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DERIVATION OF A DIAZABICYCLO[3.2.0]HEPTADIENE FROM A DIAZATRICYCLO[4.1.0.0^{2,7}]HEPTENE.

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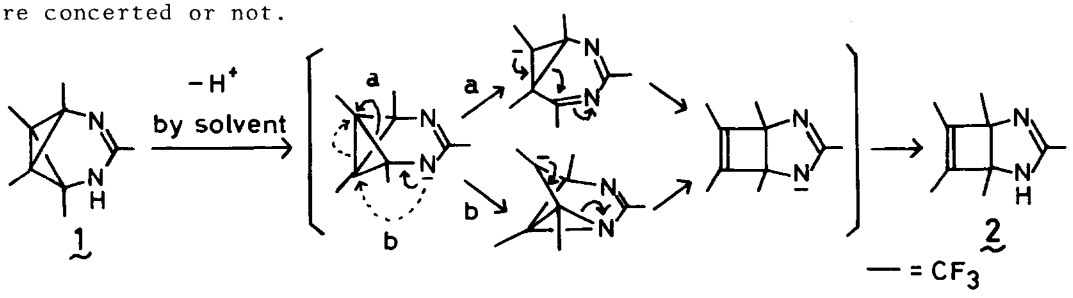
Abstract: Trifluoromethylated 3,5-diazatricyclo[4.1.0.0^{2,7}]hept-3-ene was converted thermally or photochemically to 2,4-diazabicyclo[3.2.0]hepta-2,6-diene compound. The latter was photolyzed to an imidazole compound.

In the previous paper, we reported the synthesis of 1,2,4,6,7-pentakis(trifluoromethyl)-3,5-diazatricyclo[4.1.0.0^{2,7}]hept-3-ene (**1**), a new valence bond isomer of diazepine.1) Now, we found that thermal and photochemical reactions of **1** gave another valence bond isomer of the diazepine, 1,3,5,6,7-pentakis(trifluoromethyl)-2,4-diazabicyclo[3.2.0]hepta-2,6-diene (**2**).

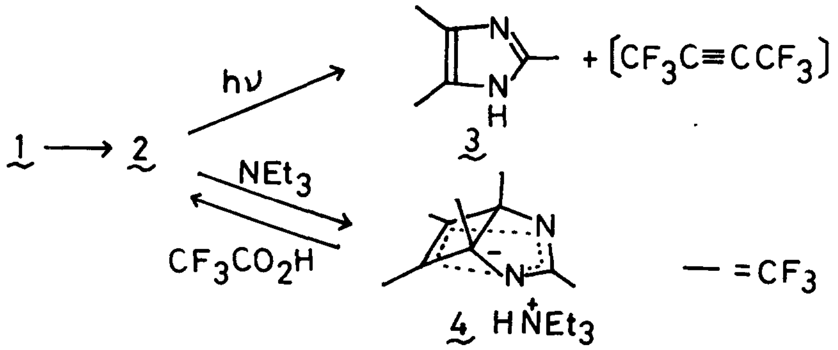
Heating a solution of **1** in ether at 140° gave **2** quantitatively. Half life of **1** at this temperature is 4.3 h. **2**: mp 138°C; ^{19}F-NMR(Et$_2$O) δ2) -0.66 (6F, m) 7.6 (3F, s) 8.6 (3F, m) 9.7 (3F, m); ^{1}H-NMR((CD$_3$)$_2$CO) δ 10.5 (bs NH); IR(Nujol) ν 3160, 1705, 1620, 1500 and 1280-1100 cm^{-1}; Mass M/e 434 (M^{+}); High resolution mass spectrum calcd. for $C_{10}HN_2F_{15}$ 433.990, found 433.992. Further, **1** isomerized rapidly to **2** in acetone or methanol. This fact suggests that this isomerization is not a free radical, but an ionic reaction. Taking this polarity-dependence and high acidity of **1** into consideration,1) the mechanism of this isomerization is speculated as route a or b in the following scheme, but we can neither distinguish these two mechanisms, nor determine whether they are concerted or not.



Irradiation of a solution of **1** in ether in a quartz tube with a low pressure mercury lamp gave **2**, which was cleaved to 2,4,5-tris(trifluoromethyl)-imidazole (**3**) and hexafluorobutyne-2 by further irradiation. **3**: mp 148-151°C (purified by bulb-to-bulb distillation at 110°C/5 mmHg); ^{19}F-NMR($(CD_3)_2$CO) δ2) -3.0 (6F, s), 1.0 (3F, s); ^{1}H-NMR($(CD_3)_2$CO) δ 5.7 (bs); IR(Nujol) ν 1320, 1280, and 1220-1150 cm^{-1}; mass M/e 272 (M^+); High resolution mass spectrum calcd. for $C_6HN_2F_9$ 272.000, found 272.000. This result is distinguished from that of photolysis of 2-oxabicyclo[3.2.0]hepta-3,6-diene, which did not give any observable changes.4)

Addition of triethylamine to a solution of **2** in ether caused quantitative precipitation of a salt **4**. **4**: mp 115°C (dec.); ^{19}F-NMR($(CD_3)_2$CO δ3) -3.0 (6F, m), 3.6 (3F, s), 6.0 (6F, m); ^{1}H-NMR($(CD_3)_2$CO) δ 1.40 (9H, t, J=7.0 Hz), 3.4 (6H, q, J=7.0 Hz), 7.36 (1H, s); IR(Nujol) ν 2700-2600, 1680, 1510, and 1280-1100 cm^{-1}; Anal, calcd. for $C_{16}H_{16}N_3F_{15}$ C, 35.62; H, 2.98; N, 7.69; F, 53.23. Found C, 35.90; H, 3.01; N, 7.85; F, 53.24.

This high acidity of **2** might be explained by bishomoaromaticity of an anion part of **4**. This hypothesis is supported by Goldstein's rule of bicycloaromaticity.5) Compound **2** was regained from **4** on treatment with trifluoroacetic acid.



References and Notes

1) Y. Kobayashi, T. Nakano, M. Nakajima, and I. Kumadaki, submitted to Tetrahedron Letters.

2) $C_6H_5CF_3$ as an external standard; upfield shifts are quoted as positive.

3) $C_6H_5CF_3$ as an internal standard.

4) Y. Kobayashi, Y. Hanzawa, W. Miyashita, T. Kashiwagi, T. Nakano, and I. Kumadaki, J. Am. Chem. Soc., 1979, 101, 6445.

5) M. J. Goldstein, J. Am. Chem. Soc., 1967, 89, 6357; M. J. Goldstein, R. Hoffmann, J. Am. Chem. Soc., 1971, 93, 6193.

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