[CONTRIBUTION FROM THE PHYSICS LABORATORY, MATERIALS CENTRAL OF WRIGHT AIR DEVELOPMENT DIVISION]

Urea Inclusion Compounds of Alkynes[1]

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Urea inclusion compounds of several acetylene derivatives have been prepared. In the monoalkyl- and dialkylacetylenes, the effect of the acetylene group increased the over-all cross-sectional diameter of the molecule. The ability of the acetylenic molecules to form a urea inclusion compound is a function of the number of consecutive —CH$_2$— groups and the over-all cross-sectional diameter of the molecule. The relative stability of the urea inclusion compounds of the position isomers of nonyne or decyne depends on the cross-sectional diameter of the molecule.

The maximum cross-sectional diameter of a hydrocarbon in the planar zigzag conformation is generally recognized as being close to the optimum cross-sectional diameter required for urea inclusion compound formation. As the maximum cross section of a molecule in the planar zigzag conformation departs from this value the ability of such a molecule to form a urea inclusion compound decreases. On this basis Truter[2] predicted that 2,4,6-octatriyne would be too slender to form a complex. We failed to complex this triyne using our standard procedure. The fact that a molecule failed to form a complex under these conditions does not preclude the possibility that a complex would form using different conditions. The maximum cross-sectional diameter of a *n*-hydrocarbon in the planar zigzag conformation is 4.6Å while the triyne and the following family of conjugated poly-ynes, $CH_3(C\equiv C)_nCH_3$, had a maximum cross-sectional diameter of 3.7Å. In the case of a mono- or dialkylacetylene the molecule arranged in an essentially planar zigzag conformation had a cross-sectional diameter as large or larger than a saturated hydrocarbon. This results from the presence of *sp* bonds in acetylene which produce a linear array of four atoms involving the two acetylenic carbons and the single atom attached to each. Consequently, the acetylene function is unique in producing molecules having both a lesser (conjugated poly-yne) or a greater (mono- or dialkylacetylene) cross-sectional diameter than a *n*-hydrocarbon.

As the over-all cross section of an *n*-alkyne is generally greater than that of a saturated hydrocarbon, we might expect that the shortest acetylenic molecule that forms an inclusion compound to contain more consecutive —CH$_2$— groups (Table II) than the corresponding alkane. Using the method described herein, we found 1-nonyne to be the shortest alkyne and *n*-octane to be the shortest alkane to form an inclusion compound. The cross-sectional diameter of the 1-nonyne was 4.7Å and for *n*-octane, 4.6Å. It would be difficult to ascribe this one-carbon difference in chain length to cross-sectional diameter alone. This is probably due to the lesser contribution of the —C≡C— over the —CH$_2$CH$_2$— group to the Van der Waals stabilization of the complex as well as the difference in cross section.

If we compare the stabilities of the complexes obtained from 1-, 2-, and 3-nonyne respectively, we find that the change in stability bears a direct relationship to the molecular cross section of the acetylene derivative. These stabilities are obtained from x-ray powder diffraction data in Table I using a method described in an earlier paper.[3]

This method is based upon the fact that the most stable complexes dissociate to a very small extent or not at all. The less stable complexes dissociate appreciably to guest and urea molecules. The x-ray data for the complex of 1-dodecyne show that it is pure complex. The X-ray data for both the 1-nonyne and *n*-octane complexes indicated the inclusion compound was present with dissociated urea in both cases. Spacings for uncomplexed urea are listed in Table I.

All acetylene compounds examined were liquid and had no powder diagrams of their own. The interplanar spacing at 4.09 to 4.15 and 7.08 to 7.19Å is roughly indicative of the amount of complex present while the 3.97 to 4.04Å spacing is roughly indicative of the amount of urea present. The relative stability of the nonyne complexes with their associated cross-sectional diameters are: 1-nonyne (4.7Å) > 3-nonyne (4.9Å) > 2-nonyne (5.2Å). The 4-nonyne treated in the same way gave pure urea only. In all three cases, uncomplexed urea was associated with the inclusion compound and resulted from the dissociation of the pure inclusion compound after filtration. We based this on the fact that in any homologous series forming urea inclusion compounds we can find a certain homologue that is the shortest that will complex. All higher homologues will also form a complex. Still shorter homologues will in some cases cause pure uncomplexed urea to crystallize from the methanol solution. The amount of urea caused to crystallize by these shorter homologues increases with successively higher homologues until we reach

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[1] Presented at the 138th meeting of the American Chemical Society, New York, N. Y., Sept. 11, 1960.

[2] E. V. Truter, *Wool Wax*, Cleaver-Hume Press Ltd., London, 1956, pp. 209, 212.

[3] J. Radell and J. W. Connolly, *J. Org. Chem.*, **25**, 1202 (1960).

TABLE I

POWDER PATTERNS OF UREA COMPLEXES OF *n*-ALKYNES

n-Alkynes	2.51-2.53[a]	2.80-2.84	3.03-3.06	3.25-3.29	3.39-3.41	3.53-3.59	3.60-3.63	3.83-3.88	3.97-4.04	4.09-4.15	7.08-7.19
1-Pentyne	0.34[c]	0.22	0.07	—	—	—	0.05	—	1.00	—	—
2-Pentyne	0.11	0.12	0.10	—	—	—	0.07	—	1.00	—	—
1-Hexyne	0.14	0.05	0.08	—	—	—	0.05	—	1.00	—	—
2-Hexyne	0.13	0.05	0.13	—	—	—	0.15	—	1.00	—	—
3-Hexyne	0.24	0.10	0.15	—	—	—	0.10	—	1.00	—	—
1-Heptyne	0.18	0.19	0.16	—	—	—	0.14	—	1.00	—	—
1-Octyne	0.17	0.10	0.24	—	—	—	0.16	—	1.00	—	—
2-Octyne	0.14	0.09	0.20	—	—	—	0.15	—	1.00	—	—
3-Octyne	0.12	0.09	0.10	—	—	—	0.06	—	1.00	—	—
4-Octyne	0.21	0.05	0.13	—	—	—	0.08	—	1.00	—	—
1-Nonyne+[b]	0.16	0.13	0.24	0.18	0.36	0.53	0.21	0.17	1.00	0.88	0.42
2-Nonyne+	0.17	0.09	0.18	—	—	0.06	0.17	—	1.00	0.05	0.04
3-Nonyne+	0.15	0.09	0.21	—	0.03	—	0.14	—	1.00	0.44	0.15
4-Nonyne	0.41	0.09	0.12	—	—	-	0.06	—	1.00	—	—
2-Decyne+	0.14	0.09	0.23	0.14	0.41	0.73	0.18	0.73	0.73	1.00	0.68
3-Decyne+	0.16	0.10	0.22	0.05	0.10	0.40	0.24	0.04	1.00	0.21	0.26
5-Decyne	0.13	0.07	0.09	—	—	—	0.07	—	1.00	—	—
1-Dodecyne+	0.05	—	—	0.06	0.37	0.58	—	0.15	—	1.00	0.61
1-Pentyne-3-ol	0.10	0.05	0.10	—	—	—	0.07	—	1.00	—	—
4-Pentyne-2-ol	0.17	0.13	0.12	—	—	—	0.05	—	1.00	—	—
1-Hexyne-3-ol	0.07	0.04	0.03	—	—	—	0.05	—	1.00	—	—
2-Octyne-1-ol	0.26	0.07	0.05	—	—	—	0.05	—	1.00	—	—
2,4-Hexadiyne	0.15	0.08	0.24	—	—	—	0.13	—	1.00	—	—
1,6-Heptadiyne	0.16	0.07	0.17	—	-	—	0.10	—	1.00	—	—
1,7-Octadiyne	0.13	0.04	0.12	—	—	—	0.07	-	1.00	—	—
1,8-Nonadiyne	0.10	0.03	0.07	—	—	—	0.06	—	1.00	—	—
Dipropargylamine	0.11	0.05	0.09	—	—	—	0.10	—	1.00	—	—
Propargyl ether	0.13	0.07	0.14	—	—	—	0.09	—	1.00	—	—
1 Chloro-4-octyne	0.13	0.08	0.10	—	—	—	0.08	—	1.00	—	—
1 Chloro-4-nonyne+	0.23	0.10	0.23	0.05	0.12	0.43	—	0.07	1.00	0.77(4.19)	0.13
1 Chloro-4-decyne+	0.08(2.63)	0.06(2.71)	—	0.05	0.11	0.23	—	0.06(3.90)	—	1.00	0.06
Octane+	0.15	0.10	—	—	0.17	0.29	—	0.10	1.00	0.48	0.29
(Urea)	(0.42)	(0.21)	(0.25)	—	—	—	(0.20)	—	(1.00)	—	—

[a] Interplanar spacings in angstroms using CuKα radiation. [b] Complex formers. [c] Relative intensities; 1.0 the strongest.

the smallest homologue forming a complex. Although the complex of this minimum homologue is associated with urea, the presence of urea disappears rapidly as we form complexes of the next two higher homologues. The third and all higher homologues above the minimum homologue show no evidence of any urea. This has been noted consistently in several series of compounds.

Urea could not have crystallized along with the complex and then have been carried mechanically along. It would be unreasonable to believe that all complexes of the higher homologues could be consistently isolated free of uncomplexed urea when the same procedure was used for preparing all complexes. We might suspect that in those cases where urea occurred along with complex, the molecule being adducted reduced the solubility of urea and caused urea to crystallize along with complex. However, this does not agree with the observation that greater amounts of urea are caused to crystallize by successively higher homologues only before we reach molecules long enough to complex. Furthermore, this explanation does not suffice because the higher homologue complexes are completely free of urea. All evidence is consistent with the supposition that only the complex forms from solution, and that free urea—if found—originates from dissociation after filtration. A similar observation was made in the case of the partially fluorinated esters.[3] Furthermore, the dissociation constant of the inclusion compounds of the lower homologues is less than for the inclusion compounds of the higher homologues. This would account for the absence of urea from the complexes of higher homologues.

Only two inclusion compounds were free from uncomplexed urea. These were the 1-dodecyne and the 1-chloro-4-decyne.

In analyzing the x-ray data the following interplanar spacings of Table I are indicative of the urea inclusion compound: 3.25 to 3.29, 3.39 to 3.41, 3.53 to 3.59, 3.83 to 3.88, 4.09 to 4.15, and 7.08 to 7.19Å. The following spacings characterize dissociated urea: 2.51 to 2.53, 2.80 to 2.84, 3.03 to 3.06, 3.60t o 3.63, and 3.97 to 4.04 Å. The 3.97 to 4.04 Å is the only exclusively characteristic line for uncomplexed urea.

In the decyne series there was available 2-, 3-, and 5-decyne only. The relative stability and cross-sectional diameters (Table II) of the complexes that formed were 2-decyne (5.1Å) > 3-decyne (5.3Å). Unfortunately the 1-decyne (4.7Å) and 4-decyne (4.9Å) were not available. The 5-decyne caused only the formation of pure urea. Both the 4-nonyne (4.9Å) and 5-decyne (5.0Å) failed to form a complex although all other position isomers examined did. It cannot be concluded that these members failed to form complexes, using the described procedure, because of cross-sectional diameter. From previous experiences we find it is necessary that a slender molecule have not only a sufficient number of —CH_2— groups, but that these groups occur in a consecutive chain of reasonable length. This is demonstrated by the $C_3F_7CO_2(CH_2CH_2O)_{10}O_2CC_3F_7$ (where each —CH_2—CH_2— group is interrupted by an oxygen atom) not forming a complex while $C_3F_7CH_2O_2C(CH_2)_7CO_2CH_2C_3F_7$ forms a complex. A possible hypothesis, consistent with the behavior of many of the other molecules examined, is that the complex originally did form for 4-nonyne and 5-decyne, but completely dissociated later. This perhaps explains why *n*-octane is the shortest hydrocarbon isolated in our laboratory by the described procedure, although previously[2] it had been reported that both *n*-hexane and *n*-heptane are capable of forming an inclusion compound.

TABLE II

SUMMARY OF COMPOUNDS FORMING COMPLEXES WITH UREA

Compound	Cross-Sectional Diameter, Å.	Urea Inclusion Compound
1-Pentyne	4.30	−
2-Pentyne	4.45	−
1-Hexyne	4.57	−
2-Hexyne	4.49	−
3-Hexyne	4.45	−
1-Nonyne	4.65	+
2-Nonyne	5.15	+
3-Nonyne	4.91	+
4-Nonyne	4.93	−
2-Decyne	5.13	+
3-Decyne	5.23	+
5-Decyne	4.95	−
1-Dodecyne	4.75	+
1-Chloro-4-octyne	4.90	−
1-Chloro-4-nonyne	4.93	+
1-Chloro-4-decyne	4.90	+
1-Pentyne-3-ol	4.73	−
4-Pentyne-2-ol	4.58	−
1-Hexyne-3-ol	5.00	−
2-Octyne-1-ol	4.95	−
2,4-Hexadiyne	3.45	−
1,6-Heptadiyne	4.87	−
1,7-Octadiyne	4.55	−
1,8-Nonadiyne	4.89	−
Dipropargylamine	5.16	−
Dipropargylether	5.18	−
2,4,6-Octatriyne	3.73	−

Two 1-chloro-4-alkynes were the only substituted acetylenes examined which formed a urea inclusion compound although three homologues were examined. The relative stability of the inclusion compound of 1-chloro-4-decyne (4.9Å) is greater than that of 1-chloro-4-nonyne (4.9Å). The 1-chloro-4-octyne (4.9Å) resulted in the crystallization of pure urea only.

Although none of the polyacetylenes, alkynols, alkyneamine, or alkyne ether formed an inclusion compound, higher homologues of these molecules would be expected to form an inclusion compound since the molecules are otherwise slender enough to fit into the channel of urea in the inclusion compound.

EXPERIMENTAL

To determine the feasibility of trapping alkynes as urea inclusion compounds, the maximum cross-sectional diameters of several unbranched molecules were measured on Stuart-Briegleb scaler molecular models arranged as closely as possible to the planar zigzag conformation. These molecules along with their cross-sectional diameters and their abilities to form an inclusion compound are listed in Table II. In all cases the presence of an inclusion compound was verified by x-ray powder diffraction data (Table I).

2,4,6-Octatriyne, 2,4-hexadiyne, dipropargyl ether, and dipropargyl amine were obtained from Professor C. J. Marsel of New York University. The remaining compounds were purchased from the Farchan Research Laboratories in Cleveland, Ohio.

Preparation of urea inclusion compounds. A urea-methanol solution was prepared by dissolving 15 g. of urea in 100 ml. of absolute methanol. If the compound examined was a liquid, 30 drops of the compound was added to 4.5 ml. of urea-methanol solution, shaken, kept in a stoppered tube at 4° for 24 hr., suction filtered, and washed with 10 ml. of 4° absolute ethanol. The crystals were vacuum dried at 4° and 3 mm. for 24 hr. If the compound examined were a solid, 2.2 g. of the compound were added to 4.5 ml. of urea-methanol solution, heated to boiling or until the solid dissolved (whichever occurred first), and then cooled at 4° for 24 hr. The same procedure is then used for both liquids and solids.

Determination of X-ray powder diffraction pattern. The urea inclusion compounds were ground into a fine powder and applied to a roughened glass slide. The interplanar spacings and relative intensities were obtained using the North American Phillips x-ray Diffraction Apparatus operated at 35,000 volts and 15 milliamps with a scanning rate of 2° per min. using CuKα radiation.

CONCLUSION

The formation of urea inclusion compounds by both monoalkyl- and dialkylacetylene as well as substituted dialkylacetylene has been demonstrated.

All monoacetylenes examined which formed an inclusion compound contained nine or more carbon atoms. The relative stability of position isomers of monoacetylenes varied with the cross-sectional diameter of the molecule determined by scalar molecular models. When the triple bond occurred at or close to the center of the molecule, no complex formed. We attributed this to an insufficient number of consecutive —CH$_2$— groups. None of the polyacetylenes studied formed an inclusion compound.

Characteristic interplanar spacings occurring in the x-ray powder diffraction analysis of the inclusion compounds were used to determine the relative stability of the inclusion compound.

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On the Titrimetric Determination of the Configuration of Bridged Diels-Alder Adducts[1a]

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By means of several examples it is shown that mixtures of *exo-endo* isomers can be analyzed iodimetrically. The results obtained emphasize that even at room temperature the Diels-Alder reaction often does not proceed in a homogeneous manner as postulated by Alder's rule.

The Diels-Alder reaction between cyclic dienes and dienophilic substances, such as maleic anhydride, may lead to two stereoisomers Ia or Ib. These stereoisomers are called *endo* and *exo* according to the system of nomenclature introduced by Bredt[2] for derivatives of camphor. The steric course of the addition reaction can be usually predicted by applying Alder's rule[3]; however, exceptions also occur depending on the conditions of the reaction (solvent and temperature) and on the type of diene used. Accordingly, it was found desirable to have a fast and exact method for the determination of the configuration of Diels-Alder adducts. Two general methods are described in the literature both of which are based on gravimetric procedures. They can be illustrated by using the *endo-exo* isomers of bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid (IIa and IIb) as an example. The first method[4] consists of an oxidative degradation of the C=C double bond with the resulting formation of a diformylcyclopentanedicarboxylic acid (IIIa and IIIb). Of these only IIIa, a derivative of the *endo*-isomer IIa, can be converted into the neutral substance IVa. This proof of the configuration is unequivocal, but the method is tedious and gives satisfying results only if the steric homogeneity of a substance with unknown configuration is beyond question. Albeit this is some-

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(2)(a) J. Bredt, *Wüllner Festschrift*, Leipzig, 1905, pp. 119–120; quoted from A. Hesse *et al.*, *Chem. Ber.*, **35**, 1132 (1906); (b) J. Bredt, *J. prakt. Chem.*, 121, 153 (1929).

(3) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(4) K. Alder and S. Schneider, *Ann.*, **524**, 189 (1936).