yields were determined for highly degassed samples sealed in Pyrex ampoules using a Perkin-Elmer MPF-2A spectrophotometer. Lifetimes for acetophenone and benzophenone were measured by pulsing the sample with the filtered output (Corning CS 7-60) of a Xenon Corp. 437A nanopulser and monitoring the transient emission at right angles with an RCA 1P28 photomultiplier through a Corning CS 3-74 filter. A Princeton Applied Research TDH-9 waveform eductor was used to average 100 or more decay transients and the output was recorded on an X–Y recorder. The single photon counting apparatus is similar to that described by Ware.[35]

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Registry No.—Acetophenone, 98-86-2; benzophenone, 119-61-9.

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Thermal Isomerizations of Dimethyl 3,4-Diphenylmuconates

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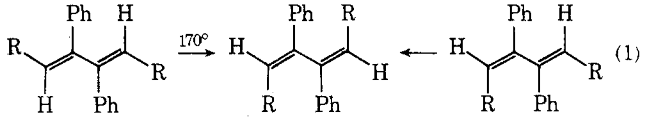
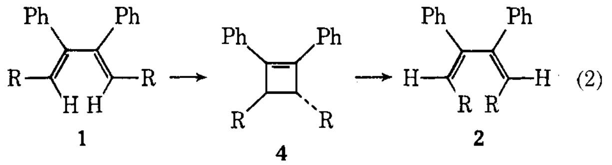
The isomerization of dimethyl (*E*,*E*)-3,4-diphenylmuconate to its *Z*,*Z* stereoisomer is shown to proceed through an isolable cyclobutene intermediate with the stereochemistry predicted by orbital symmetry rules. Rate constants and activation parameters have been obtained for the individual steps in the reversible isomerizations.

Several years ago one of us was led to a reinvestigation of the structure and reactivity of the diastereomeric dimethyl 1,3-diphenylbicyclobutane-2,4-dicarboxylates by the violations of orbital symmetry control suggested by the initial study of these compounds.[1] The major discrepancies have been resolved by subsequent work,[2,3] but the thermal interconversions of the dimethyl 3,4-diphenylmuconates **1**, **2**, and **3** which were reported[1,3] still invited explanation (eq 1, R = CO_2Me).



1 (*E*,*E*) 2 (*Z*,*Z*) 3(*E*,*Z*)

The thermal isomerization of **1** to **2** was originally observed by D'yakonov and coworkers,[1] and the conversion of **3** to **2** was postulated by them[3] to account for the observation that the thermolysis of the exo,exo- and endo,endo-substituted bicyclobutanes produced **2**, rather than **3** as predicted by orbital symmetry theory. The conversion of **1** to **2** could be accomplished by successive double-bond isomerizations involving **3** as an intermediate or by a conrotatory ring closure of **1** to cyclobutene **4** and subsequent conrotatory opening to **2** (eq 2, R = CO_2Me). The former pathway is consistent with the postulated conversion of **3** to **2**, while the latter has ample precedent in the work of Doorakian and Freedman.[4] The isomerization of **3** to **2** might proceed by a double-bond isomerization or by way of a disrotatory ("forbidden") opening of the cis isomer of **4**.

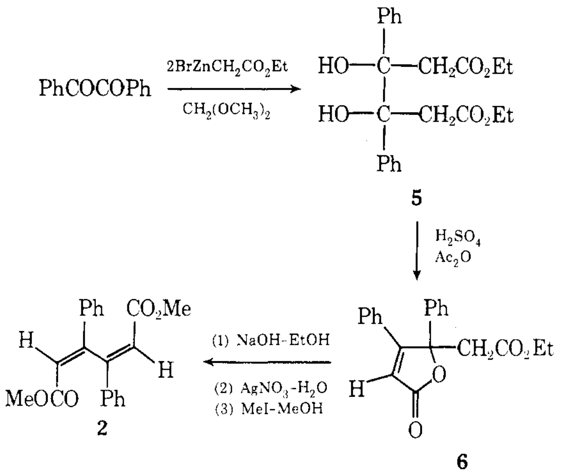


(2)

To elucidate the mechanisms of these interconversions a study of their kinetics was undertaken, and we are now able to report the results of this investigation.

As an alternative to the very inefficient synthesis *via* the bicyclobutanes,[1,2] the dimethyl 3,4-diphenylmuconates were prepared using the procedure of Beschke[5] (Scheme I).

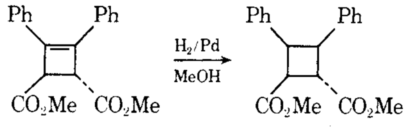
Scheme I



One significant modification of the original method was the use of dimethoxymethane as the solvent for the double Reformatsky reaction with preformed organozinc reagent.[6] This resulted in greatly improved yields and in the formation of *meso*-**5** as the only isolable product. The assignment of *Z,Z* stereochemistry to the muconate formed in this series of reactions is based on the fact that the nmr spectrum of the product indicates it is symmetric (*E,E* or *Z,Z*) and the assumption that the necessarily *Z* substitution of the double bond in lactone **6** is preserved.

The preparation of the *E,E* and *E,Z* stereoisomers, **1** and **3**, was accomplished by photochemical isomerization of **2**. Irradiation of a methanol solution of **2** at 254 nm produced a photostationary-state mixture of **1**, **2**, and **3** in a ratio of 24:30:46.[7] Separation by chromatography and fractional crystallization provided the (*E,E*)- and (*E,Z*)-muconates, **1** and **3**, needed for the study.

The thermal isomerization of **1** at 130–150° was followed by proton nmr in $CDCl_3$. It was immediately obvious that an intermediate was being formed prior to the appearance of the *Z,Z* stereoisomer, **2**. The appearance of the methine protons of the intermediate as a singlet at δ 4.18 suggested that it might be the proposed cyclobutene, **4**. That this was in fact the case was shown by its isolation and catalytic hydrogenation to the known dimethyl neotruxinate, **7**.[8]



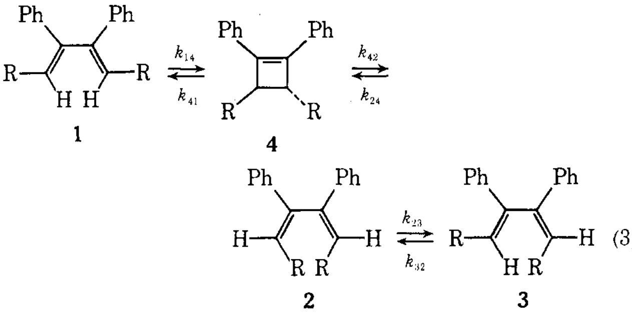
4 **7**

Table I
Rate Constants for the Interconversions of 1, 2, 3, and 4[a]

Rate constant	130.1°	139.4°	149.8°
k_{14}	20.8 ± 0.1	42.7 ± 0.6	93 ± 4
k_{41}	49 ± 2	99 ± 5	204 ± 10
k_{42}	15.9 ± 0.4	37.6 ± 1.1	94 ± 3
k_{24}	0.5 ± 0.1	1.5 ± 0.3	3.5 ± 0.1
k_{23}	1.9 ± 0.2	2.4 ± 0.5[b]	3.2 ± 0.4[c]
k_{32}	6.4 ± 0.3	13.5 ± 0.6[b]	25.1 ± 0.7[c]

[a] Rate constants in $sec^{-1} \times 10^6$. [b] $T = 138.9°$. [c] $T = 149.0°$.

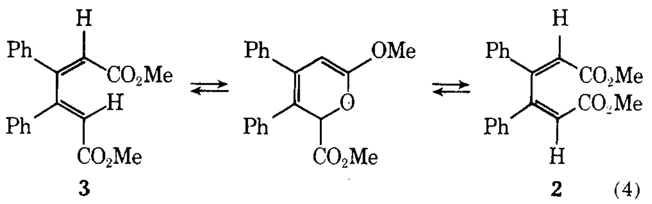
When the isomerization of **1** to **2** was followed to near equilibrium, small amounts of the *E,Z* isomer, **3**, were detectable. In order to ascertain the source of **3**, it was thermolyzed under identical conditions. The initial and only product detected for 4 half-lives of its disappearance was the *Z,Z* isomer, **2**, indicating the isomerizations can be described by eq 3 (R = CO_2Me). The equilibrium mixture at 140° consisted of the compounds **1**, **4**, **2**, and **3** in a ratio of approximately 7:3:75:15.



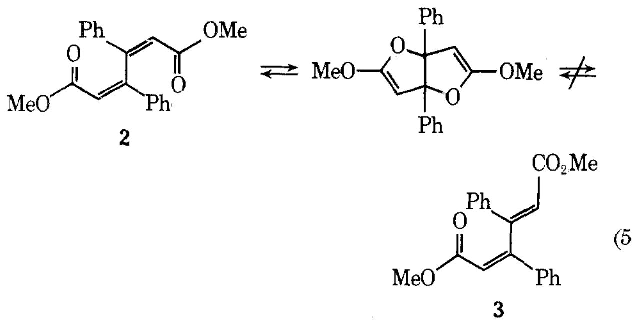
(3)

In order to characterize further this series of reactions, the nmr data were analyzed to obtain the rate constants shown in Table I. Because of the large relative errors in k_{23} and k_{24}, it was possible to calculate accurate thermodynamic constants from differences in activation parameters only for the equilibrium between **1** and **4**: $\Delta H = 1.3 \pm 0.5$ kcal/mol, $\Delta S = 1.4 \pm 1.2$ eu, $\Delta G_{415} = 0.7$ kcal/mol. It is apparent from these data that the strain between and the hindered rotation of the substituents on the butadiene skeleton in **1** nearly compensate for the strain and loss of diene rotation in cyclobutene **4**. The normally much greater stability of the butadiene tautomer is exemplified by the unsubstituted butadiene–cyclobutene system, where ΔH_{298} = 11.2 kcal/mol, ΔS_{298} = −3.6 eu, and ΔG_{298} = 12.3 kcal/mol.[9] Qualitative consideration of the data for the equilibrium between the cyclobutene, **4**, and the (*Z,Z*)-muconate, **2**, indicates that the latter's greater stability is due both to an increase in entropy and to a decrease in enthalpy of formation, *i.e.*, less strain and freer rotation of the substituents.

The kinetic parameters for the isomerization of the (*E,Z*)-muconate, **3**, to the (*Z,Z*)-muconate, **2**, are somewhat unusual for a double-bond isomerization: $\Delta H^* = 23.5 \pm 3.6$ kcal/mol, $\Delta S^* = -25 \pm 9$ eu. For comparison, the corresponding parameters for methyl *cis*-cinnamate are ΔH^* = 40.2 kcal/mol and $\Delta S^* = -14$ eu.[10] The parameters are even less consistent with an alternative mechanism of isomerization through a pyran intermediate as shown in eq 4. Such intermediates have been reported in the isomerizations of 1,4-diacylbutadienes,[11] but even less negative entropies of activation are likely for this reaction.[12] A mecha-

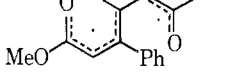


(4)



(5)

nism involving a dihydrofurofuran[11] (eq 5) might account for the large negative entropy of activation, but a concerted raction to form this intermediate from the (*E*,*Z*)-muconate, **3**, seems sterically impossible. Thus the isomerization of **2** ⇄ **3** appears most likely to occur by simple twisting about one of the double bonds going through the intermediate or particularly well-stabilized transition state, **8**, in which the rotational freedom of several of the substituents is lost.



8

Experimental Section

Infrared spectra were measured on a Perkin-Elmer 137 spectrophotometer, ultraviolet spectra were recorded on a Bausch and Lomb Model 505, and nmr spectra were determined on Varian A-60A and Perkin-Elmer R-12B spectrometers. Melting points are uncorrected.

***meso*-Diethyl 3,4-Dihydroxy-3,4-diphenyladipate (5).** A mixture of 32.5 g (0.50 g-atom) of granular zinc and 150 ml of freshly purified dimethoxymethane was heated to reflux in a 1-l., three-necked flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. To the stirred mixture 83.5 g (0.50 mol) of ethyl bromoacetate was added dropwise over 30 min. After the exothermic reaction which accompanies the addition subsided, the mixture was refluxed 1 additional hr. To the resulting solution 21.0 g (0.10 mole) of benzil in 200 ml of dimethoxymethane was added over a period of 1 hr, and the mixture was refluxed for 2 hr more. After addition of 200 ml of ice water, the mixture was transferred to a separatory funnel containing 200 ml of ether and 100 ml of 6 *N* sulfuric acid. After shaking of the mixture well, the aqueous layer was removed, and the organic layer was filtered to remove the product. The filtrate was concentrated to provide more product. The crude product was dissolved in hot benzene, which on trituration with ethanol and cooling gave 38.7 g (90%) of meso diester, **5**: mp 168–170° (lit.[5] mp 168°); ir (KBr) 3450, 1705, 1190, 1150, 752, 742, 700 cm^{-1}; nmr ($CDCl_3$, TMS) δ 7.1–8.1 (m, 10 H, Ar H), 4.55 (s, 2 H, -OH), 3.78 (q, J = 7 Hz, 4 H, -OCH_2CH_3), 3.35 (d, J = 16 Hz, 2 H), 2.27 (d, J = 16 Hz, 2 H), 0.92 ppm (t, J = 7 Hz, 6 H, -OCH_2CH_3).

Ethyl 2,3-Diphenylcrotonolactone-3-acetate (6). The lactone was prepared as described by Beschke[5] in 81% yield: mp 90–92° (lit.[5] mp 94°); nmr (CCl_4, TMS) δ 7.1–7.4 (m, 10 H), 6.24 (s, 1 H), 4.01 (q, J = 7.4 Hz, 2 H), 3.44 (d, J = 15.0 Hz, 1 H), 3.25 (d, J = 15.0 Hz, 1 H), 1.12 ppm (t, J = 7.4 Hz, 3 H).

Dimethyl (*Z,Z*)-3,4-Diphenylmuconate (2). The dimethyl ester was prepared *via* the sodium and silver salts of the diacid as described by Beschke for preparing the diethyl ester.[5] After recrystallization from methanol the ester (83% yield from **6**) had a melting point of 114–116°: lit.[1] mp 114°; uv (CH_3OH) λ_{max} 295 nm (ϵ 23,700); ir (KBr) 1710, 1630, 1610, 1185, 1160, 775, 682 cm^{-1}; nmr (CCl_4, TMS) δ 7.30 (m, 10 H), 6.44 (s, 2 H), 3.56 ppm (s, 6 H).

Dimethyl (*E,E*)-3,4-Diphenylmuconate (1). A 1% solution of **2** in spectral grade methanol was irradiated for 5 hr at 253.7 nm in a quartz tube in a photochemical reactor (New England Ultraviolet Co. Model RPR-100). Evaporation of the solvent provided a mixture of **1**, **2**, and **3** in a ratio (nmr) of 24:30:46, respectively. The mixture was separated into two fractions by dry column chromatography on silica gel (500 g of Waters Associates No. 27850/g), developing with chloroform. Elution of the band at R_f ~0.75 provided the *E,E* diester: mp 157–159° (lit.[1] mp 152°) after recrystallization from methanol; uv (CH_3OH) λ_{max} 262 nm (ϵ 14,000); ir (KBr) 1700, 1590, 1580, 1180, 1150, 750, 690 cm^{-1}; nmr (CCl_4, TMS) δ 7.32 (m, 10 H), 5.70 (s, 2 H), 3.42 (s, 6 H).

Dimethyl (*E,Z*)-3,4-Diphenylmuconate (3). The fraction at R_f 0.3–0.6 from the above chromatography was eluted with methanol. Evaporation of the solvent provided an oil consisting of **2** and **3**. After several fractional crystallizations from chloroform and methanol, the (*E*,*Z*)-muconate, **3**, was obtained: mp 96–98°; nmr (CCl_4, TMS) δ 7.2–7.6 (m, 10 H), 6.29 (s, 1 H), 6.04 (s, 1 H), 3.20 (s, 3 H), 3.15 ppm (s, 3 H). This material was contaminated with 5% of the (*Z,Z*)-muconate (by nmr) which could not be removed by further recrystallizations. This material was, however, sufficiently pure for thermolysis since the program used for analysis of the data could allow for its presence (see below).

Dimethyl 1,2-Diphenylcyclobutene-*trans*-3,4-dicarboxylate (4). A solution of 300 mg of **2** in 2 ml of chloroform was sealed in a thick-walled tube under nitrogen and heated at 140° in an oil bath for 6 hr. The resulting mixture of **1**, **2**, and **4** (65:15:20 by nmr) was separated by dry-column and preparative thin-layer chromatography (silica gel–chloroform) to provide 22.5 mg of **4**: mp 77–78° after recrystallization from methanol–water; uv (CH_3OH) λ_{max} (ϵ) 227 (20,700), 293 (14,600), 305 nm (sh) (13,500); ir (KBr) 1725, 1430, 1238, 1222, 754, 688 cm^{-1}; nmr ($CDCl_3$, TMS) δ 7.4–7.0 (m, 10 H), 4.18 (s, 2 H), 3.70 (s, 6 H); mass spectrum (70 eV) *m/e* (relative intensity) 322 (46), 290 (79), 263 (100), 262 (71), 231 (54), 203 (45), 202 (56), 129 (40), 102 (55).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 72.49; H, 5.78. Found: C, 72.46; H, 5.51.

A sample of **4** in methanol was hydrogenated at atmospheric pressure using 10% palladium on charcoal as catalyst. Trituration of the filtered solution with water provided crystals which were recrystallized from methanol to provide dimethyl neotruxinate: mp 126–128° (lit.[8] mp 127°); nmr ($CDCl_3$, TMS) δ 7.10 (br, s, 10 H), 4.0–4.4 (m, 4 H), 3.78 (s, 3 H), 3.32 (s, 3 H).

Thermolyses of 1 and 3. Solutions of 40–60 mg of **1** or **3** in 0.4 ml of $CDCl_3$ were sealed in nmr tubes under nitrogen. The tubes were placed in a thermoregulated oil bath and withdrawn at regular intervals for analysis by proton nmr. The extent of reaction and product composition was determined from the relative areas of the respective methine proton signals (**1** at δ 5.85, **2** at 6.62, **3** at 6.10 and 6.25, and **4** at 4.18 ppm). Each peak was integrated ten times using a digital voltmeter connected to the spectrometer. The standard deviation of the average was typically 0.5% of the total integral. Three separate samples of **1** were thermolyzed at each of three temperatures, 130.1, 139.4, and 149.8 ± 0.2°. Twenty points were taken over periods of 24–120 hr, depending on the reaction temperature. The temperatures used for the thermolysis of **3** were 130.1, 138.9, and 149.0 ± 0.2°. As mentioned above, the samples of **3** used in the kinetic study contained 5–10% **2**.

Kinetic Analysis of Data. The data obtained from the thermolyses were analyzed for rate constants using the general curve-fitting program of Dye and Nicely.[13] The uncertainties quoted in Table I are standard deviations calculated by the program. The criterion of fit was a minimum weighted sum of squares of deviations of all dependent variables (concentrations). The differential equations used in the analysis of the thermolyses of **1** were

$$\begin{aligned} d[1]/dt &= k_{31}[3] - k_{13}[1] \\ d[2]/dt &= k_{32}[3] + k_{42}[4] - (k_{23} + k_{24})[2] \\ d[3]/dt &= k_{13}[1] + k_{23}[2] - (k_{31} + k_{32})[3] \end{aligned}$$

To simplify the calculations, k_{23} and k_{32} were set equal to the values determined independently from the thermolysis of **3**, and the concentration of **4** was set equal to 100 − ([1] + [2] + [3]). All concentrations were expressed as per cent of the total mixture.

For analysis of the data from the thermolysis of **3**, the differential equation used was $d[3]/dt = k_{23}[2] - k_{32}[3]$.

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Registry No.—**1**, 7576-89-8; **2**, 7577-43-7; **3**, 53432-82-9; **4**, 53432-83-0; **5**, 53432-84-1; **6**, 36126-37-1; **7**, 52305-39-2; dimethoxymethane, 109-87-5; ethyl bromoacetate, 105-36-2; benzil, 134-81-6.

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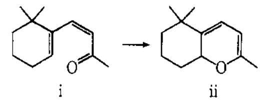

i ii

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Acylation of Vicinal Dianions. Formation of Products by Rearrangement and Proton Transfer

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The acylation of the vicinal dianions **1** and **20**, respectively derived by reductive metalation of benzophenone anil and *N*-(*p*-cyanobenzal)aniline, was examined in detail with ethyl chloroformate as the acylating agent. In the case of **1**, dimethylcarbamoyl chloride was used as well. In addition to the expected acylation at the benzylic and amine anionic sites, additional products were formed by rearrangement of the acyl group and/or proton transfer. In the case of **1**, these reactions, under certain conditions, led to triacylated semibenzene derivatives as a major product. Reaction of **20** was more complicated since the reaction products consisted of mono-, di- and triacylated derivatives. The reaction was studied by generating the individual monoanions formed as intermediates in the reaction. Proton transfer was more dominant in this reaction although migration of a carbethoxy group again occurred.

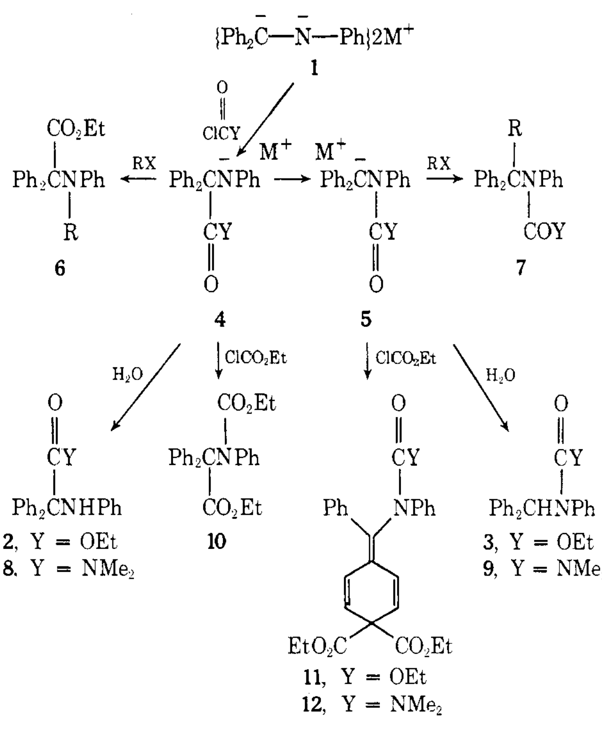
Ethyl chloroformate is a useful reagent for characterizing and functionalizing anionic species. Recently, in studies of two vicinal dianions,[1,2] some interesting deviations from the anticipated acylation were noted. This report describes these reactions which involved acyl group migration and/or proton transfer and outlines some of the factors affecting the extent of the side reactions.

Scheme I summarizes our earlier observations with ethyl chloroformate and the vicinal dianion **1** derived from benzophenone anil. Thus rearrangement of the initially formed anion **4** (Y = OEt) to **5** (Y = OEt) occurred as clearly indicated by the characterizing reactions of **4** and **5** shown in Scheme I.

This rearrangement proceeded with even greater facility with dimethylcarbamoyl chloride[3] as acylating agent. Indeed, the unrearranged anion **4** (Y = NMe_2) could only be detected under reaction conditions unfavorable to rearrangement (*i.e.*, diethyl ether as solvent, lithium as counterion).

Proton transfer was observed[1] during further acylation of the rearranged monoacylated anion **5** to produce the semibenzene derivative **11**. Again this same reaction occurred with dimethylcarbamoyl chloride to give **12**. In the case of **11** both spectral and chemical evidence supported the proposed structure (see Scheme II and Experimental Section), while structure **12** was based on the presence of four vinyl protons in the 5.8–6.8 region of the nmr spectrum and on the strong absorption band in the 320–340-nm region of the uv spectrum.[4]

Scheme I
Acylation of the Benzophenone Anil Dianion



The availability of a second vicinal dianion **20** derived from *N*-(*p*-cyanobenzal)aniline[2] prompted a comparison of its behavior toward ethyl chloroformate with that of **1**. This reaction proved quite complex. With 1 equiv of acylating agent both mono- and diacylated products **21** and **23** were isolated (see Scheme III). With 2 equiv, the additional N-monoacylated product **22**, a second diacylated derivative **24** and a triacylated compound **25** were also formed. The relative amounts of these products varied somewhat with reaction temperature (see Table I).