tert-butylcyclohexanone show almost the same catalytic effect.

In addition, if we consider only the straight chain carbons as a first approximation, a *tert*-butyl group corresponds to two carbon atoms and a *tert*-amyl group to three carbon atoms. Using this approximation, we find, on plotting log (k^{Ψ}/k^{0}) as a function of the number of "apparent" carbon atoms in the substituent, that a similar energetic increment per methylene is found as in the series of aliphatic ketones.

The results which we have obtained confirm the initial hypothesis that hydrophobic substances are solubilized in the interior of the micelle, with the hydrophobic chain or the ring oriented between the detergent carbon chains, so that the functional group is located near the surface.

The study of aromatic ketones should permit us to verify this last point: the work of Fendler et al.[19] has shown that aromatic molecules such as acetophenone are bound in the Stern layer of various surfactants. We should thus find only a small catalytic effect with benzaldehyde and acetophenone. The results are in agreement with this prediction $k^{\Psi}/k^{0} = 1.4$ for benzaldehyde and 1.5 for acetophenone.

In contrast, acetylcyclohexane gives rise to a much larger catalytic effect (3.7-fold) included between those for 2-hexanone and 2-heptanone, implying a behavior similar in the interior of the micelle.

A plausible explanation for our results is that the hydrophobic interactions of these ketones serve to orient the ketone in the micelle such that the carbonyl group is in a favorable orientation for transition state stabilization of the incipient positive charge by the negative charges on the micelle. For the ketones with carbon chains of $n > 4$, additional carbons may give rise to greater hydrophobic bonding with the micelle but apparently have no effect on the orientation of the ketone. Thus, the additional hydrophobic interactions stabilize both the initial state and the transition state equally and no further rate increase is observed.

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Registry No.—CH_3COCH_3, 67-64-1; $CH_3COCH_2CH_3$, 78-93-3; $CH_3CO(CH_2)_2CH_3$, 107-87-9; $CH_3CO(CH_2)_3CH_3$, 591-78-6; $CH_3CO(CH_2)_4CH_3$, 110-43-0; $CH_3CO(CH_2)_5CH_3$, 111-13-7; $CH_3CO(CH_2)_8CH_3$, 112-12-9; $CH_3COCH_2C(OH)(CH_3)_2$, 123-42-2; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; cyclononanone, 3350-30-9; 4-methylcyclohexanone, 589-92-4; 4-ethylcyclohexanone, 5441-51-0; 4-*tert*-butylcyclohexanone, 98-53-3; 4-*tert*-amylcyclohexanone, 16587-71-6.

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Cyclopropane Formation as Evidence for a 3-Halo 1,4-Zwitterion

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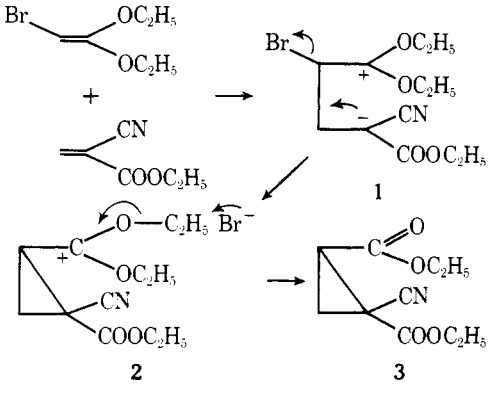
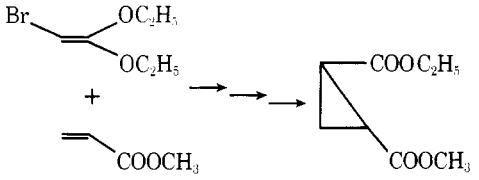
Recent investigations of the synthesis of cyclobutane derivatives by reaction of electron-rich olefins with electron-poor olefins have focused on 1,4-zwitterions as the key intermediates in these reactions.[1] As additional evidence for them, we now report that 1,4-zwitterions carrying a 3-halo substituent form cyclopropanes.

1,1-Diethoxy-2-bromoethylene reacts with ethyl α-cyanoacrylate at 0 °C during 1 h to form diethyl 1-cyano-1,2-cyclopropanedicarboxylate (**3**). The initially formed 1,4-



zwitterion **1** undergoes intramolecular displacement of bromide ion to form the dialkoxycarbenium ion **2**, which in turn undergoes dealkylation to form cyclopropane **3** and ethyl bromide.

Methyl acrylate reacts similarly with 1,1-diethoxy-2-bromoethylene to form ethyl methyl 1,2-cyclopropanedicarboxylate:



Methyl acrylate was much less reactive than methyl α-cyanoacrylate. At room temperature no reaction occurs when methyl acrylate and 1,1-diethoxy-2-bromoethylene are mixed in a 1/1 mol ratio. After heating the two compounds at 90 °C for 24 h in the presence of an inhibitor, only a trace of cyclopropane is detected by gas chromatography. The two compounds were heated without solvent in the presence of an inhibitor at 110 °C for 20 h to yield ethyl methyl 1,2-cyclopropanedicarboxylate in 50% yield. Under the same conditions, acrylonitrile gave a complex mixture of products.

In the absence of a 3-bromo substituent, analogous 1,4-zwitterions undergo ring closure to cyclobutane derivatives.[2,3] It is interesting that the 3-bromo substituent competes ef-

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fectively with a carbenium ion center at C-4; perhaps this is because bromide ion loss is irreversible, whereas cyclobutane formation is reversible.

Experimental Section

Commercial **ethyl α-cyanoacrylate** (Eastman 910 Adhesive) was distilled from phosphorus pentoxide (bp 43 °C (0.2 mm Hg)).[4]

1,1-Diethoxy-2-bromoethylene (bp 75 °C (8 mm Hg)) was obtained by dehydrobromination of 1,1-dibromo-2,2-diethoxyethane (**4**) as described by McElvain.[5] Dibromide **4** was synthesized by bromination of 2-bromo-1,1-diethoxyethane (**5**) with bromine and calcium carbonate in carbon tetrachloride. The synthesis of **5** is described by Bedoukian[6] starting from vinyl acetate.

Diethyl 1-Cyano-1,2-cyclopropanedicarboxylate (3). 1,1-Diethoxy-2-bromoethylene, 1.9 mL (10 mmol), was dissolved in dichloromethane at 0 °C in the presence of a trace of diphenylpicrylhydrazyl (DPPH) to prevent adventitious polymerization. Freshly distilled ethyl α-cyanoacrylate, 1 mL (10 mmol), was added with stirring, and the mixture was stirred for 1 h. The mixture was distilled. The first fraction contained ethyl bromide, as shown by NMR spectroscopy. Cyclopropane (**3**), 1 g (40–50% yield), was collected at 115–120 °C (1 mm Hg): IR 3100 (cyclopropane), 2250 (CN), 1735 (ester), 856 cm^{-1} (cyclopropane); NMR δ 4.25 (quadruplet, $-COO\mathbf{CH_2}CH_3$), 2.60 (two doublets, >**CH**COO–), 2.2–1.7 (multiplet, $-\mathbf{CH_2}-$), 1.30 (two triplets, $-CH_2\mathbf{CH_3}$); mass spectrum 184 ($-C_2H_3$), 166 ($-H_2O$), 137 (–HCO), 111 (–CN), 83 ($-C_2H_4$).

The IR and NMR correspond to those given by Saegusa and co-workers for dimethyl 1-cyanocyclopropane-1,2-dicarboxylate. The mass spectra further corroborate the assigned structure.[8]

Anal. Calcd: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.74; H, 6.20; N, 6.68.

Ethyl Methyl 1,2-Cyclopropanedicarboxylate. 1,1-Diethoxy-2-bromoethylene, 0.8 mL (5 mmol), was mixed with 2.7 mL (30 mmol) of methyl acrylate in a glass tube. A trace of DPPH was added. The tube was sealed under vacuum and heated at 110 °C for 20 h. The mixture was distilled, and 0.4 g (50% yield) of ethyl methyl 1,2-cyclopropanedicarboxylate, bp 70 °C (0.4 mm Hg), was collected:

Anal. Calcd: C, 55.80; H, 7.03. Found: C, 55.85; H, 7.08.

IR 1735 (ester), 860 cm^{-1} (cyclopropane); NMR δ 4.15 (quadruplet, $-COO\mathbf{CH_2}CH_3$), 3.70 (singlet, $-COO\mathbf{CH_3}$), 2.4–1.5 (multiplet, ring protons), 1.3 (triplet), $-CH_2\mathbf{CH_3}$); mass spectrum 141 (–MeO), 127 (–EtO), 113 (–COOMe), 98 (–Me).

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Registry No.—**3**, 10432-27-6; **4**, 761-17-1; **5**, 2032-35-1; ethyl α-cyanoacrylate, 7085-85-0; 1,1-diethoxy-2-bromoethylene, 42520-11-6; ethyl methyl 1,2-cyclopropanedicarboxylate, 878-14-8; methyl acrylate, 96-33-3.

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Facile Synthesis of 2′-Amino-2′-deoxyribofuranosyl Purines

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Analogues of the common ribonucleosides containing an amino group at the 2′ position have valuable potential for the investigation of chemical or biochemical problems in which the 2′ moiety is involved. Derivatization at the amino group can lead to the synthesis of antibiotics[1] and affinity labels.[2] The 2′-amino analogue of guanosine (**5**) has been isolated as an antibiotic[3] from *Enterobacter sp.*

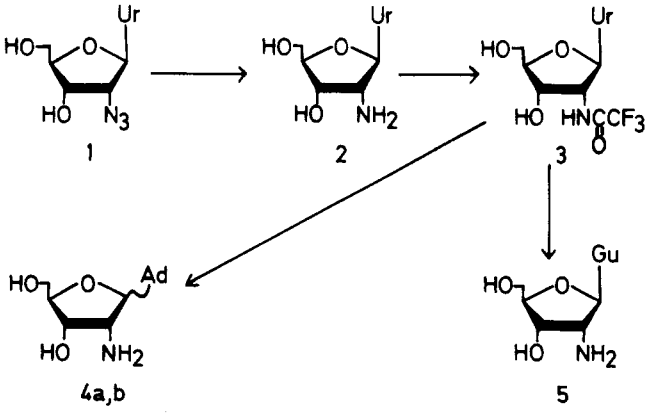
A facile synthesis of 2′-amino-2′-deoxyuridine and -cytidine via a 2,2′-cyclonucleoside has been described.[4] On the other hand, the synthesis of the corresponding purine nucleosides has been fraught with difficulty. The methods of synthesis have involved both transformations of 2′,3′-anhydronucleosides[5] or arabinonucleosides[6,7] as well as condensation of derivatives of a suitable amino sugar with a purine base.[8] All of these methods are rather lengthy and total yields are not satisfactory in most cases.

A more convenient synthesis of 2′-azido-2′-deoxy- and 2′-amino-2′-deoxyribofuranosyl purines from 2′-azido-2′-deoxyuridine,[4] which is readily available from uridine, was recently developed[9] in our laboratory. It utilizes the sugar moiety derived from the pyrimidine nucleoside for condensation with the purine bases. In order to simplify the synthesis further, we were led to investigate a direct transglycosylation reaction with purine bases instead of isolating and condensing the sugar moiety separately. Recently, we reported such transglycosylation reactions using trimethylsilyl trifluoromethanesulfonate[10] (TMSTF) as Friedel–Crafts catalyst for the synthesis of 3′-azido-2′,3′-dideoxyribofuranosyl purines.[11] The utility of the transglycosylation reaction was also demonstrated for the synthesis of unmodified purine ribonucleosides.[11,12]

Here we describe the success of this approach for the synthesis of 2′-amino-2′-deoxyadenosine (**4b**) and -guanosine (**5**) in much better yields than previously obtainable, using 2′-amino-2′-deoxyuridine (**2**) as starting material. An attempted transglycosylation reaction with 2′-azido-2′-deoxyuridine (**1**), on the other hand, failed.

2′-Azido-2′-deoxyuridine[4,9] (**1**) obtained from uridine in a yield of 50% is converted to 2′-amino-2′-deoxyuridine (**2**) by reduction with triphenylphosphine.[13] After purification over a Dowex 50 column, **2** was isolated in a yield of 91%. To protect the 2′-amino function, we selected the trifluoroacetyl group

Scheme I



Ur = uracil-1-yl, Ad = adenin-9-yl, Gu = guanin-9-yl, a = α anomer, b = β anomer.

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