proposed by Karplus and Fraenkel[11] would not be applicable to this case.

We do not have an unequivocal basis for assigning the two-proton coupling constants of 0.41 and 0.15 gauss to particular ring positions. *Assuming* that both coupling constants are negative, and taking the value of $Q_{CH}{}^{H}$ as -24 gauss, the unpaired spin density on the three rings totals 0.07. It is interesting to note that protons attached to carbon atoms *two* bonds away from the nitro group in the nitroalkane anion radicals[6] do show splittings of 0.24 gauss.

Experimental Section

The sample of 9-nitrotriptycene used in this work was provided by Professor W. Theilacker.[12] Details of electrochemical and esr instrumentation have been described previously.[13]

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Structural Directivity in Diene Syntheses. I. Addition of Monosubstituted Acetylenes to Ethyl 1,3-Cyclohexadiene-1-carboxylate

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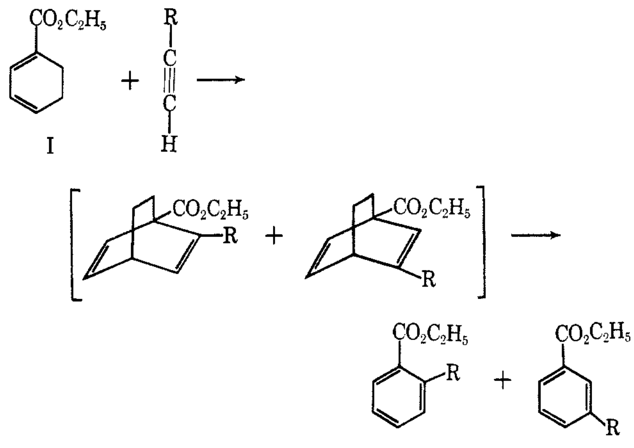
Few data are available on structural directivity in diene syntheses involving cyclic dienes. In the addition of unsymmetrical dienophiles to 9-substituted anthracenes, the ratio of "*ortho*" to "*meta*" products varies from exclusive formation of "*ortho*" isomer to complete predominance of "*meta*" isomer.[2] Completely different ratios of the structural isomers could be obtained even when the substituents in the reactants had similar electronic and steric characteristics. Kazan and Greene[3] have condensed ethyl 1,3-cyclohexadiene-1-carboxylate (I) with ethyl acrylate and obtained all four possible adducts with the "*ortho*" one predominating in a ratio of 35:9. We wish to present some data using monosubstituted acetylenes and I. It was hoped that these additions would provide syntheses of bridgehead-substituted bicyclo[2.2.2]octadienes; however, aromatization occurred at the conditions necessary for reaction.[4]

Compound I added to phenylacetylene, ethyl propiolate, and propyne to give monosubstituted aromatic esters. Mixtures of *ortho* and *meta* isomers were obtained in the following ratios (*ortho*:*meta*): R = C_6H_5, 3.4:1.0; R = $CO_2C_2H_5$, 0.96:1.0; R = CH_3, 1.0:3.2. Kazan and Greene[3] observed predominantly "*ortho*" orientation in the addition of I to ethyl acrylate. The related dienophile, ethyl propiolate, gave almost equal amounts of *ortho* and *meta* isomers. This considerable loss in selectivity is expected since a much higher temperature for reaction was used.



R = C_6H_5, $CO_2C_2H_5$, CH_3

Mechanisms which have been proposed for Diels–Alder reactions are a heterolytic process with polarization orientation of the addends and a homolytic process involving a biradical transition state.[5] An ionic mechanism is improbable since the reactions took place in the vapor phase. A biradical transition state should favor production of *ortho* isomer.[6] Steric repulsion of the substituents in the adduct should favor *meta* orientation.[7] The orienting power observed is determined by an interaction between electronic and steric effects in I and the dienophiles.

Ethyl benzoate was formed during each adduction (evidently due to aromatization of I). Dimer was produced when I was heated in benzene solution. Reversible dimerization probably occurred during each adduction; however, only the irreversibly formed aromatized adducts were isolated.

Experimental Section[8]

Product structures were determined by nmr and vpc comparisons with authentic samples. Product distribution was determined by gas chromatographic analysis.

Diels–Alder Reactions of Ethyl 1,3-Cyclohexadiene-1-carboxylate (I) with Acetylenes.—Solutions of 50 mmoles of I,[9] an

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[1] National Science Foundation Undergraduate Research Participant (Grant No. GY-38).

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[7] I. N. Nazarov, Y. A. Titov, and A. I. Kuznetsova, *Dokl. Akad. Nauk SSSR*, **124**, 586 (1959); *Chem. Abstr.*, **53**, 11268 (1959).

[8] Nmr spectra were obtained with tetramethylsilane as the internal standard using a Varian Model A-60 spectrometer. The gas chromatographic analyses were performed on an F & M Model 500, programmed-temperature gas chromatograph, using a 6-ft silicone gum rubber column. Infrared spectra were obtained from a Perkin-Elmer Model 21 infrared spectrometer. Microanalysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

[9] C. A. Grob, M. Ohta, E. Renk, and A. G. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

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 τ 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 cm^{-1} (conjugated alkene).

Anal. Calcd for $C_{18}H_{24}O_4$: 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.[1] The acylation procedures reported have used an acid anhydride or an acid chloride along with a Lewis acid catalyst. With acid anhydrides stannic chloride[2,3] and ferric chloride[4] catalysts have been used. Ferric chloride is also used with the acid chloride.[5] Reported yields are usually in the 20–30% range.[2]

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[2] 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 previously unreported methyl 4-caproylfuran-2-carboxylate. Hydrolysis of this methyl ester gave 4-caproylfuran-2-carboxylic acid (mp 176–177°, lit.[3] 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 a 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 ($CHCl_3$) showed absorption at 1830, 1720 (ester carbonyl), 1680 (aromatic ketone), 1577, 1510, 1300 (ether band), 1380 (C-methyl), 1286 and 1140 (ester), and 1438 cm^{-1} ($CH_3OC(O)X$) consistent with a caproylated methyl 2-furoate. The nmr spectrum in deuteriochloroform indicated that the material was methyl 4-caproylfuran-2-carboxylate (δ in ppm, multiplicity, number of protons, group): 0.90, triplet, three CH_3; 1.50, multiplet, six CH_2; 2.90, triplet, two $COCH_2$; 3.94, singlet, three 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 (δ in ppm, multiplicity, group): 0.93, triplet, CH_3; 1.50, multiplet, CH_2; 2.38, triplet, $COCH_2$; 3.89, singlet, 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.[6]

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 $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.49; H, 6.86.

Acknowledgment—The infrared and nmr spectra were determined and interpreted by Dr. F. J. Impastato. Elemental analysis was by W. J. Easley.

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