Tetrahedron Letters No. 13, pp 1159 - 1162, 1978. Pergamon Press. Printed in Great Britain.

DIMERIZATION- AND TRIMERIZATION PRODUCTS FROM THE REACTION OF PROPYNE WITH HCL

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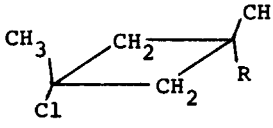
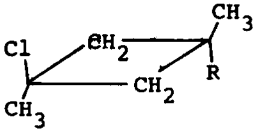
(Received in UK 23 January 1978; accepted for publication 9 February 1978)

The reaction of propyne with hydrogen chloride has been the subject of a number of investigations in the past (1-5). In early reports (1-4) 2-chloropropene and/or 2,2-dichloropropane were mentioned as the sole reaction products. More recently, however, it was shown, that under certain conditions (1:1 ratio, liquid phase) the cyclodimerization products 1a and 2a are also formed in approx. 15% combined yield, along with 10% of high boiling material. In the present paper we report the isolation and identification of ten cyclic trimerization products (viz. 1b-1f and 2b-2f) and of one linear dimerization product (viz. 3) from this high boiling material.



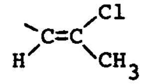
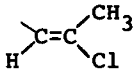
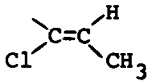
1



2

$(CH_3)_2CClCH_2CCl_2CH_3$

3

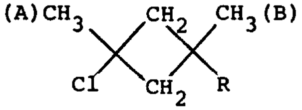
	a	b	c	d	e	f	g
R	-Cl	$-CH=C=CH_2$	$-C\equiv CCH_3$				$-COOCH_3$

Isolation of products. Crude HCl-propyne product mixture was prepared by a published procedure (5), and 90 g of it was distilled through a 15 cm packed column. By gradually lowering the pressure from atmospheric to 0.05 Torr at ambient temperature, 67 g of lower boiling material was removed. Then the bath temperature was raised and the following two fractions were collected: Fract.1: b.p. 20°-35°/0.05 Torr, 4.2 g. Fract.2: b.p. 44-46°/0.05 Torr, 4,6 g Separation of these fractions by p.g.c. (column 0.8x500 cm, 10% Carbowax 20M on chromosorb G; 60-120° at 2°/min; 150 ml N_2/min) afforded in the following order of elution: a mixture of 2b and 2c; 1b; 1c from fract.1 and 3; 2f; 2d; 1d; a mixture of 2e and 1f; 1e from fract.2. The isolated mixtures of 2b and 2c as well as of 2e and 1f were subsequently separated by p.g.c. (column: 0,8x500 cm,10% nitrilesiliconoil on chromosorb G, conditions as above). All the products isolated were colorless,mobile liquids.

Identification of products. The structures of the cyclic trimers 1b-1f and 2b-2f were assigned on the basis of the following evidence: Field ionization mass spectra showed molecular ions at m/e 156,158 for the monochloro compounds 1b, 1c, 2b, 2c and at m/e 192,194,196 for the dichloro compounds 1d-1f and 2d-2f. The pmr-spectra (Table 1) exhibited singlet signals for the methyl groups at the ring and the characteristic signals of the side-groups R. In accord with the pmr-spectra of other 1,3-disubstituted-1,3-dimethylcyclobutanes (5), all the cis-isomers of structure 1 showed AA'BB'-quartets, whereas the trans-isomers 2b-2e showed singlets for the signals of the methylene groups in the ring. In the trans-isomer 2f the CH$_2$-signal appeared as a AA'BB'-pattern, but the inner lines were very close together.

Table 1

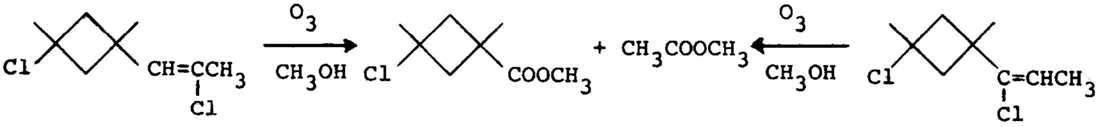
PMR-Data of 3-substituted 1-chloro-1,3-dimethylcyclobutanes (1,2)$^{1)}$



Cpd. No	Chemical shifts of structural units,ppm CH$_3$(A)	CH$_3$(B)	-CH$_2$	R
1 b	1.73 s	1.26 s	2.23; 2.70$^{2)}$	4.76 (d,J=6.0 cps,CH$_2$);5.36(t,CH)
2 b	1.70 s	1.46 s	2.50 s	4.80 (m,J=6.0 cps,CH$_2$);5.16(m,CH)
1 c	1.72 s	1.36 s	2.38; 2.96$^{2)}$	1.81 (s,CH$_3$)
2 c	1.80 s	1.48 s	2.60 s	1.88 (s,CH$_3$)
1 d	1.76 s	1.30 s	2.40; 2.86$^{2)}$	2.06 (d,J=1.3 cps,CH$_3$);5.70(q,CH)
2 d	1.66 s	1.50 s	2.60 s	2.06 (d,J=1.3 cps,CH$_3$);5.60(q,CH)
1 e	1.77 s	1.30 s	2.40; 2.80$^{2)}$	1.96 (d,J=1.2 cps,CH$_3$);5.86(q,CH)
2 e	1.70 s	1.46 s	2.56 s	1.96 (d,J=1.2 cps,CH$_3$);5.76(q,CH)
1 f	1.80 s	1.36 s	2.26; 2.96$^{2)}$	1.73 (d,J=6.0 cps,CH$_3$);5.60(q,CH)
2 f	1.63 s	1.53 s	2.56$^{3)}$	1.75 (d,J=6.0 cps,CH$_3$);5.53(q,CH)
1 g	1.78 s	1.36 s	2.30; 3.13$^{2)}$	3.80 (s,CH$_3$)
2 g	1.66 s	1.53 s	2.49; 2.90$^{2)}$	3.70 (s,CH$_3$)

1) In CDCl$_3$,TMS as internal standard. 2) δ_A and δ_B-values of an AA'BB'-system; J_{AB}=12-13 cps. 3) AA'BB'-pattern with overlapping inner lines, centered around this value.

The structural identies of the side-groups R were further verified by the following facts: The allenyl compounds 1b and 2b showed each a strong IR-band at 1960 cm^{-1}. Reaction of the propynyl compound 2c with anhydrous hydrogen chloride afforded the corresponding adducts 2d and 2f as the major products. The vinylic chlorides showed bands of the respective double bonds at 1653 cm^{-1} for the E-isomers 1e and 2e and at 1660-1665 cm^{-1} for the Z-isomers 1d, 1f, 2d and 2f. Furthermore, ozonolysis of the individual vinylic chlorides in methanol afforded the *cis*-ester 1g from the cleavage of 1d, 1e and 1f, and the *trans*-ester 2g from the cleavage of 2d, 2e and 2f. The second cleavage product was in each case methyl acetate (6):

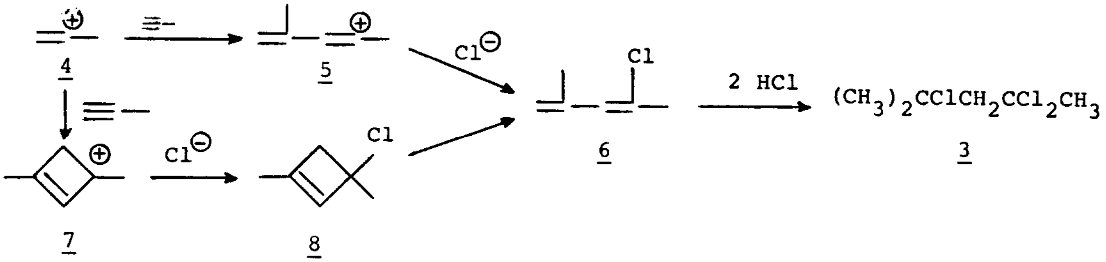


1d,e;2d,e 1g,2g 1f,2f

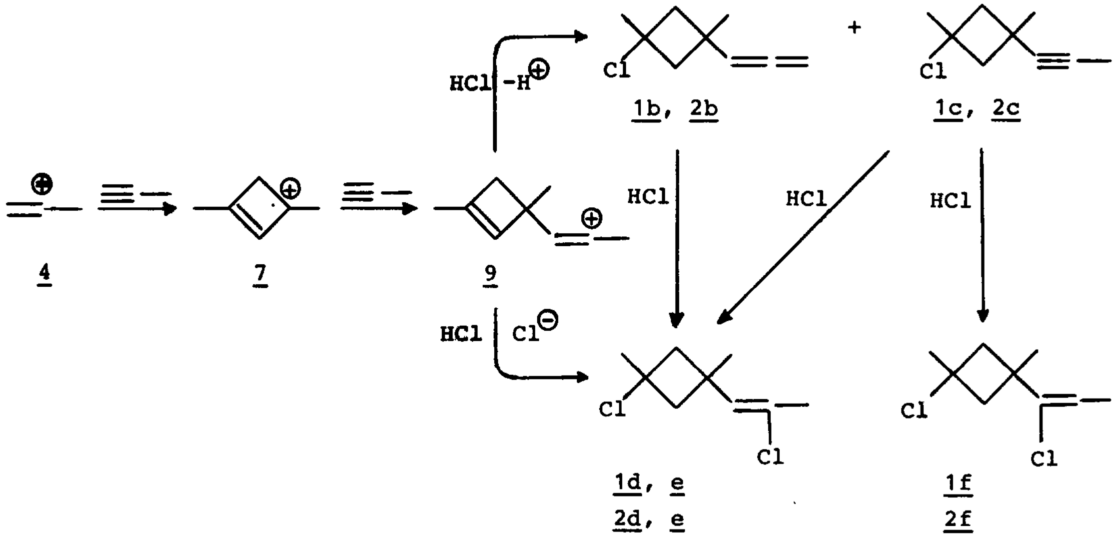
The esters 1g and 2g have been isolated as colorless liquids by means of p.g.c (carbowax-column and conditions as above). Their structures were assigned on the basis of elemental analysis, strong IR-carbonyl bands at 1745 cm^{-1} and 1740 cm^{-1}, respectively, and their pmr-spectra (Table 1). The latter showed AA'BB'-quartets for the methylene groups of both the *cis* (1g)- and the *trans*-isomer (2g).

The structure of the acyclic dimerization product 3 was assigned on the basis of its pmr-spectrum which showed three singlet signals at δ 1.80,2.36 and 2.96 ppm in the relative intensities of 6:3:2. The compound was independently synthesized by the sequential reaction of hydrogen chloride and phosphorus pentachloride with 2-methyl-2-pentene-4-one.

Rationalization of products. The formation of the dimerization product 3 can be explained in two ways, *viz.* either by reaction sequence 4→5→6→3, which involves linear alkylation of propyne by the vinyl cation 4, or, by reaction sequence 4→7→8→6→3, which involves cycloalkylation of propyne by 4, followed by ring-opening of the cyclobutene derivative 8. It appears to us that the first route *via* 5 is more likely for the following reasons: a) the reactions were carried out under rather mild conditions (ambient temperature) which should not favor step 8→6, and b) in the presence of moisture 4-chloro-4-methyl-pent-2-one was obtained as a by product. The latter was most likely derived from intermediate 5, since neither 6 nor 3 produced it upon treatment with water at ambient temperatures.



The formation of the trimerization products 1b-1f and 2b-2f can be readily rationalized by the reaction sequence depicted below: The protonation of propyne produces the vinyl cation 4, which in turn undergoes a$(\Pi 2s + \Pi 2a)$-cycloaddition with propyne to afford the dimethyl-cyclobutenyl cation 7(8). The latter then alkylates propyne to form the central intermediate 9 from which the final trimerization products are derived by the straight-forward reactions indicated in the scheme below.



Acknowledgement. Dr. A. Singh thanks the Internationales Seminar für Forschung und Lehre in Verfahrenstechnik, Technischer und Physikalischer Chemie for a fellowship.

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