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THE SYNTHESES OF NEW VALENCE-BOND ISOMERS OF PENTAKIS(TRIFLUOROMETHYL)-1,3-DIAZEPINE

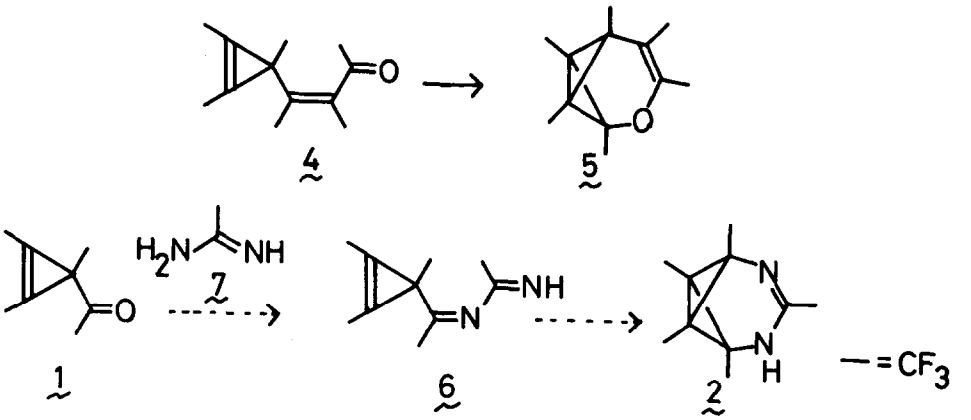
Yoshiro Kobayashi*, Takaharu Nakano, Masaharu Nakajima, and Itsumaro Kumadaki

Tokyo College of Pharmacy, Horinouchi, Hachioji, 192-03 JAPAN

Summary: A new valence-bond isomer of pentakis(trifluoromethyl)-1,3-diazepine was synthesized from tris(trifluoromethyl)cyclopropenyl trifluoromethyl ketone, and reacted with diazomethane to give an N-methylated product.

Previously, we reported that the reaction of tris(trifluoromethyl)cyclopropenyl trifluoromethyl ketone (1) with azo compounds in the presence of triphenylphosphine afforded various heterocyclic compounds.[1] We now report the syntheses of two valence-bond isomers of 1,3-diazepine derivatives; 1,2,4,6,7-pentakis(trifluoromethyl)-3,5-diazatricyclo[4.1.0.$0^{2,7}$]hept-3-ene (2) and N-methyl derivative (3) from 1.

It is known that cyclopropene derivative (4) isomerizes to hexakis(trifluoromethyl)-3-oxatricyclo[4.1.0.$0^{2,7}$]heptene (5) by heating.[2] The cyclopropene derivative (6), which might be synthesized from 1 and trifluoroacetamidine (7), was expected to isomerize to 2.

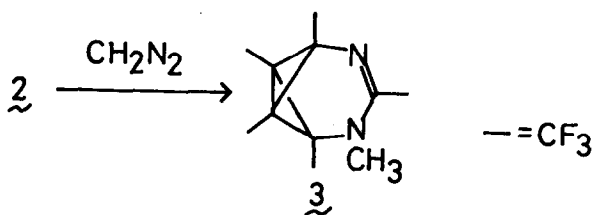


To a solution of 1 (1 eq. mole) in ether was added $TiCl_4$ (1 eq. mole), which was a good reagent for converting a carbonyl group of 1 to an imine group,[3] under argon atomosphere at -78°. A solution of 7 (3 eq. mole) in ether

was added slowly into this reaction mixture. After the addition of 7, the mixture was allowed to warm up to room temperature for 3 hrs under stirring. The reaction mixture was then poured onto ice water and the aqueous layer was extracted with ether. The ether was removed by a vacuum line. The residue was distilled and then recrystallized from ether at -30° to give 2 directly in 56.3% yield based on 1. Compound 2 is the first example of valence-bond isomers of 1,3-diazepine derivatives. Compound 6 is considered to isomerize smoothly to 2 at room temperature by a $\pi 2s+\pi 2s+\pi 2s$ mechanism. The structure of 2 was determined by the following spectral data: m.p. 112°; ^{19}F-nmr ($CDCl_3$) δ[4] +9.00(3F, s), +8.33(3F, sept., J_{F-F}=6.3 Hz), +7.07(3F, sept., J_{F-F}=6.3 Hz), -11.33 (6F, sept., J_{F-F}=6.3 Hz); ^{1}H-nmr($CDCl_3$) δ 6.33 (bs, N-H, this singal disappeared on adding D_2O); ir(nujol) ν 3200, 1600, 1530, and 1200 cm^{-1}, no absorption around 1850 cm^{-1} (CF_3-cyclopropene); mass m/e 434 (M^+).

The Diels-Alder reaction of 2 with the cyclic dienes did not give any adducts. This result is comparable to the case of 5.[5] Compound 2 easily reacted with diazomethane to give not a 1,3-dipolar cycloadduct but an N-methylated product (3) in 71% yield. 3; m.p. 67-68°; ^{19}F-nmr($CDCl_3$) δ +8.6 (3F, sept., J_{F-F}=6.6 Hz), +3.3 (3F, s), -1.3 (3F, m), -11.5 (6F, spet., J_{F-F}=6.6 Hz); ^{1}H-nmr($CDCl_3$) δ 3.3 (m, $-CH_3$); ir(CCl_4) ν 1660, 1520, 1410, 1350, and 1290-1120 cm^{-1}; mass m/e 448 (M^+).

This result shows that the proton of 2 is highly acidic. We are now investigating the photo and thermal reactions of 2 and 3.



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References

1) Y. Kobayashi, T. Nakano, K. Shirahashi, A. Takeda, and I. Kumadaki, Tetrahedron Lett., accepted.
2) Y. Kobayashi, Y. Hanzawa, W. Miyashita, T. Kashiwagi, T. Nakano, and I. Kumadaki, J. Am. Chem. Soc., 101, 6445 (1979).
3) Y. Kobayashi, unpublished data.
4) Benzotrifluoride signal is used as an external standard; upfield shifts are quoted as positive.
5) Y. Kobayashi, Y. Hanzawa, Y. Nakanishi, and T. Kashiwagi, Tetrahedron Lett., 1019 (1978).

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