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UNEXPECTED REARRANGEMENT DURING THE CYCLOADDITION OF YNAMINES WITH CYCLOBUTENONES.

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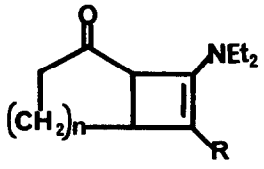
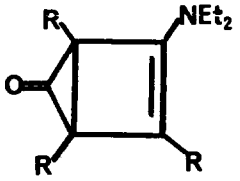
The cycloadducts 1 obtained from ynamines [1] and cyclopentenones [2] or cyclohexenones [3] are, as expected, thermally stable [4a], whereas the very strained cycloadduct 2 obtained from diphenyl-cyclopropenone [5] undergoes, in situ, a rearrangement which does not follow the selection rules [4].

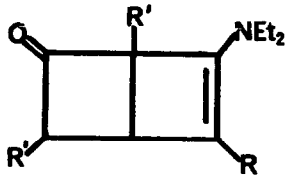


1

n = 1 or 2

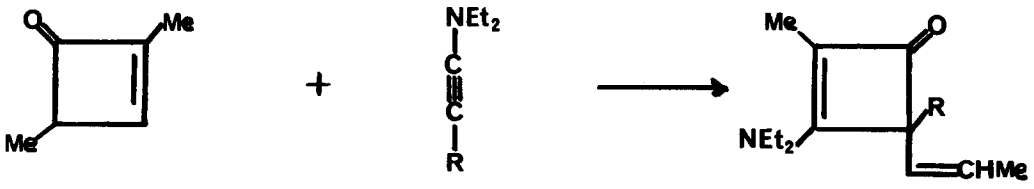


2



3

We now report the first results concerning the reaction of ynamines with cyclobutenones. These unexpected results which deal with 2,4 dimethylcyclobutenone 4 [6] and the ynamines 5 [1] show that, in all cases, the product is not an amino bicyclo (2-2-0) hexenone of type 3, but an amino-cyclobutenone 6 which arises from a very unusual rearrangement.



4 5 6

a) R=CH$_3$; b) R=SiMe$_3$; c) R=CD$_3$

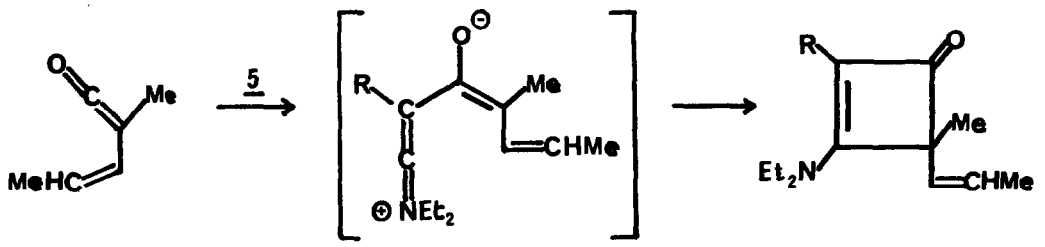
The reaction of cyclobutenone 4 [6] (1.3 equivalent of ynamines) is very fast with the reactive ynamines 5a [7] and 5c [8] (ether, -50°C, 30 min.) but slower with the less reactive ynamine 5b [9] (acetonitrile, 25°C, 20 h). The amino-cyclobutenones 6 are purified by Kugelrohr distillation :

6a : [B.p. 70°-80° (0.01 mm) ; M^+ = 207 ; 50 % yield ; IR (neat) : 1745, 1600-1570 (broad) cm^{-1} ; NMR (CCl_4) : 1.15 (t,6H), 1.26 (s,3H), 1.6 (s,3H), 1.7 (m,3H), 3.3 (m,4H), 5.45 (m,2H)]

6b : [B.p. 70°-80° (0.01 mm) ; 55 % yield ; IR (neat) : 1745, 1600-1570 (broad) cm^{-1} ; NMR (CCl_4) : 0.05 (s,9H), 1.15 (t,6H), 1.6 (s,3H), 1.7 (m,3H), 3.3 (m,4H), 5.5 (m,2H)] .

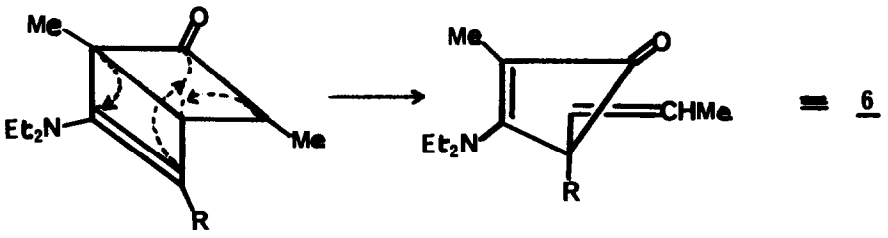
6c : [B.p. 80°-90° (0.01 mm) ; M^+ = 210 ; 55 % yield ; IR (neat) : 1745, 1600-1570 (broad) cm^{-1} ; NMR (CCl_4) : 1.21 and 1.29 (2t,6H), 1.67 (s,3H), 1.75 (d,d,3H), 3.1-3.5 (m,4H), 5.49 (m,2H)] .

The structure proposed for amino-cyclobutenones 6, is in agreement with the results of elementary analysis, Mass Spectra, IR and NMR spectroscopic data. This structure has been established by comparison with samples obtained via the reaction [10] of ynamines 5a and 5c (0.5 equivalent) with ketene 7 [11] . When R is a methyl group (5a : R = CH_3), the cycloadduct 9a is identical (IR, NMR, Mass Spectrum) with amino-cyclobutenone 6a, but when R is deuteromethyl group (5c : R = CD_3) the cycloadduct 9c : [B.p. 80°-90° (0.01 mm) ; M^+ = 210 ; 75 % yield ; IR (neat) : 1745, 1600-1570 (broad) cm^{-1} ; NMR [12] (CCl_4) 1.21, 1.29 and 1.33 (t,t and s,9H), 1.76 (d,d,3H), 3.1-3.5 (m,4H), 5.49 (m,2H)] is by contrast, very different (NMR) from its regioisomer 6c.



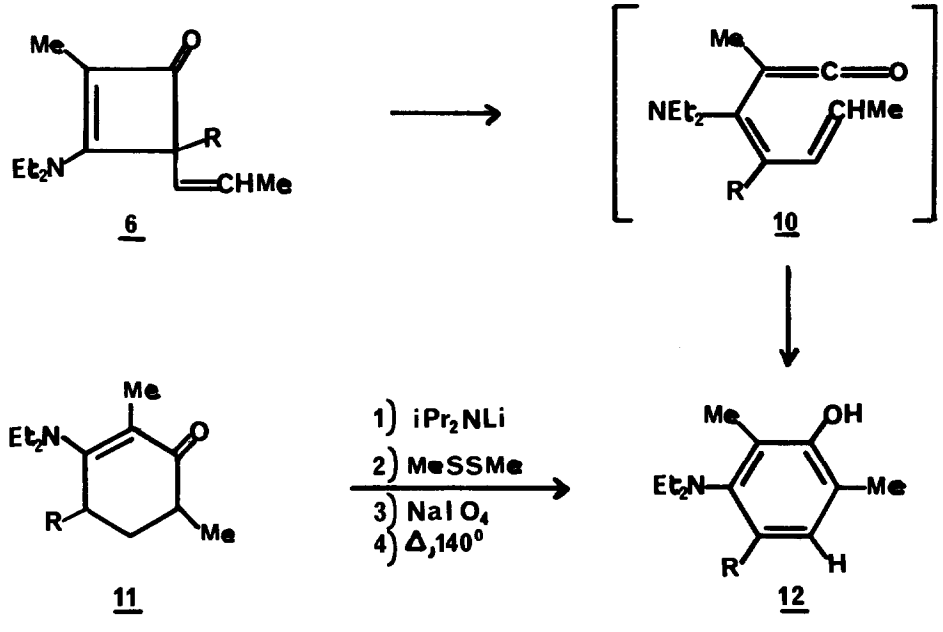
7 8 a) R=CH_3; c) R=CD_3 9

These results suggest that the initial step of the cycloaddition of ynamines with cyclobutenones is an amino bicyclo (2-2-0) hexenone such as 3. This bicyclic adduct 3 rearranges in situ, to give regiospecifically the cyclobutenone 6 by a concerted process which involves one π bond and two σ bonds ($\pi^2 + \sigma^2 + \sigma^2$). For such a process to be Woodward-Hoffmann allowed the number of suprafacial (4q + 2) elements must be odd [4b,c]. This implies that, in particular, this rearrangement might be ($\pi^2_s + \sigma^2_s + \sigma^2_s$) [13]. The aromatization of the bicyclic adduct 3 does not occur, at this temperature, for this disrotatory process which would have given phenols 12, is thermally forbidden [4a].



3 ≡ 6

By contrast, the aromatization of amino-cyclobutenone 6 is very easy and leads to phenols 12. For instance, the phenol 12a : B.p. 100°-110° (0.01 mm) ; IR (neat) : 3600-3100, 1580, 805 cm^{-1} ; NMR (CCl_4) : 0.95 (t,6H), 2.1 (s,9H), 3.05 (q,4H), 6.6 (s,1H) is obtained by heating 6a above 140°. In this case, one can assume that the easy thermal opening of the cyclobutenone ring [14] which leads to ketene 10 is followed by the cyclization [4] of the triene 10 [15]. One notices that when R is a trimethylsilyl group, it disappears during the aromatization. The phenol 12d : [B.p. 80°-100° (0.05 mm) ; IR (neat) : 3600-3100, 1585, 800 cm^{-1} ; NMR (CCl_4) : 0.85 (t,6H), 2.1 (s,6H), 2.85 (q,4H), 6.5 (d,J = 8 Hz,1H), 6.8 (d,J = 8 Hz,1H)] obtained in 60 % yield from 6b [15] is, indeed, identical with an authentic sample prepared from 11d [16], according to the pathway indicated, cf ref. 17.



a) R=Me ; b) R=Si(Me)$_3$; c) R=CD_3 ; d) R=H

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7) Commercially available from Fluka (Switzerland).

8) 5c is prepared from CD_3OTs according to : J. FICINI, C. BARBARA - Bull. Soc. Chim. France - 2787 (1965).

9) J. FICINI, A. DUREAULT - C.R. Acad. Sc. Paris - 273, 289 (1971).

10) Amino-cyclobutenones which are produced via reaction of ketenes with ynamines have a structure of type 9, see : (1), page 1469.

11) 7 is prepared according to H. MAYR - Angew. Chem. Int. Ed. - 14, 500 (1975), from 4 by refluxing in cyclohexane : after 1 h 30, 80 % (by NMR) of 4 is converted into 7.

12) NMR spectra of all compounds described in this paper are taken on a **Varian** T 60 Apparatus, except 9c and 6c taken on Cameca 250 MHz Apparatus for which we thank Dr. LALLEMAND - Ecole Normale Supérieure, Paris.

13) We thank Professor A. DEVAQUET (Université Pierre et Marie Curie, Paris) for fruitful discussions.

14) J.E. BALDWIN, M.C. DANIEL - J. Amer. Chem. Soc. - 90, 6118 (1968).

15) This type of intermediate has been assumed to rationalize for instance, the racemization of usnic acid : G. STORK - Chem. and Industry - 915 (1955) or the formation of α pyrones : J. FICINI, J. POULIQUEN, J.P. PAULME - Tetrahedron Letters - 2483 (1971).

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