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REGIOSELECTIVE COPE REARRANGEMENT OF [2+2] CYCLOADDUCT OF 2-PHENYL-2-(1,2-DIPHENYL-3-CYCLOPROPENYLIDENE)ACETONITRILE TO AN ENAMINE LEADING TO PENTALENE DERIVATIVES

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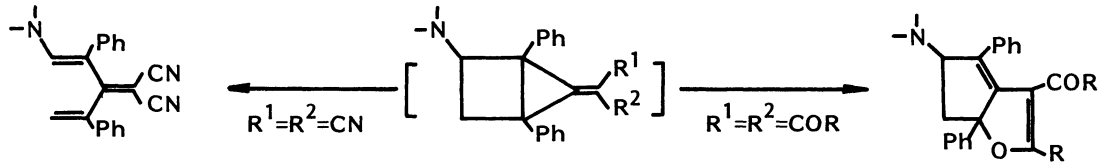
The reaction of 2-phenyl-2-(1,2-diphenyl-3-cyclopropenylidene)acetonitrile with 1-(1-pyrrolidinyl)acenaphthylene giving two isomeric tetrahydroindeno[1',2']cyclopenta-[4,5-a]acenaphthylenes is the first example in which a phenyl group on the methylene-cyclopropene ring took part in a cyclization: They are presumed to form via the regio-selective Cope rearrangement of initially formed endo [2+2] cycloadducts followed by a hydrogen shift.

Contrary to the complex reactivity of cyclopropenone and cyclopropenethione on their interaction with enamines,[1] a methylenecyclopropene as a carbon analog of them seems to show the rather simple reaction pattern: The initial interaction takes place at the endocyclic double bond in the reactions with enamines. However, the initially formed [2+2] cycloadduct, bicyclo[2.1.0]pentane intermediate, is so labile that the secondary reaction follows giving a few types of products depending upon the nature of substituents on the terminal carbon of exocyclic double bond: The dicyanomethylenecyclopropene gives cross-conjugated compounds by the ring cleavage of both three- and four-membered rings,[2] while the diacylmethylenecyclopropene yields the 5-amino-5,6-dihydro-6aH-cyclopenta[b]furans via the ring opening reactions of three-membered ring followed by the cyclization at the acyl group.[3]

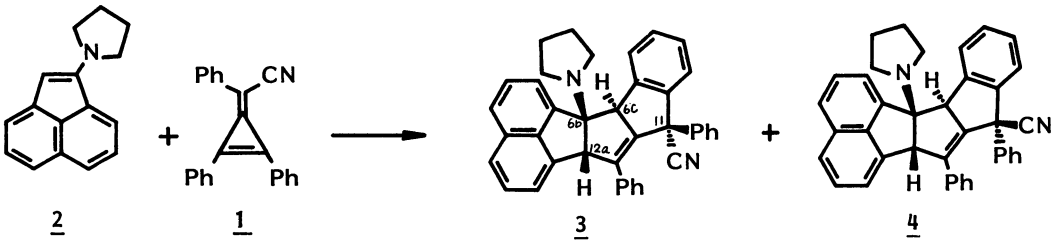


In the present communication, we wish to report the reaction of 2-phenyl-2-(1,2-diphenyl-3-cyclopropenylidene)acetonitrile 1 with 1-(1-pyrrolidinyl)acenaphthylene 2 giving tetrahydropentalene derivatives. This reaction gives the first example in which a phenyl group on the three-membered ring of methylenecyclopropene took part in a cyclization.

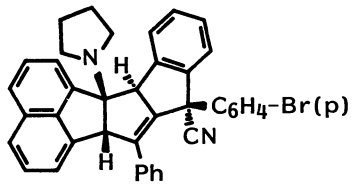
An equivalent mixture of 1 and 2 was stirred, in dry benzene under nitrogen atmosphere, at room temperature for 12 h to give two isomeric 1:1 adducts 3 (mp 258-260 °C (decomp.)) and 4 (mp 256-258 °C (decomp.)) in 57 and 33 % yields, respectively, both as colorless crystals. Their spectral data resemble each other closely enough to indicate that the both products 3 and 4 have similar structures.[4]

The major product 3 reveals two singlet signals of methine hydrogens in the ^{1}H-NMR spectrum and four signals of sp^{3} carbons except for ones of the pyrrolidine ring in the ^{13}C-NMR spectrum. These NMR spectral data conclude that one of the phenyl groups in 2 participated in the formation of 3 from the intermediary 1:1 adduct. The structure of 3 was finally confirmed to be 6b,6c,11,12a-tetrahydro-

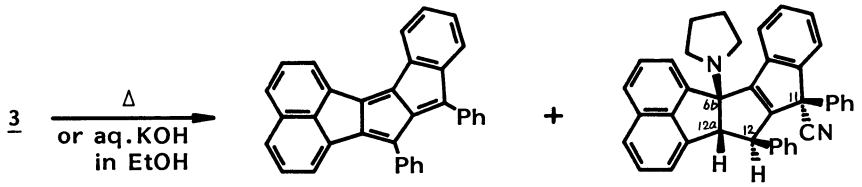
11-cyano-11,12-diphenyl-6b-(1-pyrrolidinyl)indeno[1',2']cyclopenta[4,5-a]acenaphthylene on the basis of the result of X-ray structural analysis[5] for the bromo-substituted derivative 3-Br (mp 260-262 °C (decomp.)) that was the major product from the reaction of 2 with 2-(p-bromophenyl)-2-(1,2-diphenyl-3-cyclopropenylidene)acetonitrile under the same reaction conditions.



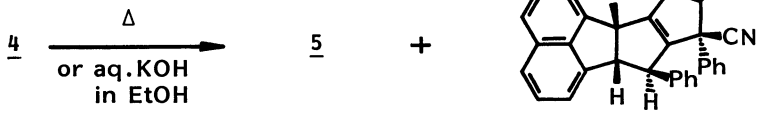
2 1 3 4



3-Br



5 6



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The geometry of ring fusion between the acenaphthene and cyclopentene rings is cis as expected and the methine hydrogens at 6c and 12a positions are trans. The former methine hydrogen is located in a shielding region of the acenaphthene ring and is assigned to the singlet signal at 4.86 ppm. The both methine hydrogens are observed as broad signals though they are not expected to couple across four single bonds in the W-configuration (W-coupling). This broadening is probably caused by a long-range coupling with the ring hydrogens on the fused benzene and acenaphthene rings. Some examples of such a long-range coupling have been reported in indene, benzofuran, and acenaphthene systems.[6]

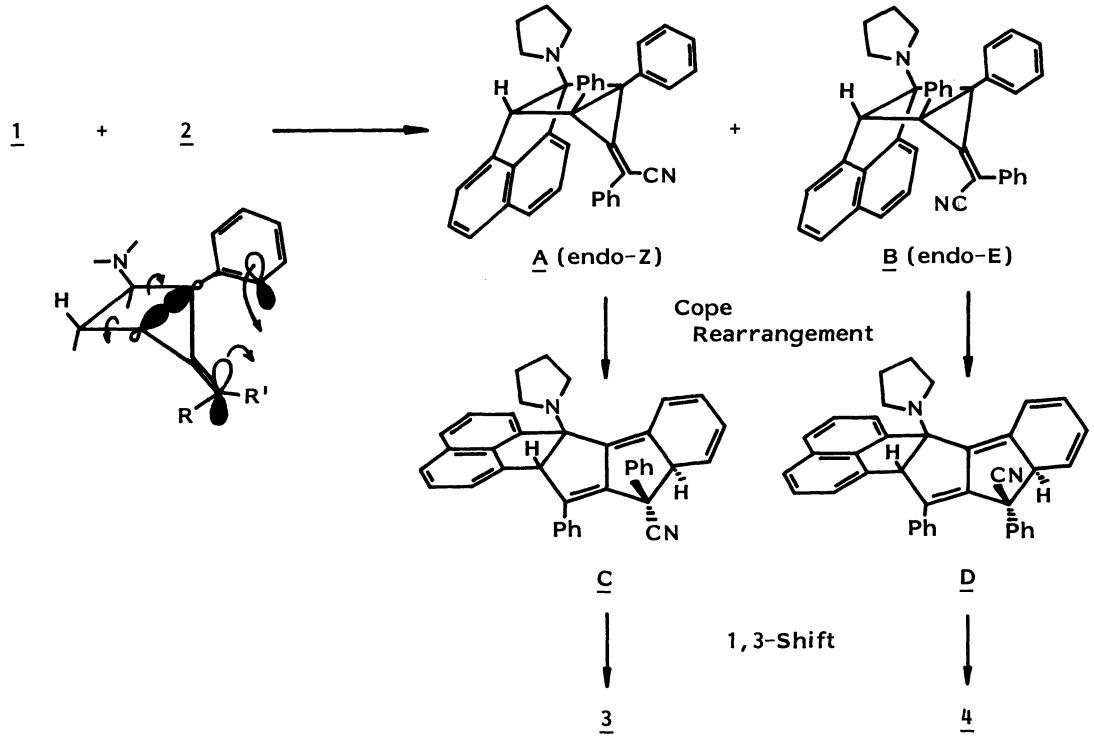
The minor product 4 also shows two singlet signals of methine hydrogens in the ^{1}H-NMR spectrum and four signals of sp^3 carbons except for ones of the pyrrolidine ring in the ^{13}C-NMR spectrum. The spectral patterns and chemical shifts for the corresponding pairs of hydrogens and carbons are extremely close between 3 and 4.[4] Especially the sp^3 carbon signals have almost the same chemical shifts meaning that the minor product 4 should be one of the stereoisomers of the major one 3.

Only the cis configuration is possible for a ring junction between the acenaphthene and cyclopentene rings.[7] No W-coupling is observed between the two methine hydrogens at 6c and 12a positions, while

they individually couple with the ring hydrogens. The hydrogen at 6c position appears at about the same position (4.76 ppm) to that of 3 indicating that this hydrogen is also trans to the 12a-H. If the 6c-H were cis to the 12a-H, it should have been observed in a considerably lower field as it is out of a shielding zone from the fused acenaphthene ring. Some examples for a similar shielding of acenaphthene ring have been reported in a recent report.[8] Thus, the minor product 4 is assigned to be a stereoisomer of 3 with a different configuration only at the 11 position.

When heated with ethanolic potassium hydroxide for 2.5 h, 3 gave a mixture of two products, 5 (mp 197-199 °C) as black needles and 6 (mp 284-286 °C (decomp.)) as colorless prisms in 6 and 82 % yields, respectively. On refluxing 3 in ethyleneglycol without potassium hydroxide, the yield of 5 increased up to 58 % with a decreased yield of 6 (37 %). Similarly 4 afforded 5 in 27 % yield and 7 (mp 214-217 °C (decomp.)) as colorless prisms in 41 % yield by heating it with ethanolic potassium hydroxide, while 5 was a sole product in ethyleneglycol.

The common product 5 is assigned to be a pentalene derivative, 11,12-diphenylindeno[1',2']cyclopenta[4,5-a]acenaphthylene, on the basis of the spectral data.[9] The other products 6 and 7 are isomers of the starting 3 and 4, and are also found to be stereoisomers each other from the close similarity of spectral data.[10] Appearance of methine signals as each doublet indicates that the migration of one of the two methine hydrogens in 3 (also in 4) occurred. Their small coupling constants (4.5 Hz in 6 and 4.0 Hz in 7) can be explained only when the hydrogen at 6c position migrates to the 12 position.[11] The products 6 and 7 have the same stereochemistry at the 6b, 12, and 12a positions but different only at the 11 position. The structures of 5, 6, and 7 can be reasonably derived from those of parent compounds 3 and 4.



The reaction pathway for the formation of 3 and 4 is deduced as follows: The enamine 2 cycloadds to the endocyclic double bond of 2 to form the endo [2+2] cycloadducts A and B. The subsequent Cope rearrangement involving the phenyl group adjacent to the pyrrolidinyl group gives the stereoselectively

rearranged products C and D. The final 1,3-hydrogen shift affords the thermodynamically stable[12] products 3 and 4. The reason why only the phenyl group adjacent to the amine substituent has been related to the Cope rearrangement may be that the phenyl group is locked by the pyrrolidinyl group in a favorable conformation for the rearrangement. Such a regioselectivity would not be expected in the exo [2+2] cycloadduct.

References

1. Th. Eicher and J. L. Weber, Topics in Current Chem., 57, 1 (1975).
2. a) J. Ciabattoni and E. C. Nathan III, J. Amer. Chem. Soc., 89, 3081 (1967); b) O. Tsuge, S. Okita, M. Noguchi, and S. Kanemasa, Chem. Lett., 847 (1982); c) O. Tsuge et al., unpublished results.
3. a) Th. Eicher and Th. Born, Tetrahedron Lett., 981 (1970) and Justus Liebigs Ann. Chem., 762, 127 (1972); b) O. Tsuge et al., unpublished results.
4. 3: IR (KBr cm^{-1}) 2225 (CN); ^{1}H-NMR ($CDCl_3$ δ ppm) 1.37-1.97, 2.10-2.90 (each 4H, m, pyrrolidinyl), 4.86 (1H, s, 6c-H), 5.44 (1H, s, 12a-H), and 6.76-7.92 (20H, m, aromatic); ^{13}C-NMR ($CDCl_3$ δ ppm) 23.6, 48.6 (each t, pyrrolidinyl), 50.7 (s, 11-C), 58.6, 64.7 (each d, 6c- and 12a-C), and 81.6 (s, 6b-C); Mass (m/e) 526 (M^+) and 220.
   4: IR (KBr cm^{-1}) 2240 (CN); ^{1}H-NMR ($CDCl_3$ δ ppm) 1.30-1.80, 1.98-2.76 (each 4H, m, pyrrolidinyl), 4.76 (1H, s, 6c-H), 5.52 (1H, s, 12a-H), and 6.90-7.90 (20H, m, aromatic); ^{13}C-NMR ($CDCl_3$ δ ppm) 23.7, 48.2 (each t, pyrrolidinyl), 51.0 (s, 11-C), 59.0, 65.7 (each d, 6c- and 12a-C), and 82.8 (s, 6b-C); Mass (m/e) 526 (M^+) and 220.
5. The results from the X-ray structural analysis of 3-Br will be reported elsewhere.
6. a) D. G. de Kowalewski, R. H. Contreras, A. R. Engelmann, J. C. Facelli, and J. C. Duran, Org. Mag. Resonance, 17, 199 (1981); b) C. L. Bell, S. Egan, and L. Bauer, J. Heterocycl. Chem., 2, 420 (1965).
7. The structural inspection using a Dreiding model shows a trans fusion between acenaphthene and cyclopentene can be constructed only with a great difficulty.
8. J. E. Shields, D. Gavrilovic, J. Kopecky, W. Hartmann, and H. G. Heine, J. Org. Chem., 39, 515 (1974).
9. 5: ^{1}H-NMR ($CDCl_3$ δ ppm) 6.64-7.76 (m, aromatic); UV ($CHCl_3$ λ_{max} nm (log ε)) 278 (5.57), 305 (4.47), 385 (4.48), 453 (3.91), 484 (3.60), and 645 (2.55); Mass (m/e) 428 (M^+).
10. 6: IR (KBr cm^{-1}) 2240 (CN); ^{1}H-NMR ($CDCl_3$ δ ppm) 1.52-1.88, 2.32-2.66 (each 4H, m, pyrrolidinyl), 4.12 (1H, d, J=4.5 Hz, 12-H), 4.67 (1H, d, J=4.5 Hz, 12a-H), and 6.68-8.05 (20H, m, aromatic); ^{13}C-NMR ($CDCl_3$ δ ppm) 23.6, 48.0 (each t, pyrrolidinyl), 52.2 (s, 11-C), 55.2, 61.4 (each d, 12- and 12a-C), and 81.8 (s, 6b-C); Mass (m/e) 526 (M^+), 456, and 378.
    7: IR (KBr cm^{-1}) 2240 (CN); ^{1}H-NMR ($CDCl_3$ δ ppm) 1.58-1.88, 2.30-2.68 (each 4H, m, pyrrolidinyl), 3.50 (1H, d, J=4.0 Hz, 12-H), 4.62 (1H, d, J=4.0 Hz, 12a-H), and 6.56-8.05 (20H, m, aromatic); Mass (m/e) 526 (M^+), 456, and 378.
11. Only this hydrogen migration gives the small coupling constant among the four possible 1,3-hydrogen shifts.
12. Each the hydrogen migrates to the anti position of pyrrolidinyl group affording the less sterically hindered framework of product.

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