

Revised Structures, Benz[*cd*]indol-2(1*H*)-ones, for the Ring-Contracted Cycloadducts from 1-Substituted Cyclohepta[*b*]pyrrol-2(1*H*)-ones with Acetylenes

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Synopsis. Formerly-proposed structures, cyclopent[*de*]-isoquinolin-3(4*H*)-ones, for ring contracted by-products obtained from 1-substituted cyclohepta[*b*]pyrrol-2(1*H*)-ones and acetylenes, were revised to benz[*cd*]indol-2(1*H*)-ones on the basis of spectroscopic analysis.

In our recent study of the cycloaddition of 1-substituted cyclohepta[*b*]pyrrol-2(1*H*)-ones (**1**) to electron-deficient acetylenes, dimethyl butynedioate (DMBD) and dibenzoylacetylene (DBA),^{1,2} we have isolated, other than the predicted azulenes and Michael-type adducts, a series of ring-contracted compounds. We have given them isoquinoline structures (**X**) mainly from an appearance of singlet signals around $\delta=8.8$, which, we thought, might be ascribable to H-5 of **X**. However, after reconsideration, we came to a view that benz[*cd*]indol-2(1*H*)-one structures were more plausible than the previously-proposed **X** in the ¹H NMR and UV spectral points of view. In this paper, we wish to correct the structures.

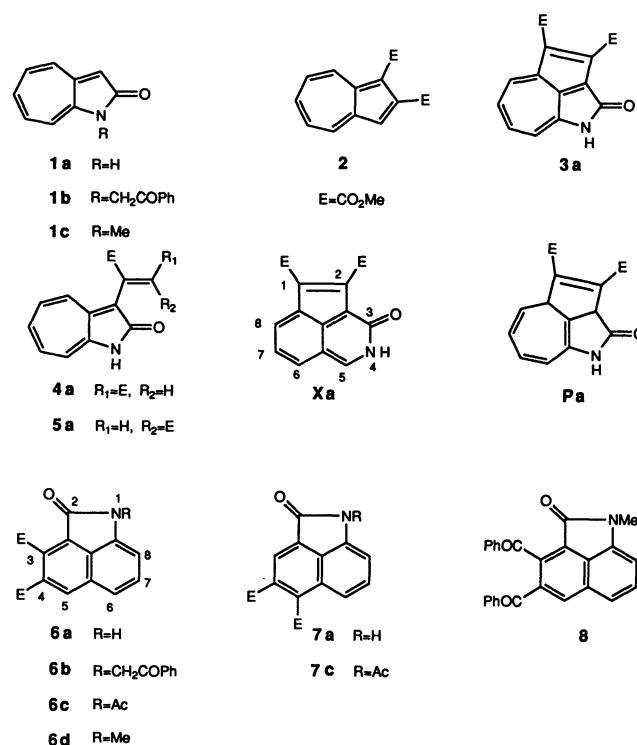
Results and Discussion

In the previous paper, we described the characterization of a series of compounds: the reaction of cyclohepta[*b*]pyrrol-2(1*H*)-one (**1a**) and DMBD after refluxing in acetonitrile for 45 h gave five products (**2**, **Xa**, and **3a–5a**) in good combined yields. However, a doubt has arisen concerning the isoquinoline structure of **Xa**.^{1,2} Namely, the structure **Xa** possesses a quinodimethane structure, and the formation of **Xa** from the protoadduct (**Pa**) involves an autooxidative dehydrogenation step. The occurrence of such a process to lead non-aromatic compounds seems unlikely. Moreover, in the ¹H NMR spectrum³ of **X**, the singlet signals, which were ascribed to H-5 signals, showed only a slight variation on changing the substituent on the nitrogen atom. In this paper, we revise the structures of **X** to **6**, benz[*cd*]indol-2(1*H*)-one derivatives, from the following evidence.

To provide more information on the structures of **X** and **6**, we extended the reaction of DMBD to 1-phenacylcyclohepta[*b*]pyrrol-2(1*H*)-one (**1b**). From **1b**, only

two products (**2** and **6b**) were isolated in 12 and 14% yields, respectively. The latter, **6b**, was identical with the sample prepared by the condensation of phenacyl bromide with **6a**. In the same time, **6a** was converted to an acetyl derivative (**6c**).^{2,4} The **6c** was identical with one of the cycloadducts by the reaction of *N*-acetylcyclohepta[*b*]pyrrol-2(1*H*)-one with 2,3-bis(methoxycarbonyl)-7-oxabicycloheptadiene under high-pressure conditions (3000 bar).⁵

Since the UV spectra of **6a** and **6c** were almost superimposable on those of corresponding dimethyl naphthostyryl-4,5-dicarboxylates (**7a** and **7c**),⁶ the same structural units in both compounds are strongly



Scheme 1.

Table 1. The UV Spectral Data of **6a**, **6c**, and the Related Compounds **7a** and **7c**^{a)}

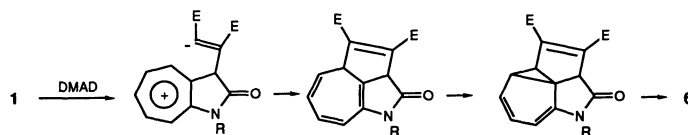
6a	6c	7a	7c
222 (41900)	221 (23400 ^{sh})	222 (46000)	233 (41800)
272 (14100)	232 (29000)	271 (13850)	255 (17880)
	255 (12600 ^{sh})	350 (2420)	
378 (3100)	349 (1900)	383 (3190)	346 (3850)

a) Solvent: **6a** and **6c** were measured in MeOH, and **7a** and **7c** were reported as in EtOH.

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Table 2. Selected NMR Data of **6** and **8**

	6a	6b	6c	6d	8
H-5	8.81	8.81	8.92	8.73	8.30
H-6	7.63	7.45	7.83	7.45	7.4
		∫		∫	∫
H-7	7.56	7.7	7.71	7.6	7.9
H-8	7.11	6.89	8.32	6.95	7.03
C-5	134.7	134.0	135.6	134.0	
C-6	120.9	121.0	123.3	120.6	
C-7	130.5	130.3	131.1	130.2	
C-8	108.6	107.8	116.7	106.9	



Scheme 2.

suggested (Table 1). This UV similarity is reasonable; since in both **6a**, **c** and **7a**, **c**, one of the methoxycarbonyl groups at C-4 or C-6, which is in an extended ortho- or para-position of the nitrogen-carrying carbon. This must largely influence the UV maxima, while the rest of methoxycarbonyl groups at C-5 in **6a**, **c** and **7a**, **c** are in the extended meta-position, having less affective on the UV maxima. Therefore, **6** are naphthostyryl derivatives. For the vicinal bis(methoxycarbonyl) naphthostyryls having three consecutive hydrogens and one isolated hydrogen, only four structures are feasible.

The ^1H NMR spectra provide diagnostic information to select the correct structure, **6**. Thus, the ^1H NMR spectra of **6a** to **6b** and the corresponding derivative (**8**) derived from DBA and 1-methylcyclohepta-[*b*]pyrrol-2(1*H*)-one (**1d**) revealed characteristic features; i.e., they showed a singlet at $\delta=8.3$ – 8.9 and aromatic proton signals at $\delta=6.9$ – 8.3 (Table 2). Among them, a doublet signal, part of the three consecutive proton system, appeared at relatively high field. It was close to a substituent on the nitrogen atom, since the chemical shifts at ca. $\delta=6.9$ or lower field were largely dependent on the *N*-substituents. The chemical shift difference, $\Delta\delta$, caused by acetylation of **6a** to **6c** was 7.11 – $8.32=-1.21$ in chloroform-*d*. Therefore, it must be ascribable to H-8.

As has already been noticed, the singlet signals were slightly sensitive to the *N*-substituents and moved to a larger extent on changing the carbonyl substituents. Therefore, the singlet signals were close to one of the methoxycarbonyl groups, and could be assigned to H-5. Accordingly, only two possibilities remain for **6**; one is the 4,5-bis(methoxycarbonyl) structure and the other the 3,4-bis(methoxycarbonyl) structure. However, the former is already known to be **7**, and the latter remaining must be **6**.

The mechanism of formation of **6** is straightforward: a valence-bond isomerization of the initial [8+2]cyclo-adducts to norcaradiene derivatives and a subsequent dehydrogenative aromatization. It is difficult to

explain the formation of any other naphthostyryl derivatives from protoproducts of **1** and DMBD.

In conclusion, cyclopent[*de*]isoquinolin-3(4*H*)-one structures, **X**, were revised to benz[*cd*]indol-2(1*H*)-one (naphthostyryl) structures, **6**, from the UV- and NMR-spectral analyses as well as the mechanistic considerations.

Experimental

Preparation of 1b. To an EtOH solution (50 cm³) of **1a** (1.08 g) was added concd NaOH (4 cm³) and the mixture was kept at room temperature for 4 h. A yellow sodium salt of **1a** (1.20 g, 97%; mp 300 °C) was collected by filtration. An anhydrous benzene suspension (50 cm³) of sodium salt (836 mg) and phenacyl bromide (995 mg) was refluxed for 12 h. The mixture was poured into water and extracted with benzene. The benzene solution was washed with dil NaOH solution, dried over Na₂SO₄, and evaporated. The residue was chromatographed on a silica-gel column to give 560 mg (43%) of **1b**: yellow needles; mp 172–173 °C; ^1H NMR³ $\delta=5.50$ (2H, s), 6.17 (1H, s), 6.66 (1H, d, *J*=9.2 Hz), 6.86 (1H, t, *J*=9.2 Hz), 7.02 (1H, t, *J*=9.2 Hz), 7.05 (1H, t, *J*=9.2 Hz), 7.51 (1H, d, *J*=9.2 Hz), 7.52 (2H, t, *J*=7.3 Hz), 7.64 (1H, t, *J*=7.3 Hz), and 8.08 (2H, d, *J*=7.3 Hz); IR ν : 1698, 1680, 802, 760, 754, and 692 cm⁻¹.

Found: C, 77.47; H, 5.01; N, 5.26%. Calcd for C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32%.

Reaction of 1b with DMBD. An anhydrous MeCN solution (30 cm³) of **1b** (500 mg) and DMBD (540 mg) was refluxed for 2 d. The solvent was evaporated and the residue chromatographed on a silica-gel column to give 56 mg (12%) of **2**,⁹ 110 mg (14%) of **6b**, and 149 mg (30%) of unreacted **1b**. **6b**: yellow needles; mp 151–153 °C; ^1H NMR $\delta=4.00$ (3H, s), 4.10 (3H, s), 5.33 (2H, s), 6.89 (1H, d, *J*=6.7 Hz), 7.45–7.7 (5H, m), 8.07 (2H, d, *J*=7.9 Hz), and 8.81 (1H, s); ^{13}C NMR $\delta=46.5$, 52.9, 53.1, 107.8, 121.0, 123.5, 126.4, 127.9, 128.1 (2C), 128.3, 128.9 (2C), 130.3, 130.9, 134.0, 134.4 (2C), 139.1, 165.4, 165.5, 166.8, and 192.2; IR ν : 1730, 1710, 1690, 1636, 790, 757, and 685 cm⁻¹.

Found: C, 68.55; H, 4.32; N, 3.32%. Calcd for C₂₃H₁₇NO₆: C, 68.48; H, 4.25; N, 3.47%.

Reaction of 6a and Phenacyl Bromide. An anhydrous benzene (30 cm³) of **6a** (18 mg), diazabicycloundecene (30 mg),

and phenacyl bromide (40 mg) was refluxed for 7 h. After removing the solvent, the residue was chromatographed on a silica-gel column to give 9 mg (35%) of **6b** and 11 mg (61%) of unreacted **6a**.

References

- 1) N. Abe and T. Takehiro, *Heterocycles*, **26**, 1727 (1987).
- 2) N. Abe and T. Takehiro, *Bull. Chem. Soc. Jpn.*, **61**, 1225 (1988).
- 3) All the NMR spectra were measured in CDCl₃.
- 4) In the previous paper,² we assigned the acetylation

product (**Xc**) of **Xa** as an *O*-acetyl derivative. However, the identity of **Xc** with **6c** was proven by direct comparisons. The observed similarity of the UV spectra of **6c** and **7c** supported to have the same naphthostyryl structures.

5) As the result, previous assignment of **Xc** as the *O*-acetyl derivative should also be revised as an *N*-acetyl derivative. The high-pressure investigation will be a matter of an independent report.

6) P. Bamfield, A. W. Johnson, and A. S. Katner, *J. Chem. Soc. C*, **1966**, 1028.
