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Unique Thermal Isomerization of the Diels-Alder Adduct of 1,1-Dicyclopropylspiro[2.4]hepta-4,6-diene with TCNE

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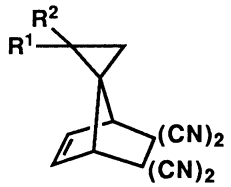
The Diels-Alder adduct of 1,1-dicyclopropylspiro[2.4]hepta-4,6-diene (**2a**) with TCNE underwent unique rearrangement to give an imine derivative, whose formation may be explained by retro-Diels-Alder-re-attack of TCNE at the β position of **2a** followed by an extensive isomerization involving the Cope rearrangement.

We found that *anti*-1,1-dicyclopropyl-4,7-vinylenespiro[2.4]heptane-5,5,6,6-tetracarbonitrile (**1a**), the Diels-Alder adduct of 1,1-dicyclopropylspiro[2.4]hepta-4,6-diene (**2a**) with TCNE, isomerized at 50-80 °C to give 4-(N-dicyclopropylmethylidenamino)-6-methylenebicyclo[3.3.0]octa-3,7-diene-2,2,3-tricarbonitrile (**3a**; 61%)[1] and a mixture of 4,4-dicyclopropylbicyclo[4.3.0]nona-1(6),7-diene-2,2,3,3-tetracarbonitrile and its 1(6),8-diene isomer (**4a-4a'**; 24%).[2] The isomerization completed after 125 min in acetonitrile whereas merely 24% conversion occurred in chloroform at 50 °C. The structure of **3a** was confirmed by the comparison of its NMR spectra[1]



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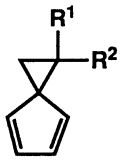

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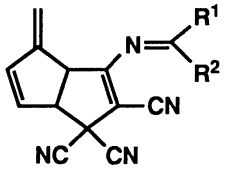

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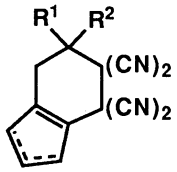

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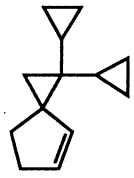
a: $R^1 = R^2$ = cyclo-Pr **c:** $R^1 = R^2$ = Me
b: R^1 = cyclo-Pr, R^2 = Me **d:** R^1 = Me, R^2 = H



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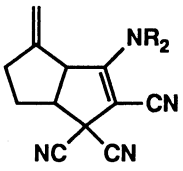

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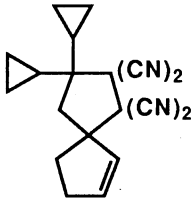

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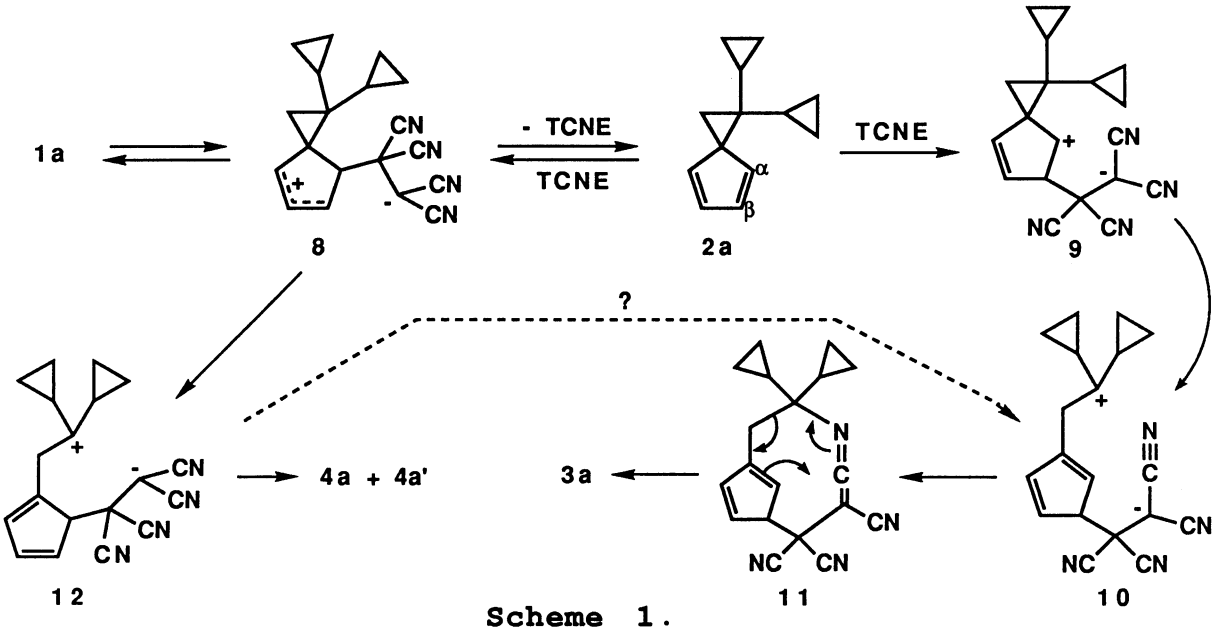
a: R_2 = (cyclo-Pr)$_2$C **b:** R = H

with those of **6a**, which was produced in 72% yield in the reaction of monoene **5** with TCNE in dichloromethane at room temperature. Acid-catalyzed hydrolysis of **6a** produced **6b** and dicyclopropyl ketone. The reaction of **5** produced also a $[\sigma 2 + \pi 2]$ adduct **7**[3] (9% yield).

Since **1a** exhibited interesting features to undergo the unique isomerization, we were interested in examining the thermal behavior of related compounds. Thus, the thermal reactions of **1b** and **1c** as well as monosubstituted **1d** were carried out under conditions similar as above. On being heated at 80 °C, **1c** and **1d** did not show any sign of isomerization, but **1b** was found to rearrange to **4b-4b'** slowly in acetonitrile. Unexpectedly, no indication for the formation of **3b** was observed in the isomerization of **1b**, and hence the rearrangement to give **3** was unique to **1a**.

The reaction courses for the isomerization might be depicted as shown in Scheme 1.[4,5] The key intermediate for the formation of **3a** would be **11**, which is transformed into **3a** by the Cope rearrangement. We have previously encountered similar transformation in the reaction of aryl-substituted vinylcyclopropanes with TCNE.[6] The formation of **4a-4a'** might be explained by a cyclization of **12** followed by a series of 1,5-hydrogen shifts.

An important point to be noted in the transformation to produce **3a** is that the TCNE derived group should change its position from α to β prior to the ring closure to give **11**. This may occur either in a 1,5-shift of the TCNE derived moiety in the intermediate (**12**⇌**10**) or in a total reversion of the Diels-Alder process followed by a re-attack of TCNE at C-5 (C_β) in **2a**.[7] We should like to propose that the latter will be the case. In fact, the retro-Diels-Alder reaction of **1a** was found to occur very readily particular-



Scheme 1.

ly in acetonitrile. This was proved by carrying out the isomerization of **1a** in the presence of **2d**, which yielded non-isomerizing **1d**. In the presence of 10 molar equivalent of **2d**, 28% of **1d** was produced just after 1 min heating of the mixture at 50 °C.[8] The generation of **2a** was confirmed by ^{1}H NMR analysis of the reaction mixture.

Moreover, we observed that small amounts of **3a** (8% in dichloromethane and 20% in acetonitrile) and **4a-4a'** (2% combined yield in dichloromethane and 7% in acetonitrile) were produced even in the Diels-Alder reaction of **2a** with TCNE *at room temperature*. Control experiments indicated that practically no isomerization of **1a** occurred at room temperature in dichloromethane. In acetonitrile, **1a** did rearrange but slowly (20% conversion after 24 h) to **3a**. However, it should be noted that the reaction of **2a** with TCNE completed almost instantly at room temperature to give **1a** and sizable amounts of **3a** and **4a**.

In the aforementioned isomerization of **1a** in the presence of **2d**, it was observed that the amount of **3a** increased gradually with time upon further heating of the mixture, while that of **1d** decreased slowly (the ratio of **1a**:**3a**:**1d** having been 38:4:58 after 10 min, 17:14:70 after 40 min, and 0:43:57 after 10 h). The observation suggests that the retro-Diels-Alder reaction of **1d** also takes place under the reaction condition to regenerate TCNE, which reacts further with regenerated **2a** to give **3a**, ultimately. After all, the retro-Diels-Alder-re-attack mechanism appeared to be more likely for the production of **3a**.

The fact that only **1a** produced **3a** suggests that the 2,2-dicyclopropylcyclopropyl group exhibits an extraordinarily large effect in the β attack of TCNE on **2a**, if the retro-Diels-Alder-re-attack mechanism is granted.[9] It should be noted that the *gem*-dicyclopropyl groups are separated from the incipient cationic center by a σ bond in the β attack. Therefore, the anomaly observed in the reaction of **2a** will require the surmises either that the cyclopropane σ bond is exceptionally effective to transmit the electronic effect[10] or that the C-1-C-3 bond stretches considerably on the β attack[5] and significant positive charge is developed at C-1 in the transition state.

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References

1) Spectral data for **3a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-1.33 (m, 10 H), 4.03 (dt, *J* = 6.6, ca. 1.0 Hz), 4.09 (dt, 1 H, *J* = 6.6, 2.2 Hz), 4.87 (br s, 1 H), 5.10 (d, 1 H, *J* = 1.0 Hz), 6.16 (dt, 1 H, *J* = 5.4, ca. 1.0 Hz), 6.32

(dd, 1 H, J = 5.4, 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 10.0 (m), 14.2 (br m), 43.2 (s), 52.9 (d), 55.1 (d), 81.7 (s), 110.5 (t), 111.9 (s), 112.4 (s), 114.4 (s), 133.3 (d), 137.3 (d), 147.1 (s), 171.5 (s), 182.5 (s); MS (70 eV) *m/z* (relative intensity, %) 300 (M^+, 5.2), 78 (100). HRMS Found: *m/z* 300.1390. Calcd for $C_{19}H_{16}N_4$: M, 300.1377. The other new compounds described in the present study gave satisfactory elemental analysis and spectral data.

2) The ratio of the two isomers was ca. 3:1 (^{1}H NMR and ^{13}C NMR), but it was difficult to assign which isomer was rich in the mixture.

3) S. Nishida, M. Murakami, H. Oda, T. Tsuji, T. Mizuno, M. Matsubara, and N. Kikai, *J. Org. Chem.*, **54**, 3859 (1989); S. Nishida, M. Murakami, T. Mizuno, and T. Tsuji, *ibid.*, **54**, 3868 (1989).

4) The retro-Diels-Alder reaction of, at least, **1a** and **1b** will be stepwise, dipolar processes. This is based on the observations that (i) **1a** and **1b** isomerized to **4a-4a'** and **4b-4b'**, respectively, which should be produced in the stepwise process; and (ii) the solvent polarity influenced the rate of isomerization of **1a**.

5) The process yielding **12** is depicted in a stepwise fashion in the scheme, but it might be possible that **12** is produced directly from **1a** and TCNE.

6) N. Shimizu, T. Fujioka, S. Ishizuka, T. Tsuji, and S. Nishida, *J. Am. Chem. Soc.*, **99**, 5972 (1977).

7) The fact that the same type of transformation took place in the reaction of monoene **5** will support the proposed process, because the β position would be the active site in **5**.

8) In these experiments, attention was focused on the formation of **3a**, but not of **4a-4a'**, because the latter lacks appropriate ^{1}H NMR peaks to carry out the analysis.

9) The possibility that the reduced reactivity in the Diels-Alder reaction forced **2a** to take the unusual reaction route is improbable because **2a-2d** exhibited similar reactivity in the Diels-Alder reaction with TCNE.

10) The conjugation can be transmitted through a cyclopropyl ring, although the consensus appears to be that this effect is small (T. T. Tidwell, "The Chemistry of the Cyclopropyl Group," ed by Z. Rappoport, Wiley, New York (1987), Part 1, Chap. 10). On the other hand, the σ^+_p values for the 2,2-dichlorocyclopropyl and 2,2-dibromocyclopropyl group (-0.02 and -0.038, respectively: Y. Kusuyama and Y. Ikeda, *Bull. Chem. Soc. Jpn.*, **46**, 204 (1973); O. G. Kulinkovich, I. G. Tishchenko, I. V. Reznikov, and A. A. Pap, *Zh. Org. Khim.*, **17**, 473 (1981)) are reported to be significantly smaller than that of the parent group (-0.46: H. C. Brown and J. D. Cleveland, *J. Org. Chem.*, **41**, 1792 (1976)). The magnitude of the electronic effect of the 2,2-dicyclopropylcyclopropyl group is currently under investigations.

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