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DIMETHOXYACETYLENE: N.M.R. SPECTRUM AND TRAPPING BY METAL CARBONYLS

A. Messeguer and F. Serratosa[+]

Instituto de Química Orgánica. Patronato "Juan de la Cierva" (C.S.I.C.). Barcelona-17

and J. Rivera

Centro Nacional de Espectrometría de Masas. Instituto de Química Orgánica.
Patronato "Juan de la Cierva" (C.S.I.C.). Barcelona-17

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In the present communication we wish to describe some experiments that complete the results reported, some years ago, by O'Connor[1] and Arens and his coworkers[2], independently, on the field of acetylene diethers. Although the authors suggested the formation of dimethoxy- and diethoxyacetylene as highly reactive and unstable intermediates, neither direct observation nor compelling evidence was presented. Working at low temperatures, we have been able to observe, for the first time, the n.m.r. spectrum of dimethoxyacetylene and to trap it by metal carbonyls.

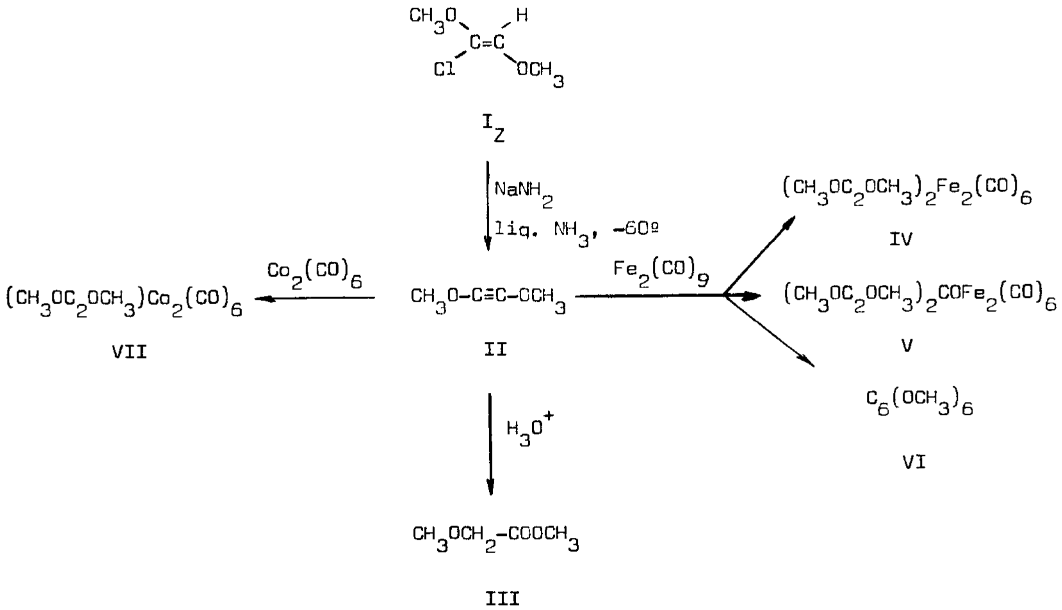
A solution of Z-1-chloro-1,2-dimethoxyethylene (I_Z) (contaminated by 6% of the E isomer) in pentane, was added to a stirred solution of sodium amide in liquid ammonia at -60º.[2] After a few minutes, crushed ice was added, the pentane layer washed with ice water and dried (at -60º). The n.m.r. spectrum at -40º of an aliquot part of the pentane solution showed that practically all the Z isomer had reacted, and a new and strong singlet at τ 6.41, that we assign to dimethoxyacetylene (II), was apparent. Using the unreacted E isomer (I_E) as internal standard (τ, 4.47 (s)(1H), 6.48 (s)(3H) and 6.54 (s)(3H)) we could calculate that the actual yield of dimethoxyacetylene was, at most, 40-50% at -40º. The peak at 6.41 slowly desappeared when the sample was allowed to warm up to room temperature, or when a trace of dilute sulfuric acid was added. In fact, a second aliquot of the pentane solution quenched at -70º with dilute sulfuric acid gave methyl methoxyacetate

(III) (v.p.c. evidence) in about 44% yield[1,2].

On the other hand, when the stirred pentane solution was treated with $Fe_2(CO)_9$ at -60º,[3] the mixture allowed to warm up slowly to room temperature (overnight), filtered off and the solution chromatographed on alumina (preparative t.l.c.) two oily fractions were isolated, which were characterized by mass spectrometry[4]:

1) Yellow fraction: characteristic fragmentation of a binuclear iron hexacarbonyl complex (molecular ion: calculated for $(CH_3OC_2OCH_3)_2Fe_2(CO)_6$ (IV), 451.912914;found, 451.903779); i.r. in CCl_4, 2080, 2038, 2000 and 1985 (strong bands) cm^{-1}; n.m.r. in CCl_4, τ 6.10 (s)(6H) and 6.32 (s)(6H).

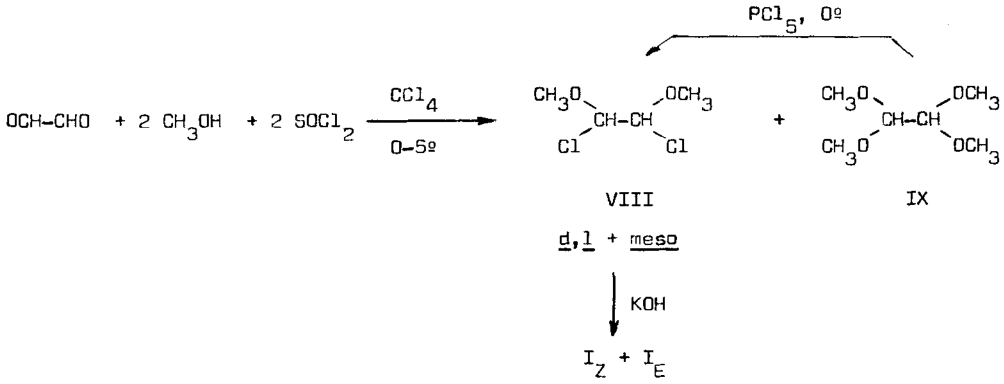
2) Red-brown fraction: mixture of a binuclear iron heptacarbonyl complex (molecular ion: calculated for $(CH_3OC_2OCH_3)_2COFe_2(CO)_6$ (V), 479.907829; found, 479.901620) and hexamethoxybenzene (VI)[5] (molecular ion: calculated for $C_6(OCH_3)_6$, 258.110340; found, 258.107721); i.r. in CCl_4, 2085, 2050, 2010, 2000, 1985 (strong bands), 1730, 1685 and 1640 cm^{-1}; λ_{max} in CCl_4, 273 and 494 nm.



The yields of the iron carbonyls complexes were very low since dimethoxyacetylene is rapidly decomposing[6] at the temperature in which the reaction with $Fe_2(CO)_9$ takes place. As anticipated[7], better results were obtained when the reaction was performed with $Co_2(CO)_8$: after a preparative t.l.c. of the reaction mixture, a crystalline compound (red needles, m. p. 62-63º) was isolated as the exclusive reaction product, which was identified as a binuclear cobalt hexacarbonyl complex (VII)(molecular ion: calculated for $(CH_3OC_2OCH_3)Co_2(CO)_6$, 371.872648; found, 371.876891); i.r. in CCl_4, 2925 (m), 2090 (s), 2050 (vs), 2025 (vs), 1595 (m), 1437 (m), 1420 (m), 1215 (s), 1190 (m) and 1160 (s) cm^{-1}; n.m.r. in CCl_4, τ 6.31 (s). Since the release of the acetylenic ligands has been accomplished in some dicobalt hexacarbonyl complexes[8], a potential and easily handled source of acetylene diethers is now available[9], which would allow to explore the chemistry of these highly elusive compounds[10].

For the preparation of the starting material we did follow a modification of the method of Baganz and Domaschke[11]. The reaction of polymeric glyoxal with methanol and thionyl chloride afforded a mixture of *meso*- and *d,l*-1,2-dichloro-1,2-dimethoxyethane (VIII), together with 1,1,2,2-tetramethoxyethane (IX). Treatment of this mixture with PCl_5 at 0º converted quantitatively IX into the *d,l* diastereomeric form of VIII[12]. After distillation, the overall yield of pure VIII was 79% (28% *meso* + 72% *d,l*).

The diastereomeric mixture VIII was treated with KOH[1] to give 50% yield of a mixture of I_Z and I_E, the former being obtained in a fairly pure form (contaminated by 6% of the *E* isomer) by fractional distillation with a spinning-band column.



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