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Evidence for an 1,7-*O,O'*-Intramolecular Acyl Migration

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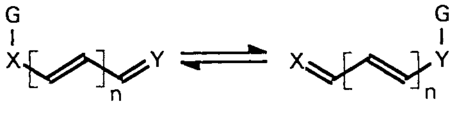
The intramolecular nature of the 1,7-*O,O'*-acyl migration observed during the column chromatography of the diazonium coupling products of methyl 3-acetoxy-6-hydroxy-2-methoxypentafulvene-1-carboxylate was determined by isotopic labeling and mass spectrometry. A cooperative transportation by the hydrazono group is proposed to explain this fact.

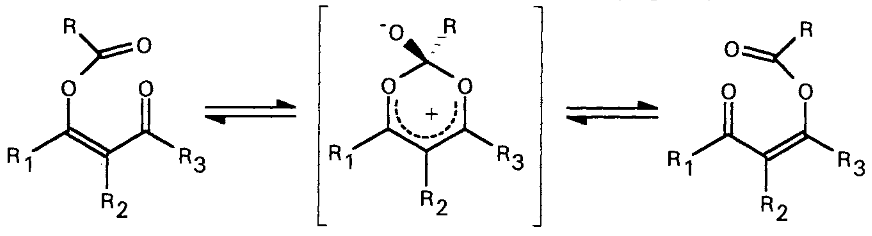
The question of whether it is possible to observe intramolecular tautomeric rearrangements **1A**→**1B** in which G is an acidic moiety led to an intensive work that has excellently been reviewed by Minkin *et al.*[1]



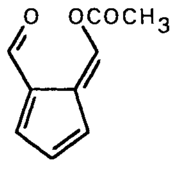
1A **1B**

X, Y = O, S, NR
G = CR_3, COR, Ar, NO, NO_2, PR_2, POR_2, SR, SOR, SOR_2
n = 0, 1, 2, 3,...

Among such tautomerisms, the *O,O'*-acyl rearrangements of compounds of general structure (**2A**) were shown to be intramolecular and to proceed through a cyclic intermediate (**2C**). A similar behavior has been observed for the 1-formyl-6-acetoxypentafulvene (**3**), and tropolone acetate (**4**),[2] the migratory ability of the acetyl group being strongly dependent on the angle of approach of the nucleophile center to the carbonyl group.[3]



2A **2C** **2B**



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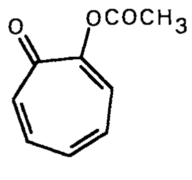

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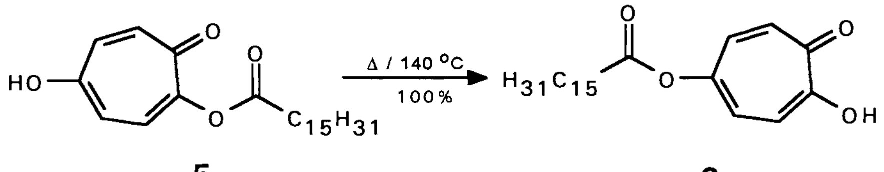
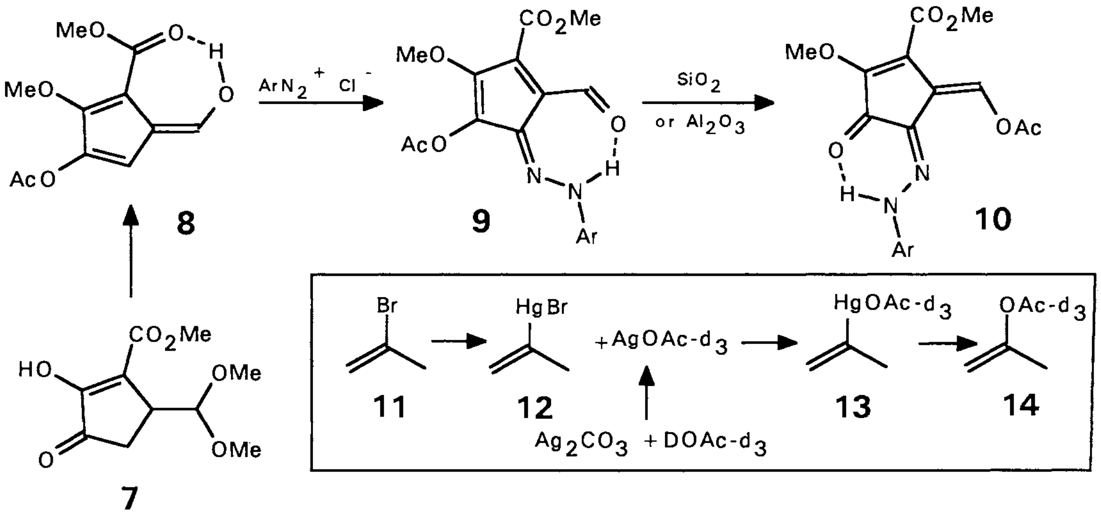
On the other hand, Takeshita *et al.*[4] have described very recently an intermolecular acyl migration for the 5-hydroxy-2-octadecanoyloxytropone (**5**) by an elimination-addition reaction. They proved the intermolecular nature of the process by mass spectrometry.



5 **6**

As a part of our study on the structure and reactivity of 2,3,6-trioxypentafulvenes[5] we found that compounds **10** were formed when methyl (*E*)-4-acetoxy-6-arylamino-1-formyl-3-methoxy-6-azapentafulvene-2-carboxylates (**9**) were column chromatographed using SiO_2 or Al_2O_3 as the stationary phase. Such transformation is the result of an 1,7-*O,O'*-acyl migration and simultaneous π-system reorganization, the intra- or intermolecular nature of which is discussed in the present communication.

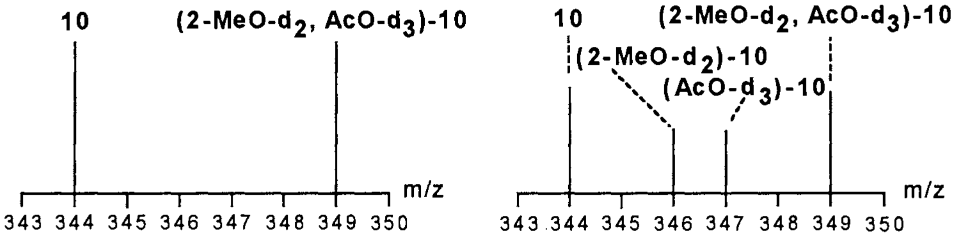
In order to solve this question we planned to prepare the pentafulvene **(2-MeO-d_2, 3-AcO-d_3)-8** using CD_2N_2[6] and isopropenyl acetate-d_3 in our synthesis[5b] of **8** from the cyclic precursor **7**. For the synthesis[7] of the not previously described isopropenyl acetate-d_3 we have modified the procedure that started with the transformation of isopropenyl bromide (**11**) to **12**.[8] Then we have treated[9] **12** with silver acetate-d_3, obtained by reaction of silver carbonate with acetic acid-d_4,[10-11] to yield isopropenylmercury acetate-d_3 (**13**). Finally we have pyrolized[12] **13** to obtain isopropenyl acetate-d_3 (**14**).



8 **9** **10** **7**

Once **(2-MeO-d_2, 3-AcO-d_3)-8** was obtained,[13] we carried out the diazonium coupling with benzenediazonium chloride to afford **(3-MeO-d_2, 4-AcO-d_3)-9**. Then an equimolar mixture of **9** and **(3-MeO-d_2, 4-AcO-d_3)-9** was column chromatographed on SiO_2 and the mass spectrum of the resulting material was recorded. The process was also carried out with pure **9** and pure **(3-MeO-d_2, 4-AcO-d_3)-9** to obtain **10** and **(2-MeO-d_2, AcO-d_3)-10**[14] for control purposes.

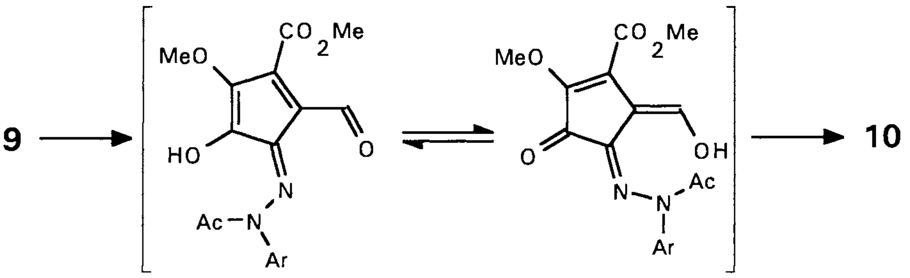
Depending on the intramolecular or intermolecular nature of the 1,7-*O,O'*-acyl migration, two different patterns may be expected in the molecular ion region of the mixture resulting from the column chromatography of **9** and **(3-MeO-d_2, 4-AcO-d_3)-9** (Scheme 1). The first one would be caused by a totally intramolecular migration, while the second one would reflect crossed intermolecular migrations by the presence of significant amounts of **(2-MeO-d_2)-10** and **(AcO-d_3)-10**.



Intramolecular *Intermolecular*

Scheme 1.

The mass spectrum[15)] of the mixture only showed fragments at m/z 344 and 349 with a strong 350, which was also observed in the MS of pure **(2-MeO-d_2, AcO-d_3)-10**, evidencing the intramolecular nature of the process. Such an 1,7-*O,O'*-intramolecular acyl migration is easily understandable in terms of a cooperative transportation carried out by the hydrazono group present in **9**. According to this hypothesis the nitrogen atom linked to the aryl group may trap the acetyl group and, through isomerization of the hydrazono group, may bring it to the other side of the molecule. A simultaneous π-system reorganization and the subsequent transfer of the acyl group to the formyl group oxygen will lead to **10**. That is to say this 1,7-intramolecular acyl migration would be the result of two consecutive intramolecular rearrangements. The driving force for this process may be the greater stability of **10** in relation to **9** that has been evaluated by semiempirical AM1 calculations[16)] in approximately 10 kcal/mol. Furthermore, the postulated intermediate **15B** is also about 10 kcal/mol more stable than **15A**.



15A **15B**

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2) S. Masamune, A. V. Kemp-Jones, J. Green, and D. L. Rabenstein, *J. Chem. Soc., Chem. Commun.*, **1973**, 283; A. Mori and H. Takeshita, *J. Am. Chem. Soc.*, **112**, 8635 (1990).

3) These angle values (θ) were evaluated by V. I. Minkin *et al* using MINDO/3 calculations.[1)]

4) H. Takeshita, R. Mori, and A. Mori, 7th International Symposium on Novel Aromatic Compounds (ISNA-7), Poster 132, Victoria, B. C., Canada, July 19-24, 1992.

5) a) P. Victory, A. Alvarez-Larena, E. Barberá, X. Batllori, J. I. Borrell, and C. Córdoba, *J. Chem. Res. (S)*, **1989**, 88, *(M)*, 0631; b) P. Victory, A. Alvarez-Larena, C. Beti, J. I. Borrell, X. Batllori, and C. Córdoba, *Chem. Ber.*, **124**, 207 (1991); c) P. Victory, A. Alvarez-Larena, X. Batllori, J. I. Borrell, A. Vidal-Ferran, and J. F. Piniella, *Anales*, **88**, 499 (1992).

6) CD_2N_2 was prepared using *N*-methyl-d_3-*N*-nitroso-*p*-toluenesulfonamide (Diazald®-*N*-methyl-d_3, Aldrich 32,990-8), sodium hydroxyde-d, and methanol-d in the procedure described by M. Hudlicky, *J. Org. Chem.*, **45**, 5377 (1980).

7) *Isopropenylmercury acetate-d_3* (**13**): To a solution of 40.3 g (0.125 mol) of isopropenylmercury bromide (**12**)[8] in 100 ml of anhydrous THF was added a suspension of 21.3 g (0.125 mol) of silver acetate-d_3 [prepared by mixing 38 g (0.14 mol) of Ag_2CO_3[11] and 20 g (0.31 mol) of acetic acid-d_4 (CEA ref. DMM-12) in 30 ml of water] in 200 ml of THF. The mixture was stirred in the dark for 15 h, then was filtered and concentrated *in vacuo* to give 32.4 g (78%) of **13** as a white solid, mp 99-101 °C (from hexane). IR (KBr) υ : 3030, 2940, 1600 (C=O), and 1335 cm^{-1}. ^1H NMR (Acetone-d_6) δ: 2.0 (m, 3H, $J_{H\text{-}Hg}$ = 93 Hz, CH_3), 5.05 (m, 1H, $J_{H\text{-}Hg}$ = 138 Hz) and 5.50 ppm (m, 1H). Ms, m/z (relative intensity): 301 (M^+, 0.3), 302 (0.4), 303 (0.4), 305 (1.0), 307 (0.5), 46 (12.7), 41 (100). *Anal.* Found: C, 19.56; O, 10.48 %. Calcd for $C_5H_5D_3O_2Hg$: C , 19.76; O, 10.54 %.

Isopropenyl acetate-d_3 (**14**): 6.0 g (0.02 mol) of **13** were heated with stirring at 125 °C to give by distillation 1.75 g (79%) of **14**, bp 94 °C. IR (film) υ: 1760 (C=O) and 1675 cm^{-1} (C=C). ^1H NMR ($CDCl_3$) δ: 2.00 (s, 3H, Me) and 5.20 (s, 2H, CH_2). Ms m/z (relative intensity): 103 (M^+, 16.7), 58 (11.7), 46 (100).

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10) R. Collongues, "Nouveau Traité de Chimie Minérale," ed by P. Pascal, Massot et cie., Paris (1957), Vol. 3, p. 622.

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12) D. J. Foster and E. Tobler, *J. Am. Chem. Soc.*, **83**, 851 (1961).

13) *Methyl 3-acetoxy-d_3-6-hydroxy-2-methoxy-d_2-pentafulvene-1-carboxylate* (**(2-MeO-d_2, 3-AcO-d_3)-8**): The procedure previously described for **8**[5b)] but using 2.30 g (0.01 mol) of **7**, CD_2N_2,[6)] 100 ml of isopropenyl acetate-d_3, and 0.2 ml of 98% sulfuric acid afforded 1.48 g (49%) of pure **(2-MeO-d_2, 3-AcO-d_3)-8**, mp 65-66 °C.

14) *Methyl (4Z,5Z)-5-(acetoxy-d_3-methylene)-2-methoxy-d_2-3-oxo-4-phenylhydrazono-1-cyclopentene-1-carboxylate* (**(2-MeO-d_2, 5-AcO-d_3)-10**): The procedure previously described for **10**[5c)] but using 0.51 g (2,1 mmol) of **(2-MeO-d_2, 3-AcO-d_3)-8** afforded 0.57 g (80%) of **(2-MeO-d_2, AcO-d_3)-10**.

15) Mass spectra were registered on a Hewlett-Packard 5989 A mass spectrometer at 70 eV by Prof. L. Comellas (Departament de Química Analítica).

16) E. Clementi, Modern Techniques in Computational Chemistry: MOTECC'91. IBM, Kingston, New York 12401, U.S.A.; M. J. S. Dewar, AMPAC, University of Florida, Gainesville, U.S.A.

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