.7 ± 0.6	−105 ± 1
CTAB	18×10^{-4}	43.8	59.6 ± 0.2	−109 ± 1

electrolyte contains a hydrophobic, water-structure-making cation but is not able to form micelles.

Following the previous kinetic approach,[3] we have measured pseudo-first-order rate constants (k_{obsd}) and isobaric activation parameters for the water-catalyzed hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (1) in aqueous solutions in the presence of 0–1.8 m n-Bu_4NBr.



1, $R_1 = R_2 = C_6H_5$

The mechanism of this reaction has been studied in some detail[7] and involves rate-determining water-catalyzed nucleophilic attack of water at the carbonyl group of the activated amide function. The data in Table I show that

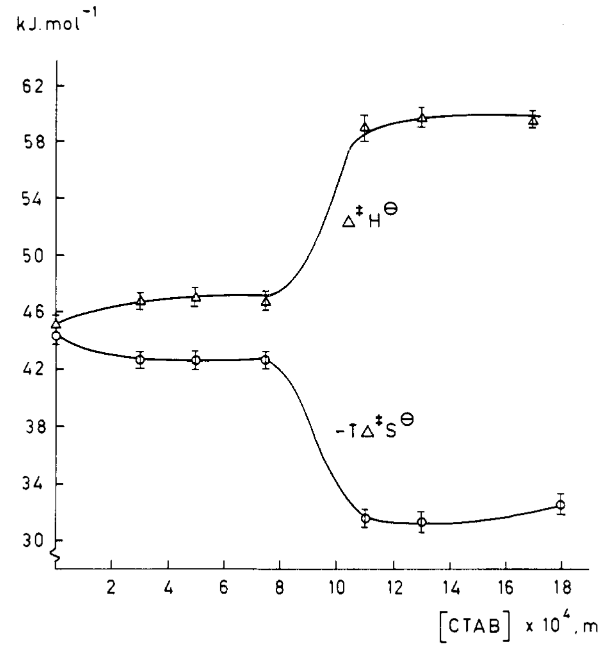


Figure 2. Plots of $\Delta^{\ddagger}H^{\ominus}$ and $-T\Delta^{\ddagger}S^{\ominus}$ vs [CTAB] for the neutral hydrolysis of 1 at 25 °C.

k_{obsd} decreases continuously with increasing concentration of n-Bu_4NBr. Plots of $\Delta^{\ddagger}H^{\ominus}$ and $-T\Delta^{\ddagger}S^{\ominus}$ vs [n-Bu_4NBr] (Figure 1) show the usual enthalpy/entropy compensatory effects, similar to those found in water-rich solutions containing a hydrophobic cosolvent like t-BuOH.[1,8] However, we note that significant changes in $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ set in only above 0.3 m n-Bu_4NBr. We contend that this threshold concentration is the chic for n-Bu_4NBr at 25 °C. If the hydrogen-bond network in the aqueous solution is characterized[4] by a single microscopic variable, α, and m_2 is the molality of n-Bu_4NBr, then $\delta\alpha/\delta m_2$ changes sign at the chic since there is no longer sufficient water for building up unperturbed hydration shells, particularly for the hydrophobic cation. As discussed by Grunwald,[4] interference of the hydration shells can only be avoided if $m_2 < 1/V_x$, where V_x is the "excluded volume", which equals about 8 times the volume of the hydration shells.[9] Rö diffraction data[10,11] for the tetra-n-butylammonium fluoride hydrate indicate that the average number of waters in the cosphere of each n-Bu moiety is 17. For the bromide ion[12] this number may be taken as 8, leading to $V_x = (8 \times 76)/55.5 = 11$ L mol^{-1}. Thus, the chic for n-Bu_4NBr will be $1/V_x = 0.1$ m. This value is in reasonable agreement with the kinetically obtained value of 0.3 m, taking into account the use of somewhat arbitrary hydration numbers,[13] the approximations in the calculation and the fact that the hydrolysis reaction will probably not respond to initially small overlap of hydration shells.

We compare the results for neutral hydrolysis of 1 in aqueous n-Bu_4NBr solutions with those for hydrolysis in

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(13) Compare: Belch, A. C.; Berkowitz, M.; McCammon, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1755.

the presence of the surfactant cetyltrimethylammonium bromide (CTAB, cmc 9 × 10^{-4} m, 25 °C). Rate constants and activation parameters are listed in Table I. As anticipated,[14] the rate of hydrolysis is retarded upon binding of 1 to the CTAB micelles. Most likely the reduced micropolarity in the Stern region of the micelles should be invoked to explain the rate inhibition.[14] Plots of $\Delta^{\ddagger}H^{\ominus}$ and $-T\Delta^{\ddagger}S^{\ominus}$ as a function of [CTAB] are depicted in Figure 2. Largely compensatory changes set in around the cmc, but, interestingly, the signs of these changes are *opposite* to those found for n-Bu_4NBr above the chic. In order to understand this difference, we note that the micellar surface may be apprehended as a concentrated electrolyte solution[15] as reflected, inter alia, in the reduced dielectric constant in the Stern region ($\epsilon \sim 32$).[16] As shown in Figure 1, the changes in $\Delta^{\ddagger}H^{\ominus}$ and $-T\Delta^{\ddagger}S^{\ominus}$ reverse their sign above the so-called "magic mole fraction" (ca. 0.85 m) for aqueous n-Bu_4NBr, and this tendency extents to 1.8 m n-Bu_4NBr. Unfortunately, no reliable activation parameters could be determined beyond this concentration because of phase separation. Therefore, $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ were measured in 2.00 m aqueous Me_4NBr (Table I) and, indeed, at this high electrolyte concentration both $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ are *larger* than in pure water in accord with the results for the hydrolysis in the Stern region of the CTAB micelles.

On the basis of the present kinetic data, the difference between aqueous solutions of n-Bu_4NBr and CTAB as reaction media can be conceived as follows. At the low concentrations of CTAB below the cmc, reaction rates hardly respond to the presence of the electrolyte. At the cmc, micelles are being formed which bind the substrate effectively.[18] The substrate then reacts in a relatively concentrated electrolyte solution at micellar binding sites of reduced micropolarity, and the rate constants are substantially reduced. In the 0–1.8 m aqueous n-Bu_4NBr solutions no micelles are formed and there is no critical concentration for the initiation of rate inhibition. Instead the rate constants decrease gradually as a result of changes in hydration effects operating on the activation process. However, there is a threshold concentration for the outset of large changes in $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ which reflects overlap of hydration shells, particularly those of the hydrophobic cations. This concentration is the chic. The activation parameters then pass through extrema at ca. 0.85 m. At still higher concentrations of n-Bu_4NBr the solutions are loosing the characteristics of typically aqueous media as dominated by the presence of extensive, three-dimensional hydrogen-bond networks. The hydrolysis then proceeds in a concentrated electrolyte solution, and the rates are more and more governed by changes in $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ which are opposite in sign to those at the lower concentrations of n-Bu_4NBr.

Experimental Section

Materials. Tetra-n-butylammonium bromide and tetramethylammonium bromide were obtained from Janssen Chimica and Fluka, respectively, and were used as such. Cetyltrimethylammonium bromide (Merck) was purified by using standard procedures.[19] 1-Benzoyl-3-phenyl-1,2,4-triazole (1) was prepared as described previously.[2,7] Demineralized water (distilled twice in an all-quartz unit) was used throughout.

Kinetic Measurements. These were performed as described previously.[2,7] All pseudo-first-order rate constants (in triplicate; in the temperature range 20–40 °C) were reproducible to within 1%. A Perkin-Elmer λ5 spectrophotometer, equipped with a Perkin-Elmer 3600 data station was employed.

Acknowledgment. We thank Dr. J. R. Haak for useful discussions.

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(14) Attempts to measure the chic via the temperature dependence of the Dimroth–Reichardt solvent parameter $E_T(30)$[3] failed because n-Bu_4NBr precipitated in the alkaline solutions.

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(18) Previously,[15] we found $K = 1.4 \times 10^5$ M^{-1}, where K is the substrate–micelle association constant divided by the aggregation number of the CTAB micelles.

(19) Duynstee, E. F. J.; Grunwald, E. *J. Am. Chem. Soc.* **1959**, *81*, 4540.

Equilibria among Anions of α-Hydroxy β-Diketones and α-Ketol Esters

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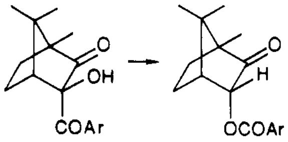
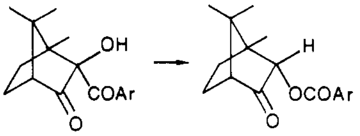
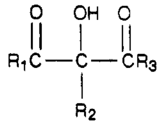
We have reported[1] thermal and base-catalyzed rearrangements of α-hydroxy β-diketones to α-ketol esters. Quantitative isomerizations of compounds **1a** to **2a**, of **1b** to **2b**, and of related compounds in the bicyclo[2.2.2]octane series resulted after 1 min at 200 °C or 10 min at room temperature in 5 × 10^{-3} N potassium hydroxide in methanol. Slower rearrangement of diacetylmethylcarbinol (**3a**) to acetoin acetate (**4a**) was also observed.



1a **2a**

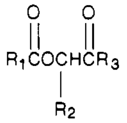


1b **2b**



$$R_1\overset{O}{\overset{\|}{C}}-\underset{R_2}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}R_3$$

3



$$R_1\overset{O}{\overset{\|}{C}}O\underset{R_2}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}R_3$$

4

a, $R_1 = R_2 = R_3 = CH_3$
b, $R_1 = R_3 = C_6H_5$, $R_2 = H$
c, $R_1 = R_3 = C_2H_5$, $R_2 = CH_3$
d, $R_1 = CH_3$, $R_2 = R_3 = C_6H_4CH_2$
e, $R_1 = C_6H_5$, $R_2 = R_3 = CH_3$
f, $R_1 = R_2 = CH_3$, $R_3 = C_6H_5$
g, $R_1 = R_3 = CH_3$, $R_2 = C_6H_5$

Three examples of thermal rearrangements of diacyl carbinols had been reported earlier. In 1936 Blatt and Hawkins[2] obtained α-hydroxyacetophenone benzoate (**4b**) from distillation of dibenzoylcarbinol (**3b**), a result which was repeated by Karrer et al.[3] in 1950; these authors also

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0022-3263/88/1953-3355$01.50/0