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UTILIZATION OF PROTOPINE AND RELATED ALKALOIDS. X.[1]
PHOTOCHEMISTRY OF 7,8-DIMETHOXY-2-METHYL-3-(4',5'-METHYLENEDIOXY-2'-VINYLPHENYL)ISOCARBOSTYRIL[2]

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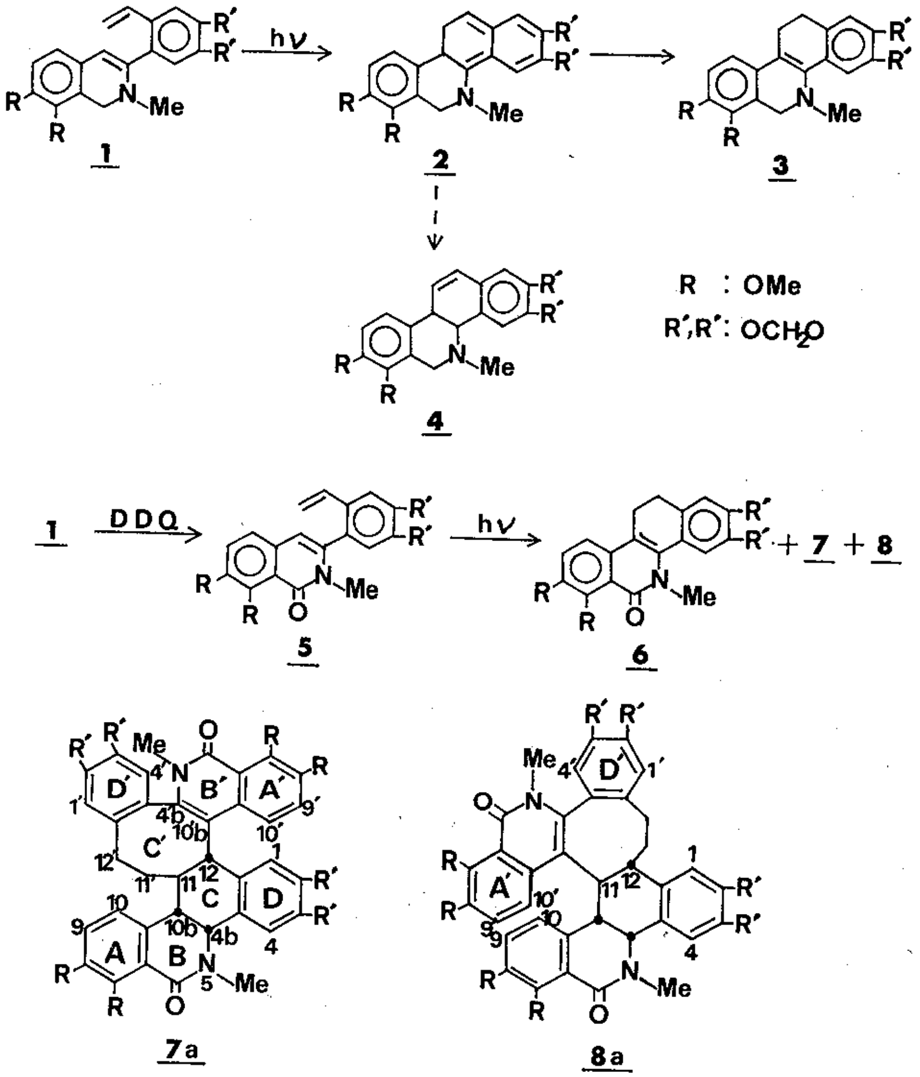
Photolysis of the isocarbostyril (5) predominantly gives the regioisomeric dimers (7) and (8). Attempts to trap the initial photo-product with the dienophiles (9) and (17) are examined and formation pathways of the resulted products are briefly commented.

We previously reported the photocyclization of the dihydroisoquinoline (1) obtained from berberinium chloride to 5,6,11,12-tetrahydrochelerythrine (3) which was considered to result from the initial product (2) by the 10b-H shift.[3] In this case, 4b,5,6,10b-tetrahydrochelerythrine (4), which is expected to arise from 2 by the 11-H shift, was not obtained. We now report the photocyclization of the isocarbostyril (5), which was achieved to compare with that of 1.

The isocarbostyril (5), mp 169-170°, was obtained in 42% yield by oxidation of 1 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Photolysis of 5 gave 5,6,11,12-tetrahydro-6-oxochelerythrine (6), mp 208-209°, 30%, and the regioisomeric dimers (7), mp 204-206°, 38%, and (8), mp 198-200°, 29%. The ^{1}H NMR spectrum of 6 shows the four-protons singlet for the 11- and 12-H_2 at δ 2.72, establishing the structure of 6.[4] The molecular formulas of 7 and 8, $C_{42}H_{38}NO_{10}$, are confirmed by their mass spectra. The ^{13}C NMR spectra of 7 and 8 are very resemble and show characteristic signals of two methylene carbons, four methine carbons and two tetrasubstituted olefinic carbons. These data lead to the structures containing a bicyclo/6.4.0/dodecatriene system in which one benzene group fuses with the six-membered ring, and one benzene and one olefin groups with the eight-membered ring, respectively. Taking into account uncrowded geometry as a whole and stable conformation of the eight-membered ring, it seems that two structures (7a) and (8a) are appropriate for the dimers. Their ^{1}H NMR spectra observed are instructive to deduce the structures. The B/C ring fusions in both compounds are cis on the basis of the coupling constant of the 4b-H's. On examination of the Dreiding model of 7a, the 1-H exists in the vicinity of the shielding zone of the double bond at the C-4'b and -10'b, being assigned for the one-proton singlet resonated at δ 6.29. Also, a close proximity of the 5-Me group and A' ring is experienced and this would be responsible for the deshieldings of the 5-Me group (δ 3.12), 9'-H (δ 7.34) and 10'-H (δ 7.41). For 8a, the 10-H (δ 6.47), 4'-H (δ 6.39) and 10'-H (δ 7.26) lie in the shielding zones of the A', A and D rings, respectively.



R : OMe
R',R' : OCH_2O

B/C/C : cis-anti-trans
D'ring/11-H : anti

B/C/C' : cis-anti-trans
D'ring/11-H : syn

Chart 1

Table 1. ^{13}C NMR Spectra of 7 and 8

	C-7,-8 -7',-8'	C-2,-3 -2',-3'	C-4a,-6a,-10a,-12a,-4'a,-6'a -10'a,-12'a,-4'b,-10'b
7	152.5 151.9 150.0 149.8	146.9 146.6 146.3 146.3	136.0 133.5 133.1 131.3 130.6 128.7 124.6 123.2 119.9 112.3
8	152.6 151.9 150.0 149.9	147.4 147.0 146.3 146.2	136.0 133.7 133.2 131.0 130.7 128.9 124.7 123.1 119.8 112.7

	C-1,-4,-9,-10 -1',-4',-9',-10'	C-10b,-11,-12	C-4b	C-11',-12'
7	120.3 118.4 117.8 115.0 109.3 109.1 107.5 107.0	43.1 37.7 34.6	60.1	28.2 27.7
8	120.3 118.4 117.6 115.0 108.8 108.6 108.5 106.7	44.2 37.9 33.6	59.6	26.4 25.1

	NMe(2)	OMe(4)	OCH_2O(2)	CO(2)
7	37.7 36.4	61.5 61.5 56.7 56.0	101.4 101.1	162.8 162.0
8	38.4 36.9	61.6 61.4 56.7 56.0	101.4 101.1	162.7 162.2

Table 2. ^{1}H NMR Spectra of 7 and 8

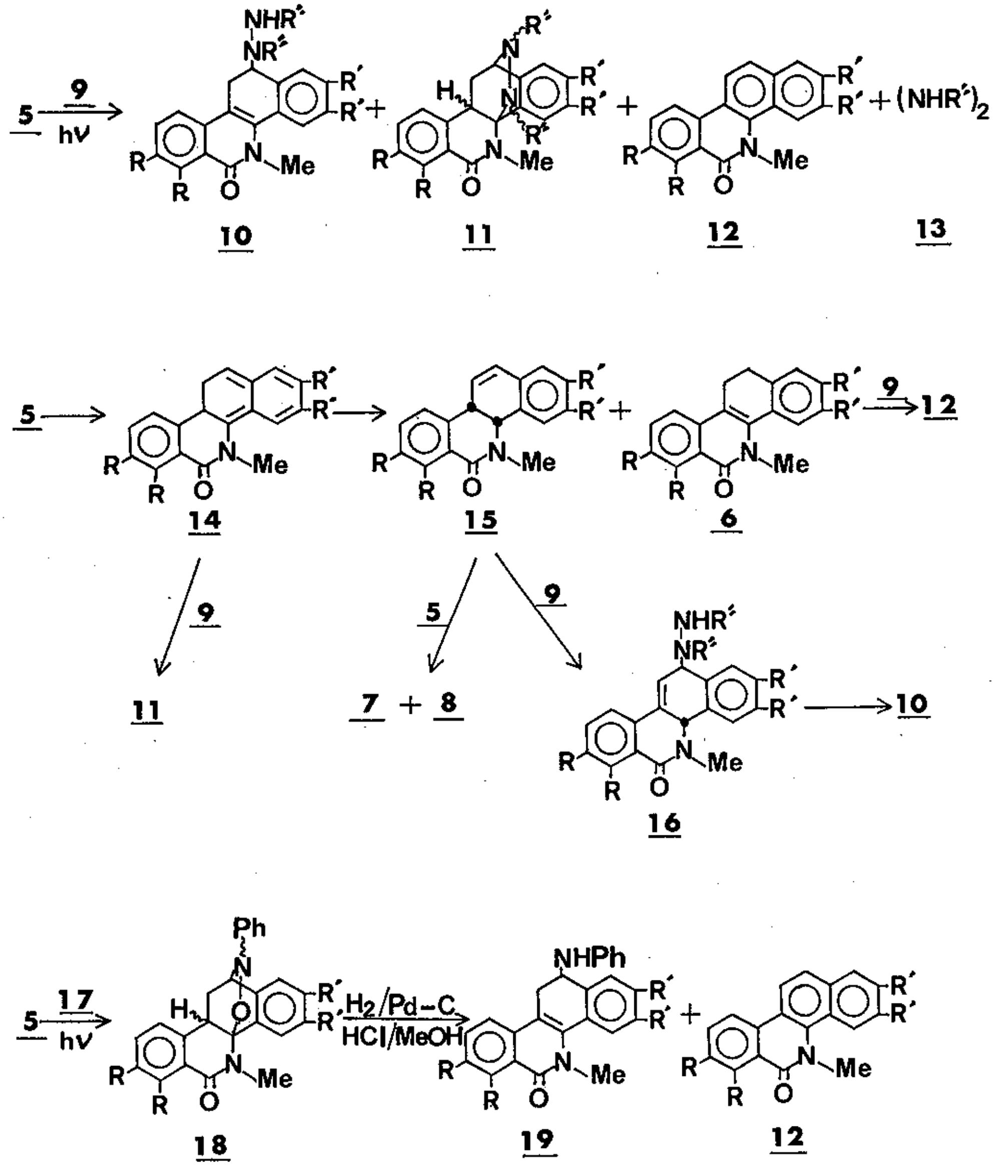
	1-H	4-H	1'-H	4'-H	9-H	10-H	9'-H	10'-H
7	6.29	6.91	6.60	6.72	6.75,d J 8 Hz	6.84,d J 8 Hz	7.34,d J 8 Hz	7.41,d J 8 Hz
8	6.62	6.93	6.62	6.39	6.84,d J 8 Hz	6.47,d J 8 Hz	7.26,s	7.26,s

	4b-H	NMe(2)
7	4.54,d J 4 Hz	3.70 3.12
8	4.45,d J 4 Hz	3.70 3.01

From these data, 7 and 8 are tentatively assigned as the structures (7a) and (8a), respectively.

Photolysis of 5 in the presence of diethyl azodicarboxylate (9) and subsequent alumina column chromatography afforded the 12-hydrazo compound (10), mp 121-123.5°, 25%, the 4b,12-hydrazo compound (11), mp 121.5-123°, 13%, 5,6-dihydro-6-oxochelerythrine (12),[5] 38%, and diethyl hydrazodicarboxylate (13), 31%. The structure of 10 is deduced from its ^{1}H NMR spectrum showing the signals for the 12-H at δ 5.42 (dd, J 8 and 3 Hz), 11-H_2 at δ 3.20-3.00 and NH at δ 1.74 (br s). The ^{1}H NMR spectrum of 11 exhibits the signals for the 12-H at δ 5.21 (dd, J 4 and 2 Hz), 10b-H at δ ca. 4.00, 11-H at δ 2.64 (ddd, J 14, 9 and 4 Hz) and 11-H at δ 2.15 (ddd, J 14, 6 and 2 Hz).

From the results obtained, the formations of these compounds are deduced as follows. The isocarbostyril (5) affords the initial product (14) which, in contrast with 2, is converted into the 4b,5,6,10b-tetrahydro compound (15) and 6 by the 11- and 10b-H shifts, respectively. Cycloaddition of 15 with 5 may give 7 and 8 in the manners of head-to-tail and head-to-head, respectively, and the fashion of reactions might be the $/2_a+6_a/$ cycloaddition followed by the 10'b-H shift. In the case of the presence of 9,[6] the Diels-Alder addition of 9 and 14 leads to 11. The ene reaction of 9 and 15 provides the 12-hydrazo compound (16) which subsequently isomerizes to 10. This would be a plausible explanation for the formation pathway of 10. Since photolysis of 6 in the presence of 9 gave 12 as sole product, a formation pathway of 12 seems to have been



R : OMe R′,R′ : OCH_2O R″: CO_2Et

Chart 2

confirmed. However, the other pathways to 12 from 14 and 15 also would not be abandoned.

Photolysis of 5 in the presence of nitrosobenzene (17) gave the 12,4b-aminoxy compound (18), mp 125-126°, 86%, resulted from the regioselective Diels-Alder addition of 14 and 17. The structure of 18 is suggested on the basis of its ^{1}H NMR signals for the 12-H at δ 4.77 (dd, J 4 and 2 Hz), 10b-H at δ ca. 3.87, 11-H at δ 3.06 (ddd, J 13, 9 and 4 Hz) and 11-H at δ 1.95 (ddd, J 13, 6 and 2 Hz). Hydrogenation of 18 over palladium-carbon in the presence of hydrochloric acid afforded the 12-anilino compound (19), mp 131-133°, 27%, and 12, 38%. The structure of 19 is deduced from its ^{1}H NMR signals for the 12-H at δ 4.65 (dd, J 10 and 5 Hz), 11-H at δ 3.12 (dd, J 16 and 10 Hz), 11-H at δ 2.69 (dd, J 16 and 5 Hz) and NH at δ ca. 4.02.

REFERENCES AND NOTES

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2 ^{1}H NMR and ^{13}C NMR spectra were taken on a JEOL JNM PS-100 at 100 and 25.1 MHz, respectively, for a deuterochloroform solution. Mass spectra were measured with a JEOL JMS-01S. Photolyses were carried out in a benzene solution under nitrogen with a 100 W medium pressure mercury lamp.

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