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REACTIONS OF CYCLIC ENAMINES WITH DICYANOMETHYLENECYCLOPROPENES. FORMATION OF MEDIUM RING COMPOUNDS AND TRANSANNULATION TO FULVENES

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Several cyclic enamines with five to seven-membered rings react with 2-(1,2-diphenyl-3-cyclopropenylidene)propanedinitrile to give medium ring compounds, showing that the latter is a versatile reagent which can insert three carbon atoms between α- and β-carbons of cyclic enamines. These medium ring compounds undergo transannular reactions on treatment with hydrochloric acid to yield fulvene derivatives with the elimination of an amine component in the enamine.

Recently, in the reactions with diphenylcyclopropenones and diphenylcyclopropenethiones, 1-(1-pyrrolidinyl)acenaphthylene 1 was reported to react in a manner quite different from ordinary enamines[1].

It is known that, in the reaction with an enamine, methylenecyclopropenes exhibit rather simpler reaction patterns compared with cyclopropenones and cyclopropenethiones[2]. For example, 2-(1,2-diphenyl-3-cyclopropenylidene)propanedinitrile 2 reacts with acyclic enamines to afford cross-conjugated dicyanomethylene compounds via 5-methylenebicyclo[2.1.0]pentane intermediates[3]. Few reactions of 2 with cyclic enamines, however, have been so far reported except for the postulation of a possible reaction pathway in a recent review[2].

We have first been interested in the reaction of 2 with the unusual enamine 1; the reaction was found to give a cross-conjugated, eight-membered cyclic compound which was readily transformed into a fulvene derivative. As an extension of the above reaction, the reactions of 2 with a variety of cyclic enamines other than 1 have also been investigated.

In the present communication we report the reactions of 2 with 1, 3-(1-pyrrolidinyl)benzo[b]thiophene 3, its dioxide 4, 3-(1-pyrrolidinyl)indene 5, 1,2-dihydro-4-(1-pyrrolidinyl)naphthalene 6, 5H-6,7-dihydro-9-(1-pyrrolidinyl)benzocycloheptene 7, 2-(1-pyrrolidinyl)indene 8, and 1,2-dihydro-3-(1-pyrrolidinyl)naphthalene 9, leading to the formation of the corresponding cross-conjugated, medium ring compounds[4]. Transannulation reactions of the medium ring compounds are also described.

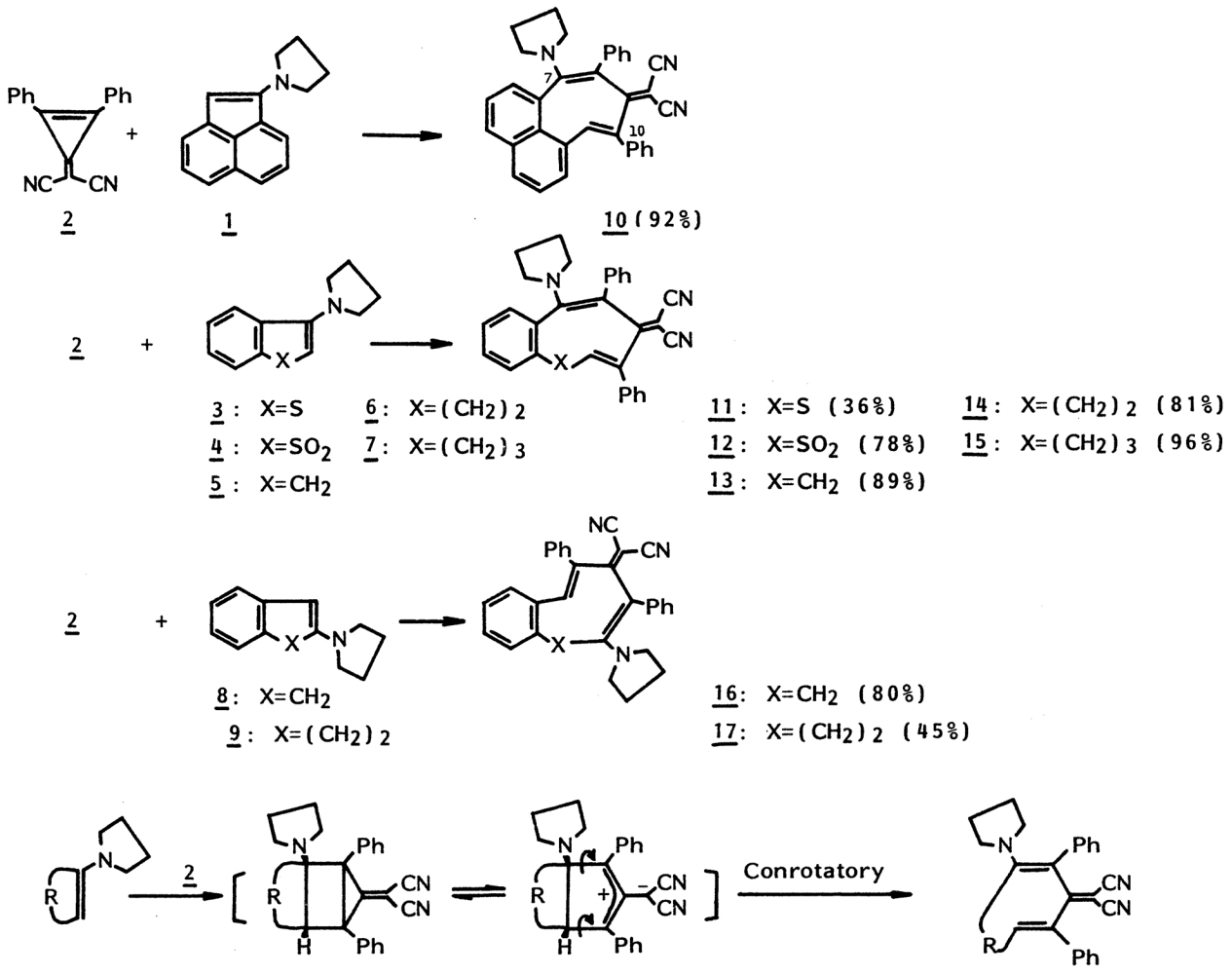
The enamine 1 readily reacted with an equivalent amount of 2 in benzene at room temperature to give a red-colored 1:1 adduct 10, mp 198 °C (dec.), which was hardly soluble in most organic solvents, in 92 % yield. No any sp^3 carbon signals other than those of the pyrrolidine ring were observed in the ^{13}C-NMR spectrum. The IR spectrum showed two absorption bands at 2130 and 2170 cm^{-1}, indicating that the two cyano groups were conjugating with an unsaturated system[5]. On the basis of spectral data[6] as well as the chemical conversion mentioned later, the structure of 10 was determined to be 9-dicyanomethylene-8,10-diphenyl-7-(1-pyrrolidinyl)-9H-cycloocta[1,2,3-ij]naphthalene.

The enamines 3 and 4 were less reactive toward 2 than 1. The reaction of 3 or 4 in refluxing benzene for 24 h or 3 h afforded the corresponding cross-conjugated heterocyclic compound 11, mp 166-169 °C (dec.), or 12, mp 178-181 °C (dec.), in 36 or 78 % yield, respectively[7]. Structural elucidation

of 11 and 12 was accomplished on the basis of spectral data[8].

It should be emphasized that 2 is a versatile reagent which can insert three carbon atoms between α- and β-carbons of cyclic enamine. Thus, further extension to other cyclic enamines was investigated. As expected, cyclic enamines 5-9 reacted with 2 in benzene at room temperature for 24 h to give good yields of the corresponding eight to ten-membered, cross-conjugated compounds 13-17 whose structures were again identified on the basis of spectral data[9].

An inspection of Dreiding models of eight-membered ones indicates that the structure having 7-cis and 10-trans configurations is the most favorable one for 10. This stereochemistry of 10 can be attributable only to a conrotatory ring opening of zwitterionic intermediate arising from the initial cis-fused [2+2] cycloadduct as shown in Scheme 1[10]. The similar stereochemical inspections of 14-17 show that the cross-conjugated parts of them can lie in a plane when one of the double bonds is trans. Their geometry seems to be consistent with the electronic spectral data in which all the cross-conjugated compounds reveal their absorption maxima in wave length longer than 470 nm[9].

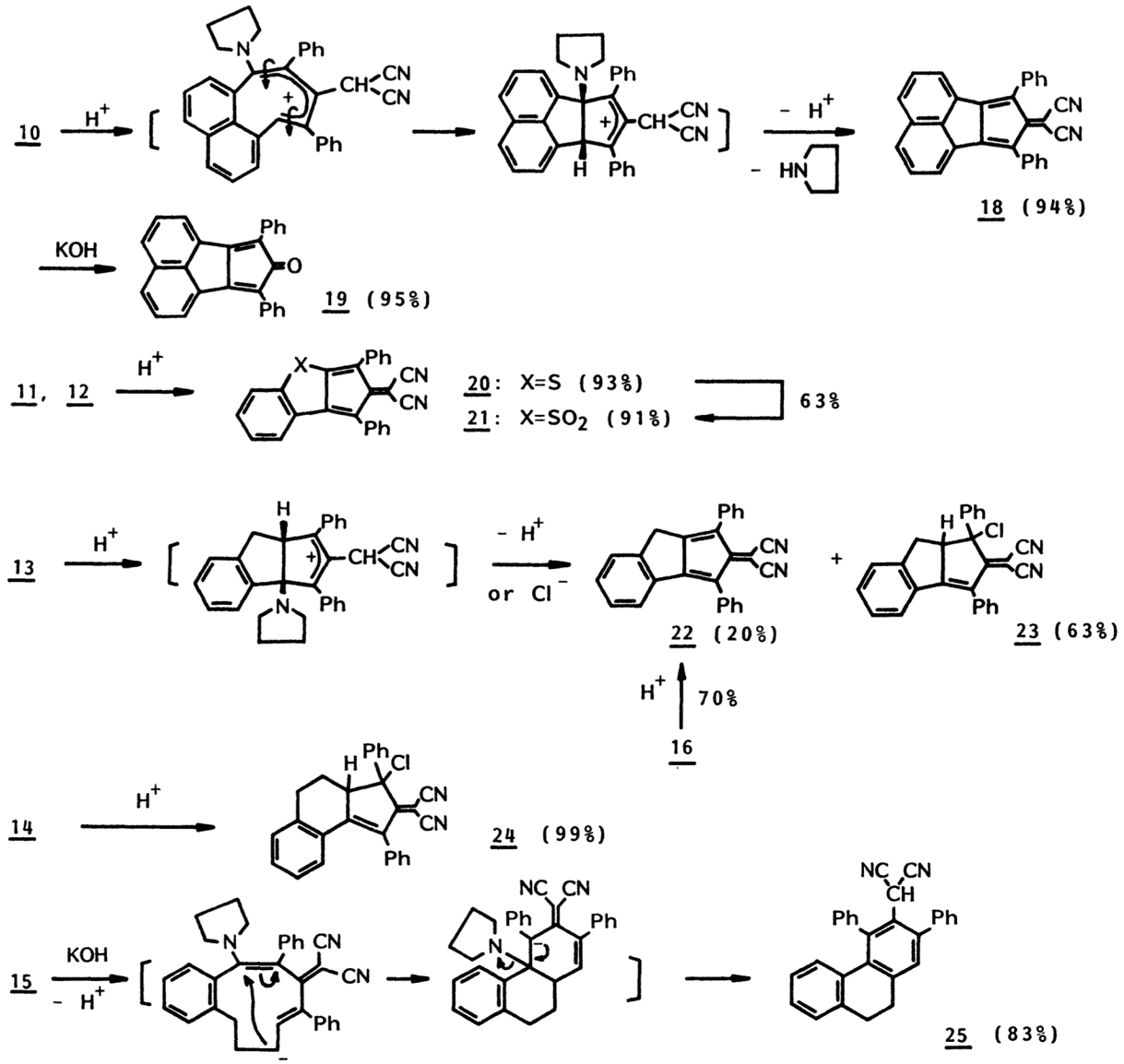


Scheme 1

Heating 10 in acetic acid in the presence of hydrochloric acid gave a deaminated product 18, mp 286-288 °C, as black needles in 94 % yield. Structural determination of 18 was made by its alkali hydrolysis into a known compound, 7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one 19[11] and on the basis of

spectral data[12]. The acid-catalyzed transannular reaction probably started by protonation onto a terminal carbon of the exocyclic double bond of 10 to generate a cyclic pentadienyl cation intermediate which then cyclized with a conrotatory rotation. Similar acid-catalyzed deamination reactions of 11 and 12 afforded the fulvene derivatives 20, mp 221-223 °C (dec.), and 21, mp 256-257 °C (dec.), respectively, the former being oxidized by hydrogen peroxide in acetic acid to give the latter in 63 % yield.

The dicyanomethylenebenzocyclooctene 13 was also deaminated on treatment with hydrochloric acid to give a mixture of fulvene 22, mp 219-221 °C (dec.), and 1-chloro-2-cyanomethylene-1,2,8,8a-tetrahydro-1,3-diphenylcyclopenta[a]indene 23, mp 196-199 °C (dec.), in 20 and 63 % yields, respectively[13]. The latter 23 is believed to form by nucleophilic attack of chloride ion to the allyl cation intermediate from which the fulvene 22 is also formed. The isomeric 1:1 adduct 16 gave 22 under the same conditions. When treated with hydrochloric acid in ethanol, the benzocyclononenes 14 and 17 yielded no fulvene derivatives but only 14 gave a chloro-substituted compound 24, mp 197-198 °C (dec.), in quantitative yield.



Scheme 2

The ten-membered cross-conjugated compound 15 is inert against hydrochloric acid, while, on heating with alcoholic potassium hydroxide, it was transformed into a deaminated compound 25, mp 203-204 °C, in 83 % yield. The structure of 25 was assigned as 3-dicyanomethyl-2,4-diphenyl-9,10-dihydronaphthalene on the basis of spectral data [14]. This transannular reaction is probably initiated by proton abstraction at the 10 position as shown in Scheme 2 [15].

References

1. O. Tsuge, S. Okita, M. Noguchi, and H. Watanabe, Chem. Lett., 1981, 1439.
2. Th. Eicher and J. L. Weber, Topics in Current Chem., 57, 1 (1975).
3. J. Ciabattoni and E. C. Nathan III, J. Amer. Chem. Soc., 89, 3081 (1967).
4. 9-(1-pyrrolidinyl)phenanthrene did not react with 2 under various conditions.
5. Splitted absorptions are observed for stretching vibration of cyano group in the following cases: 1 (2190 and 2200 cm^{-1}) and thiazolium 3-dicyanomethylide (2130 and 2180 cm^{-1}).
6. 10: ^{1}H-NMR in CF_3COOH: δ 1.96-2.30, 3.30-3.65 (each 4H, m, pyrrolidinyl), 5.71 (1H, s, 9-H), and 7.00-8.20 ppm (16H, m, aromatic); ^{13}C-NMR in CF_3COOH: δ 25.4, 48.9 (each t, CH_2) and 67.8 ppm (s, $=C(CN)_2$); IR: 2130 and 2170 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 292 (4.15), 380 (3.70), and 534 nm (3.28); MS: m/e 475 (M^+).
7. Although nucleophilicity of the β-carbon of enamine 4 may be reduced, this enamine was found to be more reactive than 3.
8. 11: ^{1}H-NMR in $CDCl_3$: δ 1.60-2.00, 2.90-3.30 (each 4H, m, pyrrolidinyl), 6.72 (1H, s, -H), and 6.90-7.85 ppm (14H, m, aromatic); ^{13}C-NMR in $CDCl_3$: δ 25.3, 51.0 (each t, CH_2) and 89.7 ppm (s, $=C(CN)_2$); IR: 2210 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 245 (4.31), 271 (4.25), 382 (3.86), and 515 nm (3.47); MS: m/e 457 (M^+).
   12: ^{1}H-NMR in $CDCl_3$: δ 1.60-2.00, 2.80-3.28 (each 4H, m, pyrrolidinyl), 6.88 (1H, s, 2-H), and 7.00-8.24 ppm (14H, m, aromatic); ^{13}C-NMR in $CDCl_3$: δ 25.4, 51.5 (each t, CH_2) and 85.8 ppm (s, $=C(CN)_2$); IR: 2200 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 253 (4.34), 333 (3.94), and 515 nm (3.77); MS: m/e 489 (M^+).
9. The spectral data of 13 and 16 are given below as typical examples:
   13: mp 175-180 °C (dec.); ^{1}H-NMR in $CDCl_3$: δ 1.60-1.92, 2.70-3.30 (each 4H, m, pyrrolidinyl), 3.52 (1H, dd, J=9 and 16 Hz, one of CH_2), 3.97 (1H, dd, J= 3 and 16 Hz, the other of CH_2), 6.43 (1H, dd, =CH), and 6.90-7.70 ppm (14H, m, aromatic); ^{13}C-NMR in $CDCl_3$: δ 25.4, 50.9 (each t, CH_2 of pyrrolidine), 34.5 (t, CH_2), and 88.9 ppm (s, $=C(CN)_2$); IR: 2225 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 243 (4.46), 298 (3.93), 330 (3.98), 352 (3.88), and 500 nm (3.69); MS: m/e 439 (M^+).
   16: mp 184-187 °C (dec.); ^{1}H-NMR in $CDCl_3$: δ 1.50-2.04, 2.70-3.56 (each 4H, m, pyrrolidinyl), 4.03 (2H, broad d, CH_2), and 7.00-8.16 ppm (15H, m, =CH and aromatic); IR: 2200 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 263 (4.34), 332 (3.85), 348 (3.78), and 470 nm (4.40); MS: m/e 439 (M^+).
   The melting points and absorption maxima of the other compounds 14, 15, and 17 are given as follows:
   14: mp 173-174 °C (dec.); 481 nm (4.44).
   15: mp 239-241 °C (dec.); 482 nm (4.39).
   17: mp 160-165 °C; 470 nm (3.80).
10. Trans ring fusion at the 1,2-bond of acenaphthene seems impossible because of rigidity of the five-membered ring of acenaphthene.
11. W. Dilthey, I. ter Horst, and W. Schommer, J. prak. Chem., 143, 189 (1935).
12. 18: ^{1}H-NMR in $CDCl_3$: δ 7.20-7.80 ppm (16H, m, aromatic); IR: 2230 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 250 (4.34), 332 (4.68), and 635 nm (2.58); MS: m/e 404 (M^+).
13. 22: ^{1}H-NMR in $CDCl_3$: δ 3.76 (2H, s, CH_2) and 7.00-7.50 ppm (14H, m, aromatic); IR: 2210 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 269 (4.25), 348 (4.28), and 595 nm (3.15); MS: m/e 368 (M^+).
    23: ^{1}H-NMR in $CDCl_3$: δ 2.20 (1H, dd, J=16.5 and 7.5 Hz, one of CH_2), 3.00 (1H, dd, J=16.5 and 7.5 Hz, the other of CH_2), 4.73 (1H, t, CH), and 6.90-7.70 ppm (14H, m, aromatic); IR: 2220 cm^{-1} (CN); UV in $CHCl_3$: λmax (logε) 298 (3.78), 313 (3.76), and 390 nm (4.50); MS: m/e 406 (M^++2) and 404 (M^+).
14. 25: ^{1}H-NMR in $CDCl_3$: δ 2.84 (4H, broad s, CH_2), 5.11 (1H, s, CH), and 6.50-7.60 ppm (15H, m, aromatic); IR: 2270 cm^{-1} (CN); MS: m/e 396 (M^+).
15. The another possible pathway which is initiated by base-catalyzed hydrolysis of the enamine moiety is excluded, since the nine-membered analog 14 was not hydrolyzed on a similar treatment being recovered in a quantitative yield.

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