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A COMPARISON OF THE UREA INCLUSION COMPOUND FORMING ABILITY OF BUTANEDIOIC, BUTENEDIOIC AND BUTYNEDIOIC ACIDS ESTERS

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Abstract—The ease of formation of urea inclusion compounds of the dialkyl esters of succinic, fumaric, maleic and acetylenedicarboxylic acids has been determined using the size of the smallest chain length including all the chain atoms except the terminal hydrogens, which in the diester proved capable of forming a urea complex. The shorter the chain length required, the greater the ease of complex formation. The following are the shortest diesters forming a complex (in parenthesis the cross-sectional diameter which determines the chain length required): diethyl succinate (5·0 Å), diethyl fumarate (5·1 Å), di-n-propyl acetylenedicarboxylate (5·2 Å) and di-n-butyl maleate (5·3 Å). The formation of urea inclusion compounds was established by X-ray powder diffraction patterns.

IN AN earlier study[4] the effect of *cis trans* isomerism in olefines on urea inclusion compound formation was determined, and it was concluded that the ease of the inclusion compound formation was related to the maximum cross-sectional diameter of the molecule in its least voluminous conformation. The ease of complex formation was determined by finding the shortest chain length including all the chain atoms except the terminal hydrogens, which as dialkyl maleate and fumarate, respectively, would form an inclusion compound. X-ray powder diffraction patterns, showed that the ease of formation was inversely proportional to the cross-sectional diameter of the molecule, the chain length of the lowest complexing homologue being proportional to the cross-sectional diameter of the molecule. Moreover, when the comparison was extended to include the urea inclusion compound of the "shortest" diester of the corresponding saturated dibasic acid, succinic acid,[5] the minimum required chain length for complex formation was again found to be proportional to the molecular cross-sectional diameter. On the other hand, the ease of formation was inversely proportional to the cross-sectional diameter of the molecule. In view of the fact that earlier research[6] had demonstrated the feasibility of preparing urea inclusion compounds of alkynes and particularly non-terminal alkynes, the study of the ease of formation of the urea inclusion compounds of dialkyl acetylenedicarboxylates was undertaken. In this way, a systematic comparison could be made of four families of

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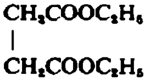
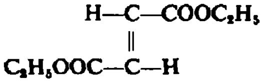
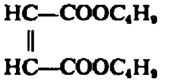
[4] J. Radell, J. W. Connolly and W. R. Cosgrove, Jr., *J. Org. Chem.* **26**, 2960 (1961).

[5] R. P. Linstead and M. Whalley, *J. Chem. Soc.* 2987 (1950).

[6] J. Radell, J. W. Connolly and L. D. Yuhas, *J. Org. Chem.* **26**, 2022 (1961).

compounds, differing only in the nature of the central C—C bond (saturated, *cis* and *trans*-ethylenic, acetylenic).

Five di-n-alkyl acetylenedicarboxylates were prepared and treated with a methanolic solution of urea. Whilst the dimethyl and diethyl esters produced no crystalline material, crystalline urea inclusion compounds were obtained from di-n-propyl, -butyl and -amyl acetylenedicarboxylates. This was verified by the presence of interplanar spacings at 4·11, 7·13 and 3·39–3·40 Å in the X-ray powder patterns of the crystals (Table 1). None of the complexes was contaminated with free urea, which is easily identifiable by its most intense interplanar spacing at 4·00–4·01 Å (Table 1). The absence of this spacing proves the spacing at 3·56–3·58 Å which is characteristic of both the free urea and the inclusion compound, is actually due to the latter. The spacing at 2·06 Å is weak and has previously been found characteristic of urea inclusion compound.[7]

Compound	Cross Section, Å	Chain Length[8]
 $\begin{array}{l} CH_2COOC_2H_5 \\ \vert \\ CH_2COOC_2H_5 \end{array}$	5·0	10
 $\begin{array}{l} \quad H{-}C{-}COOC_2H_5 \\ \qquad \Vert \\ C_2H_5OOC{-}C{-}H \end{array}$	5·1	10
$C_3H_7OOCC{\equiv}CCOOC_3H_7$	5·2	12
 $\begin{array}{l} HC{-}COOC_4H_9 \\ \Vert \\ HC{-}COOC_4H_9 \end{array}$	5·3	14

The explanation previously given[4] for the freedom from urea of even the shortest maleate and fumarate applies equally to the complexes of the acetylenedicarboxylates. The ability to form inclusion compounds was found to be related to the cross-sectional diameters of the molecules. This is shown again by comparing the size of the molecules and chain length of the shortest complexing homologues.

The shortest homologues capable of complex formation in the succinate and fumarate series are the diethyl esters which have the "slenderest" cross sections. The acetylenedicarboxylate system has a sufficiently greater girth to require as a minimum the di-n-propyl ester. Finally the maleate with the largest cross section requires a minimum of a di-n-butyl ester for complex formation. This comparison further points out the importance of geometry in urea channel complex formation, as the change in complexing ability is not related to the change in character of the bond but rather to the change in cross section of the molecule produced by this change in chemical structure, an increase in the cross section making formation more difficult. Consequently, the compensatory stabilization by a greater number of methylene groups is required for complex formation in the molecules of bulkier girth. While the succinate and fumarate esters can easily assume a planar zigzag conformation to produce a slender molecule, the acetylenedicarboxylate has a linear array of four atoms making one leg of the zigzag longer than all the others. Consequently the acetylenedicarboxylate acid ester has a slightly greater cross section than the succinate and fumarate

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[7] J. Radell, B. W. Brodman and E. D. Bergmann, *Tetrahedron* in press (1963).

[8] The chain length is the total number of atoms in the chain excepting hydrogen.

esters. The maleates, due to their *cis*-configuration, are the least slender molecules when the alkyl chain is extended, although slender enough to qualify as guests in the host channel of urea.

TABLE 1. X-RAY POWDER DIFFRACTION PATTERNS OF UREA INCLUSION COMPOUNDS OF $ROOCC\equiv CCOOR$

n-R	2·06[a]	2·17	2·53–2·56	2·61–2·62	2·70	3·26–3·27	3·39–3·40	3·56–3·58	3·86	4·00–4·01	4·11	7·13
C_3H_7	0·08[b]	0·10	0·08	0·12	0·08	0·12	0·28	0·55	0·15	—	1·00	0·21
C_4H_9	0·05	0·04	0·04	0·06	0·07	0·06	0·12	0·45	0·07	0·07	1·00	0·15
C_5H_{11}	0·05	—	—	—	—	—	0·10	1·00	—	—	0·64	0·34
(urea)[c]	—	—	(0·07)	—	—	—	—	(0·06)	—	(1·00)	—	—

[a] Interplanar spacings in Å using CuKα radiation.

[b] Relative intensities; 1·0 being the strongest.

[c] Additional minor spacings for free urea occurred at 2·00, 2·83, 3·04 and 3·63 Å.

EXPERIMENTAL

Di-n-alkyl acetylenedicarboxylates. The esters were prepared by a previously described procedure.[8] Attempts to distill di-n-hexyl acetylenedicarboxylate under reduced pressure resulted only in decomposition. Incidentally, this ester was also not reported by Jeffrey and Vogel.[8]

Urea inclusion compounds. To a weighed amount of the acetylenedicarboxylates, in a screw cap vial, 4·5 ml urea-methanol solution (0·15 g urea/ml methanol) was added. The vial was capped, shaken vigorously for 30 sec, and then allowed to stand at 29–30° for 3–4 hr. Then the compounds were kept at 4° for 24 hr. Crystals which formed were filtered by suction using a rubber sheet as an air-tight cover over the funnel to reduce the possibility of the mother liquor evaporation on the residue during the filtration. The quantity of $ROOCC\equiv CCOOR$ used and the quantity of complex isolated was:

n-R	Grams of guest	Grams of complex
CH_3	0·521	0
C_2H_5	0·530	0
C_3H_7	0·560	0·226
C_4H_9	0·593	0·114
C_5H_{11}	0·566	0·317

X-ray powder diffraction measurements. The interplanar spacings were determined on a North American Phillips Co. X-ray Diffractometer (Model 5001) which was equipped with a high angle goniometer and a proportional counter. CuKα radiation was obtained by operating the copper tube at 35 K.V. and 15 m.a. using a nickel filter and passing the radiation through a 1° slit. The goniometer scanning speed was 1°/min. Samples were mounted on a roughened glass slide using a spatula and enough pressure to make the sample stick to the slide.

Cross-sectional diameters. These measurements were made on scalar molecular Fisher-Taylor-Hirschfelder models according to a previously described procedure.[5]

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[8] G. H. Jeffrey and A. I. Vogel, *J. Chem. Soc.* 674 (1948).