7-METHYL-TRICYCLO[5.3.0.0.^{1,6}]DECA-2,4-DIEN-8-ONES: THE FIRST EXAMPLES OF TRICYCLONORCARADIENONES IN TAUTOMERIC EQUILIBRIUM WITH THE 7-METHYL-BICYCLO[5.3.0]1,3,5-DECATRIEN-8-ONES

Antonio Saba

Dipartimento di Chimica, Via Vienna, 2 1-07100 Sassari Italy

Summary: Introduction of a methyl group at the C_7 position of bicyclo[5.3.0.] 1,3,5-decatrien-8-one results in a stabilization of the norcaradienic structure which causes equilibrium between the two cyclotautomers whose populations were determined in the case of 3c.

The selective intramolecular addition of the carbenoid species, derived by catalytic decomposition of the diazomethyl ketone 1a, leads to the tropilidenic (T) 2,3-dihydro-1(2H)-azulenone 2a(T)[1] which rearranges to 2-tetralone on brief exposure to trifluoroacetic acid[2]. Both these reactions need the intermediacy of the norcaradienic (N) tricyclo [5.3.0.0.^{1,6}] deca-2,4-dien-8-one 2a(N), but no traces of this form have been detected. Also the cycloaddition carried out with PTAD (4-phenyl-1,2,4-triazoline-3,5-dione) and $^1O_2$, useful dienophiles for studying these valence equilibria[3], selectively afforded products of formal [4+2] or [6+2]-tropilidenic addition[4].

Herein is reported evidence that the 7-methyl-bicyclo[5.3.0]1,3,5-decatrien-8-ones 3b-d exist in equilibrium with the corresponding norcaradienic forms.

1	a	b	c	d	e
R^1	H	H	Me	H	H
R^2	H	H	H	Me	Me
R^3	H	Me	Me	Me	H

3	b	c	d
R^1	H	Me	H
R^2	H	H	Me
R^3	Me	Me	Me

| 2	a[1]	e
R^1	H	H
R^2	H	Me

The title systems were prepared by catalytic decomposition of the diazo ketones **1b, 1c,** and **1d** (obtained from the corresponding hydrocinnamic acids)[5]. Dropwise addition of a dichloromethane solution of the diazo ketones **1b-e** (0 5 ml, 1 mmol) to a refluxed solution of rhodium acetate dimer (0.01 mmol), filtration on neutral alumina, and flash chromatography on silica gel (petroleum ether-diethyl ether 95:5) gave the compounds **3b-e** which appeared homogeneous to TLC.

The first sign of the presence of a cyclotautomeric equilibrium **2(N)** $\rightleftharpoons$ **3(T)** came by observing the ^{1}H NMR peaks assigned to the H-1 protons of the compounds **3b, 3c,** and **3d**[6]. The corresponding resonances, observed at δ 4.35, 3.86 and 4.28 ppm respectively, were not in agreement with those expected for a tropilidenic structure nor with those of a norcaradienic one[7]. Therefore, starting from these results, an investigation of the relative reactivity of the equilibrium tautomers toward the PTAD was performed.

Dropwise addition of a dichloromethane solution of PTAD (1 mmol) to an ice cooled and stirred solution of **3b-d** in the same solvent (1 mmol) showed instantaneous decoloration of the brick-red colour of the dienophile. The resulting 1 to 1 adducts were purified by silica gel column chromatography eluting with a mixture of dichloromethane-ethyl ether 8:2 and recrystallizing from ethanol.

All these cycloadditions selectively afforded the formal [4+2] norcaradienic adducts **4b-d,** dirty white crystals, m.p. 166-167°C, 164-165°C and 171-172°C respectively[8]. This behaviour was in line with the presence of the **2(N)** isomer, the planar diene moiety is well known to be more reactive toward the dienophiles than the twisted tropilidenic form[3].
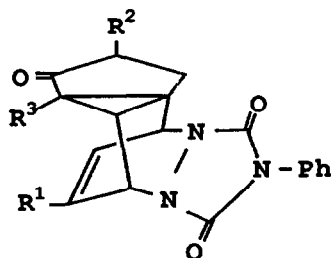
4	b	c	d
R^1	H	Me	H
R^2	H	H	Me
R^3	Me	Me	Me

5	a(4a)	e
R^1	H	H
R^2	H	Me

4
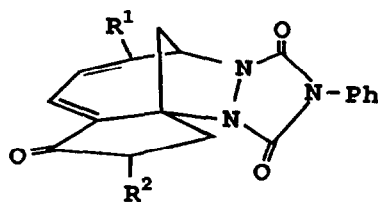
5

The structures of the adducts were assigned on the basis of elemental analysis and ^{1}H NMR spectroscopy and substantiated by decoupling experiments and by the absolute value of the coupling constants which were in good agreement with the literature data[9]. Particularly diagnostic is the

presence of two olefinic proton resonances at 6.36 and 6.34 in the case of **4b** and **4d** and only one at 5.97 ppm for **4c**, thus excluding the formal [4+2] or [6+2] tropilidene-type additions. The doublets observed at 1.63 ppm (J= 4.5 Hz), 1.60 ppm (J= 4.5Hz) and 1.66 ppm (J= 4.3Hz) for **4b, 4c** and **4d** respectively, coupled with the allylic protons at 5.34 ppm (J= 4.5Hz), 5.08 ppm (J= 4.5Hz) and 5.30 ppm (J= 4.3Hz) were also in accordance with the (**N**) form.

To determine the configuration of cyclopropanic carbon bearing the methyl group, recourse was made to nuclear Overhauser effect (n.O.e.) experiments. Irradiation of the above methyl resonances brought about a positive effect on the olefinic protons showing it to be directed toward the unsaturated bonding.

Further evidence for the valence tautomerism was obtained for **3c** by observing the ^{1}H NMR signals of H-1 at various temperatures in $CS_2/CDCl_2$ (3:1 v/v) at 300 MHz. As the temperature was lowered, these signals broadened and after passing the coalescence point (-65-70°C) new signals appeared at 5.60 ppm and 2.20 ppm at -95°C which, on the basis of the literature data[10], could be assigned to the tropilidene and norcaradiene forms respectively with a population of 15:85 (obtained by signals integration at -95°C). At lower temperatures a series of signal splittings is clearly observable which is consistent with the existence of other isomers probably due to ring inversion.

The low temperature ^{13}C NMR spectra of **3c** in $CS_2-CD_2Cl_2$ (3:1 v/v) at 25 MHz were in accordance with these results also being typical of an equilibrium system: at 25°C the C-1 carbon exhibited a broad signal at 82 ppm which disappeared as the temperature decreased and then two new resonances appeared at 32 ppm and 125 ppm which may be assigned to (**N**) and (**T**) tautomers respectively[10].

By use of the chemical shift data for H-1 the equilibrium constant for **3c** was calculated as 0.942 at 25°C.

The decomposition product of **1e** was identified as 9-methyl-bicyclo [5.3.0.]1,3,6-decatrien-8-one **2e** without traces of the related tricyclic (**N**) tautomer. The structure of the cycloheptatriene moiety of **2e** was assigned by ^{1}H NMR spectroscopy by comparison with data of **2a**[1a,b,11]. Also in this case the absence of any detectable equilibrium was substantiated by the cycloaddition with PTAD, performed following the above procedure (dichloromethane, 0°C). This reaction selectively afforded the formal [6+2]-tropilidene adduct **5e**, of which the structural assignment was again attributed on the basis of elemental analysis and ^{1}H NMR spectroscopy. The three olefinic resonances at 5.61, 6.13 and 6.53 ppm were particularly diagnostic for the structure of **5e**, confirmed by decoupling experiments and

by the absolute value of the coupling constants in agreement with those of **4a** and literature data[3,9].

It is clear that the presence of a methyl group on 7-tropilidenic carbon in these condensed systems plays a very important role in stabilizing the **(N)** tautomers. That substitution, by fixing the cyclopentanone annelation at C_6-C_7 of cycloheptatriene, causes the contemporary presence at C7 of a carbonyl group, which is found, by its π-acceptor effect, to exert a strain reducing function[12]. Instead, in the case of compounds **2a,e**, the different cyclopentanone annelation, which does not involve the tropilidenic sp^3 carbon, results in a stabilization of the **(T)** tautomers[13].

References and notes

1. a)A. Constantino, G. Linstrumelle, and S. Julia, Bull. Soc. Chim. Fr., 907 (1970). b)L.T. Scott, J.C.S. Chem. Commun., 882 (1973). c)L.T. Scott, M.A. Minton and M.A. Kirms, J. Am. Chem. Soc., 102, 6311 (1980).
2. M.A. McKervey, S.M. Tuladhar, and F. Twohig, J.C.S. Chem. Commun., 129 (1984).
3. See for example W. Adam, M. Balci and B. Pietrzak, J. Am. Chem. Soc., 101, 6285 (1979).
4. a)A. Saba and O. De Lucchi, Heterocycles, 26, 2339 (1987). b)L.T. Scott and C.M. Adams, J. Am. Chem. Soc., 106, 4857 (1984). c)N. Akbulut, A. Menzek and M. Balci, Tetrahedron Lett., 28, 1689 (1987).
5. The diazo compounds **1b-e** were obtained from the corresponding hydrocinnamic acids by the well known procedures. They exhibit the characteristic diazo-stretching vibrations at 2120-2130 cm^{-1}.
6. All new compounds presented correct composition by elemental analysis and spectral data in accordance with the proposed structure. As example the ^{1}H NMR and ^{13}C NMR spectra of compound **3c** are reported. ^{1}H NMR (CD_2Cl_2) δ: 6.10 (2H, q, J= 8.1, H-C-4, H-C-5); 5.87 (1H, d, J= 7.8, H- C-2); 3.86 (1H, d, J= 7.8, H-C-1); 2.63-2.22 (4H, m); 2.02 (3H, s); ^{13}C NMR (CD_2Cl_2) δ: 10.81, 22.99, 27.31, 33.94, 82.05, 123.98, 124.11, 126.3, 126.4, 128.9, 134.6, 192.42.
7. See for example: G. Jenner and M. Papadopulos, J. Org. Chem., 51, 585 (1986).
8. As example the ^{1}H NMR and ^{13}C NMR spectra of the adduct **4b** are reported. ^{1}H NMR (CDCl3) δ: 7.43 (5H, m); 6.36 (m, H-3 and H-4, $J_{2,3}$= 4.2, $J_{3,4}$= 3.9; $J_{3,5}$= 5.1; $J_{4,5}$= 5,4); 5.34 (m, H-2, $J_{1,2}$= 4.5, $J_{2,3}$= 4.2, $J_{2,4}$= 4.8); 5.21 (q, H-5, $J_{3,5}$ = 5.1, $J_{4,5}$= 5.4); 2.35-2.16 (4H, m); 1.63 (d, H-1, $J_{1,2}$= 4.5); 1.26 (3H,s); ^{13}C NMR (CDCl3) δ: 20.81 (Me); 24.11 , 25.73, 32.65, 36.66, 40.13, 53.57, 57.29, 125.46, 128.30, 128.90, 129.10, 129,70, 131.60, 156.71.
9. See for example : G. Crow, R. Rodebaugh, M. Grippi, G. De Vicaris , C. Hyndman and J. Marakowsky, J. Org. Chem., 38, 3094 (1973). K.Arano, M.M. Yasuda, and K. Kanematsu, ibid., 47, 3736 (1982).
10. a)K. Takeuchi, M. Arima, and K. Okamoto, Tetrahedron Lett., 22, 3081 (1981). b)K. Takeuchi, T. Kitagawa, T. Toyama, and K. Okamoto, J.C.S.Chem. Commun., 313, (1982). c)K. Takeuchi, T. Kitagawa, Y. Senzaki, H. Fujimoto, and K. Okamoto, Chem. Lett., 69 (1983). d)K. Takeuchi,T. Kitagawa, Y. Senzaki, K. Okamoto, Chem. Lett., 73 (1983). e)K. Takeuchi, Y. Senzachi, and K. Okamoto, J.C.S. Chem. Commun., 111 (1984). f)K. Takeuchi, H. Fujimoto, T. Kitagawa, H. Fujii, and K. Okamoto, J.C.S. Perkin Trans. II, 461(1984).
11. Compound **2e**: ^{1}H NMR (CDCl3) δ: 6.83-6.02 (3H, m); 5.55-5.16 (1H, m) ;3.11 (1H, q, J= 7Hz); 2.76 (2H, d, J= 5Hz); 2.60-1.83 (2H, m); 1.13 (3H, d, J= 7Hz).
12. E. Ciganeck, J. Am. Chem. Soc., 89, 1454 (1967).
13. G. Mayer, Angew. Chem. Internat. Edit., 6, 402 (1967).