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MOLYBDENUM HEXACARBONYL-INDUCED REACTIONS OF 3-ARYL-2H-AZIRINES AND ACETYLENES

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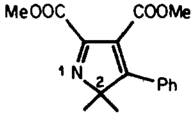
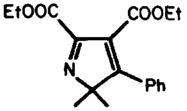
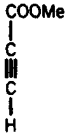
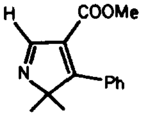
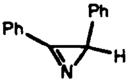
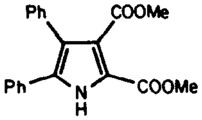
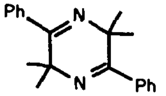
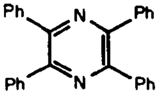
Summary.- In the presence of molybdenum hexacarbonyl, 3-phenyl-2H-azirines and acetylene carboxylic acid esters react via the unusual splitting of the C,N-double bond to give 2H-pyrroles or pyrroles.

2H-Azirines have been shown to undergo C-C bond cleavage photolytically, whilst in ground-state reactions all three types of ring opening are known. These reactions have been used to synthesize a variety of heterocycles.[1)] Recently, interesting intra- and inter-molecular reactions of 2H-azirines in the presence of transition metal carbonyls such as $Fe_2(CO)_9$[2)], $Co_2(CO)_8$[3)], and $M(CO)_6$ (M = Mo, Cr, W)[4)] have been reported. In a previous paper,[5)] we have shown that $Fe_2(CO)_9$-induced coupling reactions of 3-aryl-2H-azirines and acetylenes yield diiron-hexacarbonyl complexes. It seems that all these metal carbonyl-induced reactions proceed by C-C bond cleavage or C-N bond cleavage of the azirine ring.

In the present paper we wish to report that $Mo(CO)_6$-induced reactions of 3-aryl-2H-azirines and acetylenes lead to pyrrole derivatives via splitting of the C=N bond of the azirine.[6)] Thus, 2,2-dimethyl-3-phenyl-2H-azirine (1a) or 2,3-diphenyl-2H-azirine (1b) and acetylene carboxylic acid esters (2) react in the presence of $Mo(CO)_6$ (ratio of 1:2:$Mo(CO)_6$ = 1:2:1) in dry benzene at 35-50° during about 3 days, to give the 2H-pyrroles 3 and pyrrole 4, respectively. Without the acetylenic compound, 1a or 1b and $Mo(CO)_6$ yield known pyrazine derivatives (5).[4)] The resulting products are summarized in Table I.

The structures of the 2H-pyrroles 3a-3c were deduced from the following facts: Photolysis of 1a in the presence of either 2a or 2c has been reported to give 6a and 6b (and the isomeric 6c, Fig. I), respectively, via C-C bond cleavage of the azirine ring.[7)]

Table I

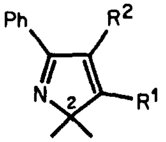
azirine (1)	acetylene (2)	product[a]	yield (%)	mp.
 **1a**	 **2a**	 **3a** [b]	28	103.5-105°
1a	 **2b**	 **3b** [b]	20	92.5-93°
1a	 **2c**	 **3c** [b]	5	59-61°
 **1b**	**2a**	 **4** [c]	20	186-187° 8)
1a	—	 **5a** [c]	25	126-127° 9)
1b	—	 **5b** [c]	18	250-251° 10)

[a] All new compounds give correct analytical results.

[b] The 2H-pyrroles (3a, 3b, 3c) show the following spectral data. 3a: mass. 287(M^{+}); λmax(MeOH)(logε)=293(3.57); ν(KBr): 1750,1715 cm^{-1}; ^{1}H-NMR ($CDCl_3$,δ): 1.50 (2Me,s),3.71,4.01 (2COOMe,2s), 7.04-7.56 (arom. H); 3b: mass. 315(M^{+}); λmax(MeOH)(logε)=292(3.67); ν(KBr): 1745,1715 cm^{-1}; ^{1}H-NMR ($CDCl_3$,δ): 1.07,1.41 ($2COOCH_2\underline{CH_3}$, t, J=7), 1.46 (2Me,s), 4.11,4.41 ($2COO\underline{CH_2}CH_3$, 2q, J=7), 7.05-7.60 (arom. H); 3c: mass. 229(M^{+}); λmax(MeOH) (logε)=280(3.59);ν(KBr): 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$,δ): 1.32 (2Me,s), 3.60 ($COOCH_3$,s), 7.00-7.57 (arom. H), 8.15 ($\underline{H}C=N$,s).

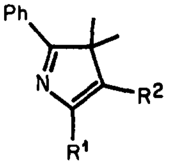
[c] Identified by comparison of mp. and spectral data with literature.

Fig. I



6

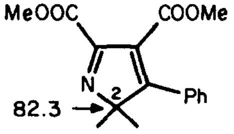
a: $R^1=R^2=COOMe$
b: $R^1=H, R^2=COOMe$
c: $R^1=COOMe, R^2=H$
d: $R^1=R^2=H$



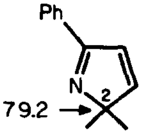
7

The similarity between the spectral properties of 3a, 3c and 6a, 6b suggest that the former are five-membered heterocycles isomeric with 6a, 6b. Whereas, for example, 6a is formed via fission of the azirine C-C bond, the other isomer can be built up via cleavage of either the C,N-double bond or the C,N-single bond. In the former case, the 2H-pyrrole 3a is the product whilst in the latter, the 3H-pyrrole 7a is to be expected. The structure of 7a can be excluded by the ^{13}C-NMR data ($CDCl_3$,δ): The sp^3-hybridized ring carbon appears at 82.3 ppm,[11] comparable with the corresponding chemical shift in other 2H-pyrroles, e.g. 6d [12] (Fig. II).

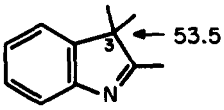
Fig. II



3a



6d

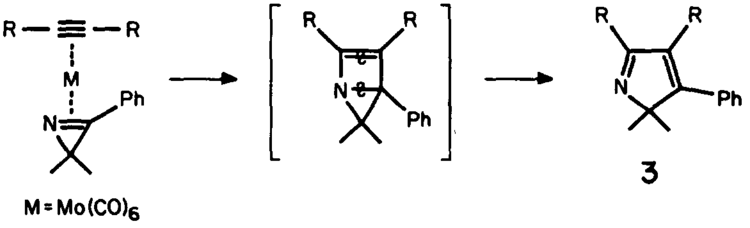


8

In the alternative 3H-pyrrole (7a) the sp^3-carbon (C(3)), attached to only carbon atoms, may be expected to absorb at higher field. For example, C(3) in the indolenine derivative 8 appears at 53.5 ppm.[13] Furthermore, in the ^1H-NMR spectrum of 3c the azomethine H (H-C(5)) appears at 8.15 ppm; in the case of the alternative structure 7b (or 7c), no azomethine H is present.[14] These results prompt us to formulate the new adducts as 2H-pyrroles (3a-3c). In the reaction of 1b and 2a, the primarily formed 2H-pyrrole leads to the pyrrole 4 by means of a H-migration.

A tentative mechanism for the formation of 2H-pyrroles of type 3 via cyclobutane intermediates is formulated in Fig. III.[15]

Fig. III



References and Notes

1) See for example: P. Gilgen, H. Heimgartner, H. Schmid, and H.-J. Hansen, Heterocycles 6, 143 (1977); A. Padwa, Accounts Chem. Res. 9, 371 (1976); V. Nair and K.H. Kim, Heterocycles 7, 353 (1977); H. Taniguchi, K. Isomura, and T. Tanaka, ibid. 6, 1563 (1977); D.J. Anderson and A. Hassner, Synthesis 1975, 483.

2) H. Alper and J.E. Prickett, Inorg. Chemistry 16, 67 (1977); F. Bellamy, J.C.S. Chem. Comm. 1978, 998.

3) H. Alper and J.E. Prickett, Tetrahedron Letters 1976, 2589.

4) H. Alper, J.E. Prickett, and S. Wollowitz, J. Amer. Chem. Soc. 99, 4330 (1977).

5) Y. Nakamura, K. Bachmann, H. Heimgartner, H. Schmid, and J.J. Daly, Helv. Chim. Acta 61, 589 (1978).

6) Recently, Ni-complex induced reactions of 1b and activated ketones have been reported to occur via C=N bond cleavage of the azirine; see P.F. dos S. Filho and U. Schuchardt, Angew. Chem. 89, 672 (1977).

7) U. Gerber, H. Heimgartner, H. Schmid, and W. Heinzelmann, Helv. Chim. Acta 60, 687 (1977).

8) J.B. Hendrickson, R. Rees, and J.F. Templeton, J. Amer. Chem. Soc. 86, 107 (1964).

9) D.G. Farnum and G.R. Carlson, Synthesis 1972, 191.

10) N. Gakis, M. Märky, H.-J. Hansen, and H. Schmid, Helv. Chim. Acta 55, 748 (1972).

11) The other C-atoms show the following chemical shifts (ppm): 22.3 ($\underline{C}H_3$), 52.0, 52.8 ($COO\underline{C}H_3$), 126.9, 128.3, 128.8, 132.7 (arom. C, C(3)), 160.7, 162.7, 163.6 ($\underline{C}OOCH_3$, C(4)), 177.0 (C(5)).

12) W. Stegmann, P. Gilgen, H. Heimgartner, and H. Schmid, Helv. Chim. Acta 59, 1018 (1976).

13) V. Dave, J.B. Stothers, and E.W. Warnhoff, Tetrahedron Letters 1973, 4229.

14) The vinyl-H of the isomeric 3-methoxycarbonyl- and 2-methoxycarbonyl-4,5-diphenyl-pyrroles appear at 7.90 and 7.29 ppm, respectively (see ref. 7).

15) In some cases, $Mo(CO)_6$ has been used for metathesis reactions. However, the mechanism of these reactions is not definitely resolved yet (cf. A. Mortreux and M. Blanchard, J.C.S. Chem. Comm. 1974, 786; T.J. Katz and J. McGinnis, J. Amer. Chem. Soc. 99, 1903 (1977).

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