

equivalent amount of the acetylene, and 10 ml of benzene were heated at 320° for 1 day in sealed tubes. The products were distilled and the yields of aromatized adducts from phenylacetylene, ethyl propiolate, and propyne were 30, 21, and 7.0%, respectively. Some phthalic anhydride was produced in the reaction using ethyl propiolate. Column temperatures used, respectively, for the determination of the isomer ratios were 225, 200, and 125°. Isomer ratios (*ortho:meta*) were 3.4:1.0, 0.96:1.0 (diethyl phthalate and phthalic anhydride), and 1.0:3.2, respectively.

**Dimerization of I.**—Propyne and I did not condense when heated for 2 days at 215° and the chief product was dimerized I. When propyne was omitted, 1 day of heating at 215° converted I into a 57% yield of colorless liquid, bp 148–149° (0.5 mm). Nmr analysis showed vinyl protons centered about  $\tau$  3.6 (poorly defined), methylene protons centered about 5.8 (a pair of overlapping quartets), and the remaining protons in a band from 7.1 to 8.9. The integrated ratio of these three groups was 2.8:3.9:17, respectively (*cf.* 3:4:17 for a dimer structure). Characteristic infrared absorptions appeared at 1720 (nonconjugated ester), 1710 (conjugated ester), 1645 (nonconjugated alkene), and 1620  $\text{cm}^{-1}$  (conjugated alkene).

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_4$ : C, 71.02; H, 7.95. Found: C, 70.96; H, 7.90.

### Directive Effects in Acylation of Methyl Furan-2-carboxylate

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Acylation of methyl furan-2-carboxylate has been reported to give exclusively 5-acylation in spite of the expected deactivating effect at the 3 and 5 positions of the carbomethoxy grouping. Resonance arguments have been advanced to explain this unexpected result.<sup>1</sup> The acylation procedures reported have used an acid anhydride or an acid chloride along with a Lewis acid catalyst. With acid anhydrides stannic chloride<sup>2,3</sup> and ferric chloride<sup>4</sup> catalysts have been used. Ferric chloride is also used with the acid chloride.<sup>5</sup> Reported yields are usually in the 20–30% range.<sup>2</sup>

We have examined in detail the products from acylation of methyl furan-2-carboxylate with caproic anhydride and stannic chloride. The procedure of Kawabi, Suzui, and Iguchi<sup>2</sup> was followed. We found the products to be more complex than expected. The vpc trace of the crude product mixture showed three product range peaks in the height ratio 1.9:3.1:1 in order of increasing retention time. Distillation gave a mixture of the first two products. The product of highest retention time remained in the pot and was not isolated. Recrystallization of the crude semisolid distillate from ethanol gave the material of lowest retention time as a crystalline solid. Detailed nmr examination of this solid dissolved in deuteriochloroform showed it to be the pre-

viously unreported methyl 4-caproylfuran-2-carboxylate. Hydrolysis of this methyl ester gave 4-caproylfuran-2-carboxylic acid (mp 176–177°, lit.<sup>3</sup> mp 166° for 5-caproylfuran-2-carboxylic acid). Examination of the crude distilled methyl ester product by nmr showed that the material formed in highest yield was the expected 5-caproyl isomer.

These results show that, at least for caproylation, acylation of methyl furan-2-carboxylate gives a 38:62 mixture of 4- and 5-acylated product. Therefore, caution must be used in identifying the products of acylation of alkyl furan-2-carboxylates. The preference for 5-acylation is weak and the product isolated may in fact be the 4 isomer owing to normal differences in solubilities and melting points. The high proportion of 4 acylation is probably due to normal deactivation of the 5 position of the furan ring by the electron-withdrawing carbomethoxy group. Resonance arguments predicting the contrary are incorrect at least in this case.

### Experimental Section

**Caproylation of Methyl Furoate.**—Into an erlenmeyer flask was put 5 g (40 mmoles) of methyl furoate, 8.5 g (68 mmoles) of caproic anhydride, and 20 ml of benzene. The flask was sealed with a serum rubber cap and cooled in an ice bath. Then 5.0 ml of stannic chloride was slowly added from a hypodermic syringe. The reaction mixture was allowed to warm to 25° and was then stirred for 4 days. The resultant dark brown solution was washed repeatedly with water and then with sodium carbonate solution. The crude neutral solution was examined by vpc (15-ft SE-30 column, 15°/min from 100°). Product peaks were noted at 11.8, 12.5, and 16.4 min (relative peak heights 0.61:1:0.32). Distillation of the product (18-in. spinning-band column) gave 1.9 g (21%) of caproylation product, bp 89–95° (0.07 mm), mp 46°. Only the 11.8- and 12.5-min retention time peaks were noted in the distilled product with relative peak heights 0.55:1 (yields by vpc are 7.5 and 14.5%). Two recrystallizations from absolute ethanol gave white plates, mp 76–77°, corresponding to the 11.8-min retention time product. The infrared spectrum ( $\text{CHCl}_3$ ) showed absorption at 1830, 1720 (ester carbonyl), 1680 (aromatic ketone), 1577, 1510, 1300 (ether band), 1380 (C-methyl), 1286 and 1140 (ester), and 1438  $\text{cm}^{-1}$  ( $\text{CH}_3\text{OC(O)X}$ ) consistent with a caproylated methyl 2-furoate. The nmr spectrum in deuteriochloroform indicated that the material was methyl 4-caproylfuran-2-carboxylate ( $\delta$  in ppm, multiplicity, number of protons, group): 0.90, triplet, three  $\text{CH}_3$ ; 1.50, multiplet, six  $\text{CH}_2$ ; 2.90, triplet, two  $\text{COCH}_2$ ; 3.94, singlet, three  $\text{OCH}_3$ ; 7.20, singlet, two furyl protons. The chemical shifts of the furyl protons were the same. These were not adjacent since first-order coupling did not occur. Examination of the crude distilled product by nmr showed in addition to the above peaks for pure methyl 4-caproylfuran-2-carboxylate a second group of peaks consistent with the presence of methyl 5-caproylfuran-2-carboxylate ( $\delta$  in ppm, multiplicity, group): 0.93, triplet,  $\text{CH}_3$ ; 1.50, multiplet,  $\text{CH}_2$ ; 2.38, triplet,  $\text{COCH}_2$ ; 3.89, singlet,  $\text{OCH}_3$ ; 6.81, quadruplet, furyl protons. The furyl proton quadruplet showed lines at 6.44, 6.50, 7.12, and 7.18 ppm giving chemical shifts of 6.47 and 7.15 ppm ( $J = 3.6$  cps). These are predicted shifts and coupling constants for protons at the 3 and 4 positions.<sup>6</sup>

**4-Caproylfuran-2-carboxylic Acid.**—A solution of 0.5 g (10.2 mmoles) of sodium hydroxide and 0.5 g (2.23 mmoles) of methyl 4-caproylfuran-2-carboxylate in 10 ml of methanol was allowed to stand for 14 hr at 25°. Dilution with water and acidification yielded a thick mass of white crystals, mp 173–176°; recrystallization from methanol gave mp 176–177°.

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_4$ : C, 62.84; H, 6.71. Found: C, 62.49; H, 6.86.

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