HETEROCYCLES, Vol. 29, No. 2, 1989

THE DI-π-METHANE REARRANGEMENT IN 3,4-DIBENZYL-2(5H)-FURANONE

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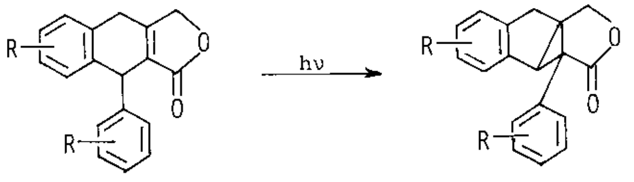
Abstract - The photo-irradiation of 3,4-dibenzyl-2(5H)-furanone (5) in acetone or in methanol resulted in selective rearrangement of the 4-benzyl and gave 1-benzyl-5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (7) along with cis- and trans-3,4-dibenzyldihydro-2(3H)-furanone (8a and 8b). Attempted rearrangement of the 3-benzyl system (13) resulted only in photo-reduction or photo-addition of solvent and gave no evidences for the di-π-methane rearrangement.

In a previous paper,[1] we have reported the regiospecific di-π-methane rearrangement of β-apolignan (1) into a tetrahydrocycloprop(a)indene (2) and have revealed that the rearrangement is common among β-apolignans irrespectively of their ring substituents and that only the pendant phenyl migrates among three possible di-π-methane systems found in the β-apolignan system. On the other hand, the photo-rearrangement of the 4-benzyl-2(5H)-furanone system (3) into a 5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (4), a type reverse to the one in the case of β-apolignan, has been reported.[2]



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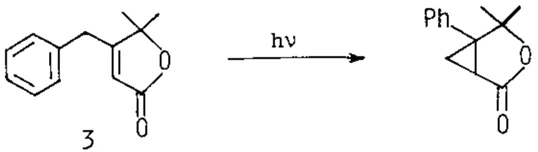

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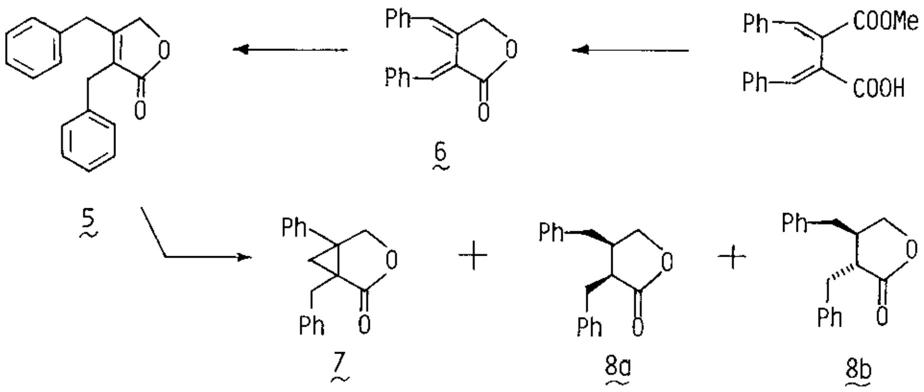
Consequently, we have assumed that this feature of rearrangement in β-apolignan is closely associated with the stereochemistry of the β-apolignan system capable of the quasi-axial conformation of its pendant phenyl ring. We examined the photoreaction of 3,4-dibenzyl-2(5*H*)-furanone (**5**), the system lacking the rigidity in stereochemistry essential to such a conformation responsible for the migratory aptitude of the system, and found that only the 4-benzyl migrated and no rearrangement was detected with the 3-benzyl in contrast to the case of β-apolignan.

The furanone **5** was prepared as follows. The selective reduction of methyl hydrogen α,β-bisbenzylidenesuccinate[3] with Super-Hydride at -10° ∼ 0°C and subsequent tosic acid-catalyzed lactonization of the resulting hydroxy acid afforded a butyrolactone (**6**),[4] which was converted by action of sodium borohydride into the desired furanone **5** in 85% yield from **6**.



5 **6** **7** **8a** **8b**

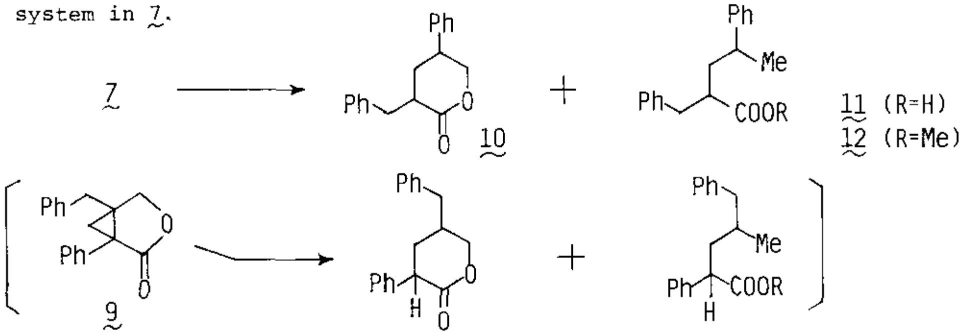
The photo-irradiation of **5** in acetone through a Pyrex filter for 6 h[5] gave a rearranged photo-product (**7**), in 27% yield, and stereoisomeric dihydrofuranones (**8a**[6] in 8% yield and **8b** in 21% yield). In methanol, the irradiation for 24 h gave **7**, **8a**, and **8b** in 6%, 6%, and 20% yield, respectively. In benzene, the photo-irradiation resulted in complete recovery of the starting material.

The Birch reduction of **5** by application of an incomplete reaction period gave the same members of dihydro products as those obtained from the photolysis of **5**. The major product of the reduction was identical with **8b** and was assigned the *trans* stereochemistry.[7]

The photo-product (**7**) displayed an ir absorption[8] for a lactone carbonyl at 1759 cm^{-1} and no olefinic band in the region of 1650 - 1620 cm^{-1}. The ^{1}H-nmr spectrum[8] displayed a pair of one-proton doublets for the cyclopropane proton at 1.32 and 1.62 ppm, a pair of one-proton doublets due to the benzyl methylene at 2.62 and 3.04 ppm, and a pair of one-proton doublets due to the lactonic γ-methylene at 4.36 and 4.45

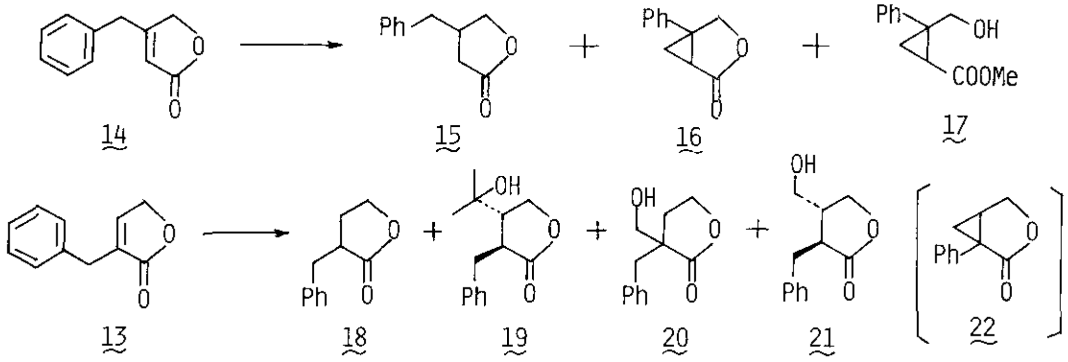
ppm. Moreover, the compound displayed a ms peak[8] due to the molecular ion at m/z 264 (51%) and a fragment peak due to tropylium at m/z 91 (100%).

The furanone 5 has two di-π-methane systems capable of transformation into 7 or its alternative (9), and it was difficult from the above spectral data to discriminate between 7 and 9. Thus, we examined the hydrogenolytic cleavage of the cyclopropane system in 7.



Catalytic hydrogenation of the lactone (7) over palladium on carbon gave a diastereomeric mixture of lactones (10), in 39% yield, and a diastereomeric mixture of carboxylic acids (11), in 57% yield. The lactones displayed the ir absorption for their lactone carbonyl at 1723 cm^{-1}. The ^1H-nmr signals for the major counterpart of lactone 10 appeared as a one-proton multiplet, at 2.84-2.92 ppm, due to the methine α to its lactonic carbonyl and as a pair of one-proton ones consisting of a doublet of doublets for the benzylic methylene at 2.80 and 3.47 ppm. In addition, lactone 10 displayed a ms peak due to the molecular ion at m/z 266 (36%) and a fragment peak due to tropylium at m/z 91 (29%). The acids (11) were converted, without separation, into the corresponding methyl esters (12) by use of diazomethane, which displayed the ir absorption at 1724 cm^{-1} for the ester carbonyl. The ^1H-nmr signals for the major counterpart of ester 12 appeared as a three-proton doublet for the methyl attached to a benzylic carbon, at 1.20 ppm, and as a one-proton doublet of doublets of doublets of doublets (J=10.0, 8.0, 7.0, 4.0 Hz), due to the methine α to an ester carbonyl, centered at 2.48 ppm. Moreover, ester 12 displayed a ms peak due to the molecular ion at m/z 282 (12%) and that due to tropylium at m/z 91 (15%). After all, both lactone 10 and ester 12 displayed no nmr signals for any α-methine proton of the phenylacetate system resulting possibly from the hydrogenolysis of 9. In addition, one of the benzyl protons in 10 is shifted to much lower field (3.74 ppm) possibly by the deshielding effect of the lactone carbonyl. These evidences indicate the '3-benzyl' structure for cyclopropane 7.

In order to confirm the selectivity in migratory aptitude for the 4-benzyl in 5, the di-π-methane rearrangement was examined for 3- and 4-benzyl-2(5*H*)-furanone (13[9] and 14[10]).



The irradiation of 14 in acetone through a Pyrex filter for 6 h gave a butanolide (15)[11a] in 8% yield and a cyclopropanolactone (16)[12] in 23% yield. In methanol, the irradiation for 24 h gave 15, 16, and methyl 2-(hydroxymethyl)-2-phenylcyclopropane-1-carboxylate (17) in 18%, 11%, and 7% yield, respectively. Compound 15 displayed the ir absorption for a lactone carbonyl at 1778 cm^{-1} and no olefinic band. The ^1H-nmr spectrum displayed a pair of one-proton doublet of doublets for the lactonic α-methylene at 2.29 and 2.61 ppm, a three-proton multiplet for the benzyl methylene and β-methine in butanolide at 2.74-2.92 ppm, and a pair of one-proton doublet of doublets indicative of a lactonic γ-methylene at 4.04 and 4.34 ppm. In addition, lactone 15 displayed a ms peak due to the molecular ion at *m/z* 176 (32%) and that due to tropylium at *m/z* 91 (100%). On the other hand, compound 16 displayed the ir absorption for a lactone carbonyl at 1768 cm^{-1} and no olefinic band. The ^1H-nmr displayed a one-proton doublet of doublets due to the highly shielded methine α to carbonyl at 1.38 ppm, a pair of one-proton signals consisting of a doublet of doublets of doublets for the cyclopropane proton at 1.70 and 2.32 ppm, and a pair of one-proton signals consisting of a doublet of doublets indicative of a lactonic γ-methylene at 4.47 and 4.51 ppm. The ms of compound 16 displayed its molecular ion peak at *m/z* 174 (56%) and a peak due to tropylium at *m/z* 91 (28%). On the basis of these spectral evidences, we assigned the structures 15 and 16. The structure of 17 was assigned on the basis of its ir band (CO at 1722 cm^{-1}), ^1H-nmr signals (cyclopropane CH_2 at 1.36 and 2.10 ppm as a pair of doublet of doublets, COCH at 1.74 ppm as a doublet of doublets, $C\underline{H}_2OH$ at 3.57 and 3.80 ppm as a pair of doublets, and OCH_3 at 3.43 ppm as a singlet), and ms peaks [*m/z* 206(5%)

and 91(66%)].

The irradiation of **13** in acetone through a Pyrex filter for 6 h gave a butanolide (**18**)[11] and 3-benzyl-4-(2-hydroxy-2-propyl)dihydro-2(3*H*)-furanone (**19**), and the irradiation in methanol for 24 h gave **18**, 3-benzyl-3-(hydroxymethyl)dihydro-2(3*H*)-furanone (**20**), 3-benzyl-4-(hydroxymethyl)dihydro-2(3*H*)-furanone (**21**), and some unidentified products, but we could not detect any evidences for formation of a cyclopropanolactone (**22**).[13]

Consequently, on the photolysis of the aryl-butenolidyl di-π-methane system such as **5**, **13**, and **14** which lack the rigidity in stereochemistry, the migratory aptitude is reversed as compared with the β-apolignan system. As for the rearrangement of β-apolignan, it seems conclusive that the pendant phenyl being fixed in quasi-axial conformation[14] is essential for the rearrangement and fulfils the special stereoelectronic requirement.

NOTES AND REFERENCES

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3. Prepared from dimethyl *trans*-benzylidenesuccinate (T. Momose, K. Kanai, T. Nakamura, and Y. Kuni, *Chem. Pharm. Bull.*, 1977, **25**, 2755) by the Stobbe condensation with benzaldehyde in the presence of potassium *t*-butoxide. The preparation *via* half esterification of α,β-bisbenzylidenesuccinic acid was reported: K. Freudenberg and T. Kenpermann, *Ann.*, 1957, **602**, 184.
4. Compound **6** was described without description of experimental details: H.G. Heller and M. Szewczyk, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1487; H.G. Heller and P. J. Strydom, *J. Chem. Soc., Chem. Commun.*, 1976, 50.
5. The photochemical reaction was carried out in an immersion apparatus fitted with an Ishii UV-HT 200 W high-pressure mercury lamp.
6. Mp 78-79°C (prisms from ethanol). The value reported: mp 80.5-81°C; see M. Masamura, *Nippon Kagaku Zasshi*, 1955, **76**, 1381.
7. The *trans* mode of stereochemistry in the butanolide system was also assigned by inspection of the feature of its ^{13}C-nmr spectrum: the mode of *cis* and *trans* geometry in 3,4-disubstituted butanolides has been well examined in the light of carbon nmr spectroscopy; see S. Nishibe, M. Chiba, A. Sakushima, S. Hisada, S. Yamanouchi, M. Takido, U. Sankawa, and A. Sakakibara, *Chem. Pharm. Bull.*, 1980, **28**, 850; S. Nishibe, K. Okabe, and S. Hisada, *Chem. Pharm. Bull.*, 1981, **29**, 2078.

8. Infrared (ir) spectra were recorded on a Shimazu IR-435 grating spectrophotometer, and nuclear magnetic resonance (nmr) spectra were obtained with a JEOL JNM-GSX 270 and JEOL JNM-GSX 500 spectrometer with tetramethylsilane as an internal standard. Mass (ms) spectra were recorded on a JEOL JMS-HX 100 spectrometer.
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11. a) T. W. Frechtner, *J. Org. Chem.*, 1977, **42**, 901; b) R. E. Galady and Z. P. Kortylewicz, *Biochemistry*, 1984, **23**, 2083.
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13. G. Mouzin, H. Cousse, and H. Bonnaud, *Synthesis*, 1978, 304.
14. In such a conformation, the spatial requirement for rearrangement of the system that has been proposed by Zimmerman and coworkers can be fulfilled: see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531.

Received, 28th October, 1988