Tetrahedron Letters No.30, pp. 3357-3358, 1968. Pergamon Press. Printed in Great Britain.

PHOTOAMIDATION OF ACETYLENIC COMPOUNDS

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(Received in UK 29 March 1968; accepted for publication 29 April 1968)

Reactions of free radicals and acetylenic compounds usually lead to 1:1 adducts which result from addition to the acetylenic bond of one molecule of the substrate (1). In some cases 1:2 adducts, derived from one molecule of the acetylenic compound and two molecules of the addend, are also formed (2). Kharasch and co-workers (3) found that polyhalomethanes and some acetylenes can form under free radical initiation a 2:1 adduct by the condensation of two molecules of the alkyne and one molecule of the halide.

The light-induced addition of formamide to olefins ("photoamidation") leads to the formation of the corresponding higher amides (4). We wish to report now the ketone-initiated photochemical addition of formamide to terminal acetylenes which leads predominantly to 2:2 adducts. Similar reactions with nonterminal acetylenes yield 1:2 adducts (one mole of the acetylene and two moles of formamide) as the predominant products. Irradiation (Hanau Q81) of a mixture of formamide (40 g), 1-heptyne (4.8 g; 1.9 g could be recovered after irradiation), t-butyl alcohol (40 ml) and benzophenone (4 g) led to the formation of 0.7 g of I ($R=C_5H_{11}$)*, m.p. 288-290° (a similar experiment in sunlight yielded 1.5 g of I). N.m.r. (TFA, TMS internal): peaks at τ 1.9 (4H, $-CON\underline{H}_2$, broad), 4.15 (2H, vinyl protons, multiplet), 6.3 and 6.9 (2H, $-C\underline{H}\ CONH_2$, multiplets), 7.8 and 8.6 (16H, methylenes, broad and sharp signals, respectively), and 9.1 (6H, terminal methyls, triplet). Catalytic hydrogenation of I over palladium in t-butyl alcohol gave the dihydroadduct, m.p. 320° (dec). N.m.r.: peaks at τ 7.1 (2H, $-C\underline{H}CONH_2$ broad), 8,6 (20H, methylenes, sharp), and 9.05 (6H, terminal methyls, triplet). The dimethyl ester obtained after hydrolysis of the dihydroadduct was identical with dimethyl-2-heptyl-3-pentylsuccinate. Ozonolysis of I in t-butyl alcohol-methyl alcohol mixture gave hexanal (2,4-dinitro-phenylhydrazone, m.p. 102-103°) and pentylsuccinamide (m.p. and m.m.p. 218-219°), which results from 2-carboxy-3-pentylsuccinamide through the loss of carbon dioxide. α,β-Unsaturated amides (II) and monoalkylsuccinamides (III) were isolated as by products. Similarly, 1-hexyne and 1-octyne reacted with formamide to give the corresponding 2:2 adducts. The reaction of a terminal acetylene with formamide in the presence of a ketone under ultraviolet irradiation can thus be summarised as follows:

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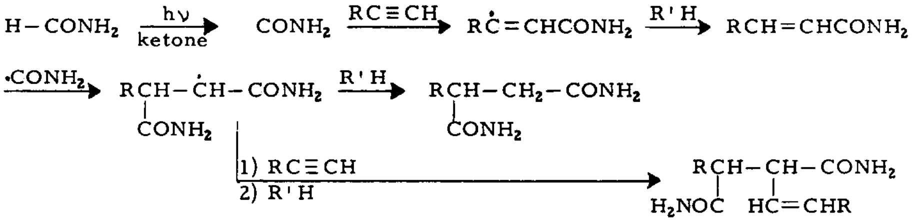
* All new compounds gave satisfactory analytical data, including molecular peak (mass spectrum).

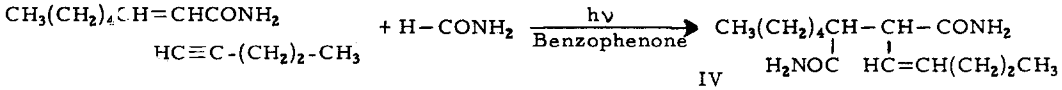


$$H-CONH_2 \xrightarrow[\text{ketone}]{h\nu} CONH_2 \xrightarrow{RC\equiv CH} R\dot{C}=CHCONH_2 \xrightarrow{R'H} RCH=CHCONH_2 \quad \text{II}$$

$$\xrightarrow{\cdot CONH_2} \underset{CONH_2}{RCH}-\dot{C}H-CONH_2 \xrightarrow{R'H} \underset{CONH_2}{RCH}-CH_2-CONH_2 \quad \text{III}$$

$$\xrightarrow[2)\ R'H]{1)\ RC\equiv CH} \underset{H_2NOC}{RCH}-\underset{HC=CHR}{CH}-CONH_2 \quad \text{I}$$

The proposed mechanism, involving addition of a carbamoyl radical to an α, β-unsaturated amide followed by addition of the resulting radical to an acetylene, was further supported by the photo-reaction of 2-octenamide, 1-pentyne and formamide in the presence of benzophenone which yielded a "crossed" product (IV), m.p. 287-289°, [Calcd for $C_{14}H_{26}N_2O_2$; mol.wt., 254. Found: mol.wt., 254 (mass spectrum)] as the one corresponding to a 2:2 adduct.



$$\begin{matrix} CH_3(CH_2)_4CH=CHCONH_2 \\ HC\equiv C-(CH_2)_2-CH_3 \end{matrix} + H-CONH_2 \xrightarrow[\text{Benzophenone}]{h\nu} CH_3(CH_2)_4\underset{H_2NOC}{CH}-\underset{HC=CH(CH_2)_2CH_3}{CH}-CONH_2$$

IV

The strong hydrogen atom abstracting ability of open-chain vinyl radicals has been demonstrated recently (5). Such a process should facilitate the formation of I and II in the present reaction rather than the formation of higher telomeric products.

Conversely, nonterminal isolated acetylenes were found to yield 1:2 adducts, i.e. the derived dialkylsuccinamides, under similar reaction conditions (6). Thus, 4-octyne and formamide when irradiated in the presence of acetone gave 2,3-dipropylsuccinamide while no 2:2 adduct was detected.

The synthetic potentialities of this photo-reaction leading to 2:2 adducts are being explored. Besides alkynes, olefinic compounds which have been shown to be intermediate in the reaction path, are also being used as starting materials in attempts to extend the scope of the reaction to encompass three-component free radical condensations.

Acknowledgement

The authors are grateful to Professor Dov Elad for valuable advice and encouragement.

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