Tetrahedron Letters No.23, pp. 1811-1814, 1969. Pergamon Press. Printed in Great Britain.

THE CHEMISTRY OF CYANOACETYLENES III. A NOVEL SYNTHESIS OF 4-CYANOMETHYLENE-1,4-DIOXOLANES FROM CYANOACETYLENE

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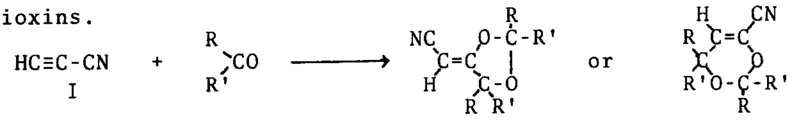
(Received in Japan 6 December 1968; received in UK for publication 4 April 1969)

In a previous paper (1), we reported on the strong resistance to acidic hydrolysis of a cyano group in cyanoacetylene I. When treated with bases like primary and secondary amines, I is known to afford Michael-type addition products (2) and the treatment with aqueous alkalis resulted in the formation of intractable tars. This paper deals with the results of its basic hydrolysis using an anion-exchanger, since some aliphatic nitriles are successfully hydrolyzed to the corresponding amides by this resin (3).

To an acetone solution of I was added Dowex-1 (hydrate form) as an anion-exchanger and the reaction mixture was kept standing at room temperature for 24 hr. The worked-up product was a colorless crystal of mp 46° and the yield was 65%. Its microanalysis and mass spectrum showed $C_9H_{13}O_2N$ (M.W. 167), a 1:2 adduct of I and acetone. Similar treatment of I with acetaldehyde and formaldehyde afforded the corresponding 1:2 adducts, IIb of mp 34° (bp 63~65/0.4 mm), $C_7H_9O_2N$ (139) and IIc of mp 123°, $C_5H_5O_2N$ (111). The yields were both 85%. These three products showed common infrared absorptions at 2220 (CN), 1660 (vinyl), 1230, 1120, and 1250 (ether) cm^{-1}. Disappearance of those at 2130 (C≡C) and 3300 (≡C) cm^{-1} in these products indicates that the reactions have occurred at the triple bond of I. Further structural elucidation was carried out by their NMR spectral inspection; from simple patterns of IIa and IIc, as shown in Figure, we assumed for IIa and IIc either of two ring systems, five-membered 1,3-dioxolanes or six-membered

1,3-dioxins.



1,3-dioxolane 1,3-dioxin

IIa: $R=CH_3$, $R'=CH_3$
b: $R=CH_3$, $R'=H$
c: $R=H$, $R'=H$

In the NMR spectrum of IIa, three signals at τ 8.44 (6 H), 8.55 (6 H), and 5.83 (1 H) could be assigned to two $-C(CH_3)_2$ groups and an olefinic proton in either 1,3-dioxolane- or 1,3-dioxin-structure respectively. However, in that of IIc, a singlet at τ 4.52 (2 H) should be assigned to a methylene at the C-2 of 1,3-dioxolane- rather than of 1,3-dioxin-structure (4). The appearance of a doublet at τ 5.38 (2 H, J = 1.5 c.p.s.) and a triplet at 5.52 (1 H, J = 1.5 c.p.s.) could be explained by allyl coupling. Their similar NMR patterns to 2-trichloromethyl-4-methylene-1,3-dioxolane (5) might substantiate the veridity of five-membered structure for IIa and IIc. The NMR spectrum of IIb exhibited a more complicated pattern than those of IIa and IIc, indicating a mixture of cis and trans isomer, the ratio of which was calculated on the basis of each assignment given similarly as above (see Figure), and finally IIb was concluded to be a mixture of 70% of cis and 30% of trans isomer, assuming that cis is more stable than trans isomer, as judged from the Dreiding stereomodel (6).

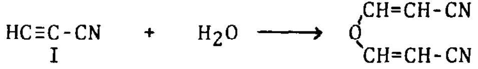
Upon similar treatment of I with other carbonyl compounds like benzophenone, acetophenone, methyl ethyl ketone, benzaldehyde and cyclohexanone, as well as that of acetone with chlorocyanoacetylene, phenylacetylene and dimethyl acetylenedicarboxylate were all recovered the starting materials.

When I was treated with a mixture of tetrahydrofuran and water in the presence of Dowex-1, the colorless product III of mp 165∿166° was obtained in a 60% yield; III was characterized as 3,3'-oxodiacrylonitrile on the basis of the microanalysis and the following spectral data: in the NMR spectrum in deuteriochloroform, a signal at τ 2.55 (doublet, 2 H, J = 6.4 c.p.s.) was assigned to olefinic protons adjacent to ether oxygen and that at 5.03

(doublet, 2 H, J = 6.4 c.p.s.) was assigned to other olefinic protons, taking each olefinic proton a cis-configuration similar to that of cic-cis-dimethyl 3,3'-thiodiacrylate (7,8) or of cis-cis-3,3'-thiodiacrylonitrile (9). In the infrared spectrum (KBr pellet), III showed characteristic absorptions at 2235 (CN) and 1620 (CH=CH) cm^{-1}, being consistent with the above structure.

When I was treated with a mixture of acetone and water in the presence of Dowex-1, the product was exclusively IIa, but when I was treated with aqueous alkali in the absence of Dowex-1, the main product was intractable tars **with** a trace amount of III. Dowex-1 could be replaced with Triton-B in the above reactions. This indicates that the initial attack of quarternary amine hydroxide to I plays a very important role in the formation of II.

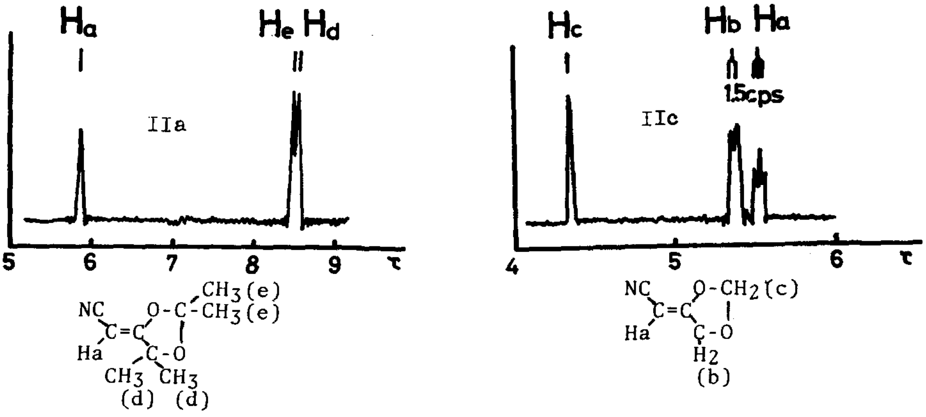
II showed a strong resistance to catalytic hydrogenation; no reactions occurred in the presence of Adams platinum, palladium on charcoal, and Raney nickel at room temperature in the atmospheric pressure of hydrogen. No reduction was observed with alkali metal hydrides. Furthermore, neither Diels-Alder reactivity with isoprene or butadiene even on warming in a fused tube, nor additivity to acetylenic alcohols, different from 2-trichloromethyl-4-methylene-1,3-dioxolane (5) could be observed about II. However, its acidic hydrolysis and its bromination with bromine or N-bromosuccinimide led to a mixture of many products, from which any definite product could not be identified.

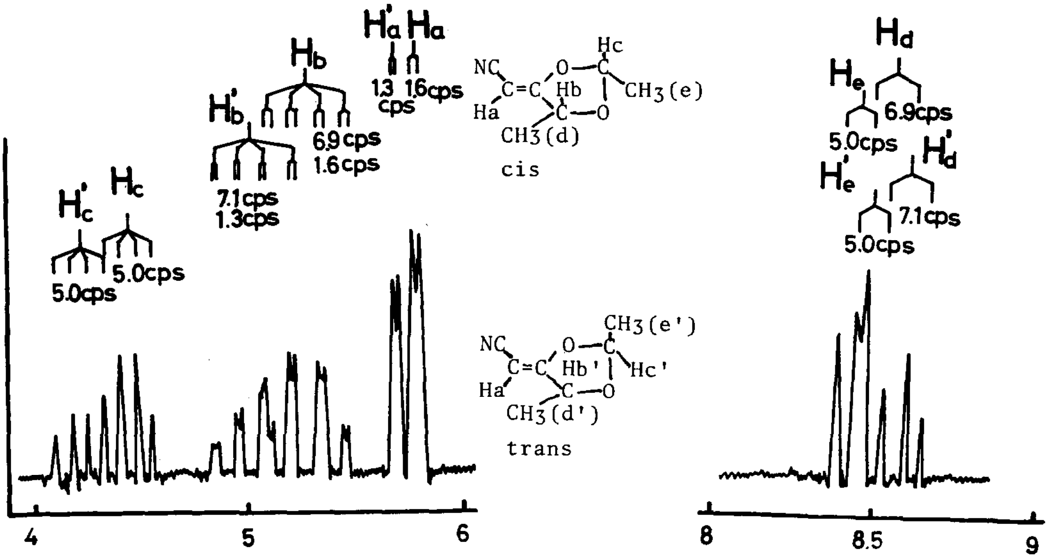


$$\underset{\mathrm{I}}{\mathrm{HC{\equiv}C\text{-}CN}} + \mathrm{H_2O} \longrightarrow \mathrm{O}\begin{matrix}\diagup\mathrm{CH{=}CH\text{-}CN}\\ \diagdown\mathrm{CH{=}CH\text{-}CN}\end{matrix}$$

III

FIGURE NMR Spectra of IIa and IIc
($CDCl_3$; TMS as an internal standard)





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(6) The observed values of the cis/trans ratios for Ha, Hb, Hc, Hd and He to Ha', Hb', Hc', Hd' and He' from the NMR spectrum in Figure were 2.30, 2.64, 2.86, 2.50 and 2.48 respectively, indicating that the above assignments were reasonable. Taking 2.55 on the average, we concluded that IIb was a mixture of 70% of cis and 30% of trans isomer, which was further confirmed by gas-liquid chromatography.

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