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THE FINAL PRODUCT OF PHOTOCYCLIZATION OF 3,4-BISARYLMETHYLENEDIHYDRO-2(3H)-FURANONE

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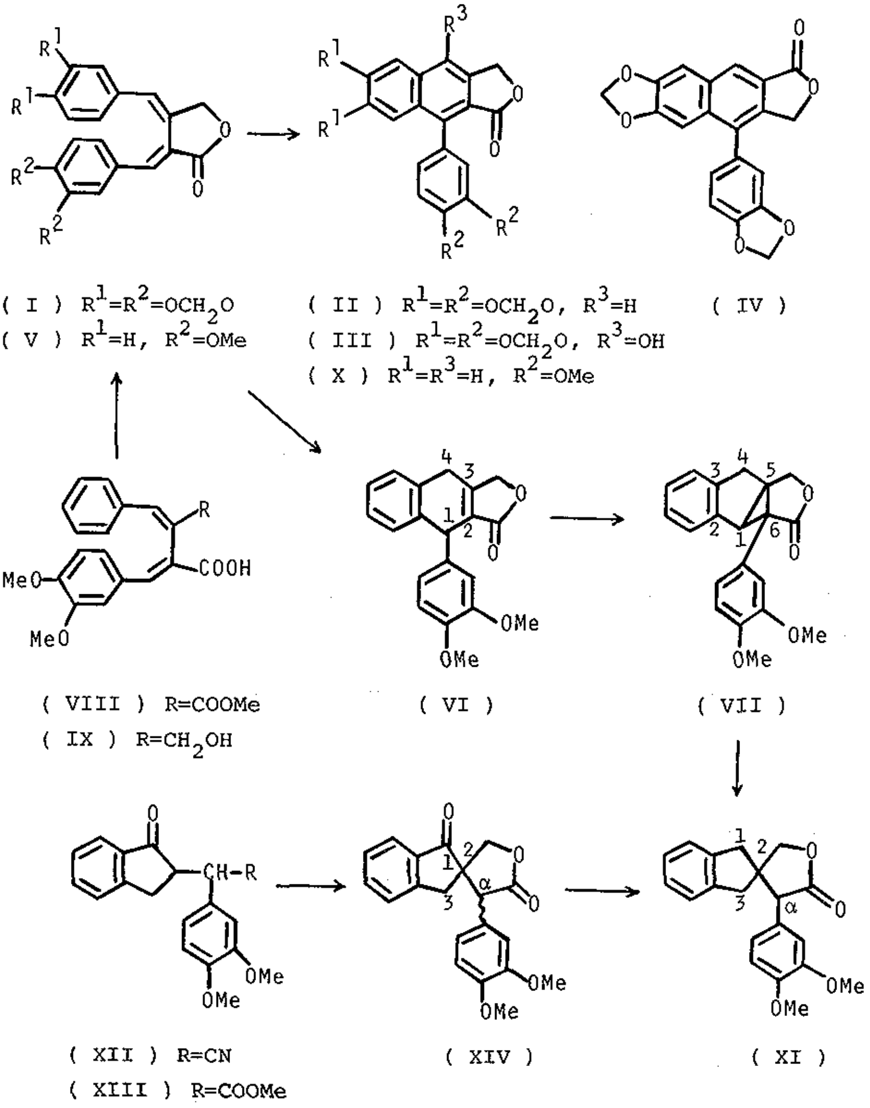
Irradiation of 3,4-bisarylmethylenedihydro-2(3H)-furanone afforded selectively β-apolignan, but was accompanied by subsequent transformation into benzobicyclo[3.1.0]hex-2-ene system via novel degenerate photorearrangement.

In 1967, Lin and his co-workers isolated taiwanin A (I), C (II) and E (III) from Taiwania cryptomerioides Hayata and discovered the selective phototransformation of I into 1-aryl-2,3-naphthalides (II and III).[1] The result suggests that a preferential activation of the olefinic system conjugated with the carbonyl group in 3,4-bisarylmethylenedihydro-2(3H)-furanones in the light is responsible for the selective formation of 1-aryl-2,3-naphthalides (II or III) instead of 4-aryl-2,3-naphthalides (IV). In the photocyclization of 1,4-diphenyl-1,3-butadienes[2] are observed significant effects of ring substituents upon orientation in ring closure. However, bisbenzylidenesuccinic anhydrides[3] cyclize comparably at both phenyl rings, the orientation being irrespective of such effects. The facts also indicate the leading role of the conjugated enone system in the cyclization. The concept appears to explain the fact that most of natural naphthalide lignans belong to type II or III rather than type IV.[4]

In a photochemical experiment associated with the preferential excitation of the enone system[5] in 3,4-bisarylmethylenedihydro-2(3H)-furanone (V), we have found that a selectively formed β-apo-naphthalide (VI) is subsequently transformed into the benzobicyclo[3.1.0]hex-2-ene system (VII) via novel degenerate photorearrangement.

The half ester (VIII) prepared from dimethyl 3,4-dimethoxybenzylidenesuccinate[6] was reduced with lithium aluminum hydride at -20° to give a hydroxy acid (IX)[mp 102-105°; IR($CHCl_3$)cm^{-1} 1682(C=O); NMR($CDCl_3$)δ 3.70(3H, OMe, s), 3.80(3H, OMe, s), 4.24 (2H, $-C\underline{H}_2OH$, broad s), 7.83(1H, $-C\underline{H}=\overset{|}{C}-$, s), 6.7-7.7(9H, Ar-H & $-C\underline{H}=\overset{|}{C}-$, m)], treatment of which with p-toluenesulfonic acid in the dark gave V [mp 87-93°; IR(KBr)cm^{-1} 1765(C=O), 1624(C=C); NMR($CDCl_3$)δ 3.54(3H, OMe, s), 3.78(3H, OMe, s), 5.02(2H, $-C\underline{H}_2O$-CO-, d, J=2Hz), 6.62(1H, $-C\underline{H}=\overset{|}{C}-$, t, J=2Hz), 7.64(1H, $-C\underline{H}=\overset{|}{C}-$, broad s); UV λ_{max}^{EtOH} nm(log ε) 279(3.70)].

The cis,cis-configuration[7] for V was assigned based on comparative NMR data as in the case of taiwanin A (I).[8] The olefinic protons in VIII and one of those in IX and V resonate at the field closely similar to that for the β-proton in methyl trans-cinnamate (δ 7.71)[9] rather than in methyl cis-cinnamate



(I) $R^1=R^2=OCH_2O$
(V) $R^1=H$, $R^2=OMe$

(II) $R^1=R^2=OCH_2O$, $R^3=H$
(III) $R^1=R^2=OCH_2O$, $R^3=OH$
(X) $R^1=R^3=H$, $R^2=OMe$

(IV)

(VIII) R=COOMe
(IX) R=CH_2OH

(VI)

(VII)

(XII) R=CN
(XIII) R=COOMe

(XIV)

(XI)

(δ 6.93).[10]

A solution of V in benzene was irradiated with a 100 W high-pressure mercury lamp with Pyrex filter[11] in the presence of 1,4-diazabicyclo[2.2.2]octane.[12] During irradiation, the solution was flushed with dry and oxygen-free nitrogen. Chromatography of the crude product gave VI, in 24% yield, [mp 168-169°; MS m/e 322(M^+); IR(KBr)cm^{-1} 1752(C=O), 1694(C=C); NMR($CDCl_3$)δ 3.80(3H, OMe, s), 3.82(3H, OMe, s), ca. 3.84(2H, C_4-H, m), 4.85 (2H, -$C\underline{H}_2$OCO-,s), ca. 4.93(1H, C_1-H, m)] and VII, in 24% yield, [mp 195-196°; MS m/e 322(M^+); IR(KBr)cm^{-1} 1750(C=O); NMR($CDCl_3$) δ 2.96(1H, C_4-H, d, J=18Hz), 3.38(1H, C_4-H, d, J=18Hz), 3.09(1H, C_1-H, s), 3.64(3H, OMe, s), 3.73(3H, OMe, s), 4.63(2H, -CH_2OCO-, s)].

The structure of VI was established by its aromatization with lead tetraacetate into the known lignan (X).[13] The intermediacy of VI in the phototransformation of V into VII was confirmed by its independent irradiation to give VII almost quantitatively. The final product (VII) gave, on catalytic hydrogenation over palladium on carbon, the dihydro compound (XI) as sole product [mp 105-106°; MS m/e 324(M^+); IR(KBr)cm^{-1} 1768 (C=O); NMR($CDCl_3$)δ 2.68 and 2.71(2H, C_1-H, each s), 3.02(1H, C_3-H, d, J=16Hz), 3.20(1H, C_3-H, d, J=16Hz), 3.76(1H, C_α-H, s), 3.82(3H, OMe, s), 3.84(3H, OMe, s), 4.20(1H, -$C\underline{H}_2$OCO-, d, J=9Hz), 4.27(1H, -$C\underline{H}_2$OCO-, d, J=9Hz)], which was synthesized as given below.

Hydrocyanation of 3,4-dimethoxybenzylidene-1-indanone[14] and subsequent treatment of the resultant keto nitrile (XII)(a diastereomeric mixture) with methanolic hydrogen chloride gave a keto ester (XIII). Condensation of the crystalline major isomer of XIII with aqueous formaldehyde in the presence of potassium carbonate gave a keto lactone (XIV) [mp 206-207°; MS m/e 338(M^+); IR(KBr)cm^{-1} 1767, 1707(C=O); NMR($CDCl_3$)δ 3.31(1H, C_3-H, d, J=18Hz), 3.49(1H, C_3-H, d, J=18Hz), 3.76(3H, OMe, s), 3.78 (3H, OMe, s), 3.93(1H, C_α-H, s), 4.30(1H, -C$\underline{H}_2$OCO-, d, J=10Hz), 4.58(1H, -C$\underline{H}_2$OCO-, d, J=10Hz)]. Hydrogenolysis of XIV over palladium chloride on carbon yielded quantitatively XI, which was identical with the reduction product from VII with regard to mp, TLC, and IR and NMR spectra.

The conversion of VI to VII is the first example of a photoinduced 1,2 aryl migration to α-position of the enone system.[15] Further studies on the detailed aspects of the novel photorearrangement of VI and related compounds are currently in progress.

NOTES AND REFERENCES

1. Y. -T. Lin, T. -B. Lo, K. -T. Wang, and B. Weinstein, Tetrahedron Letters, 1967, 849.

2. C. C. Leznoff and R. J. Hayward, Canad. J. Chem., 1970, **48**, 1842.

3. F. G. Baddar, L. S. El-Assal, N. A. Doss, and A. H. Shehab, J. Chem. Soc., 1959, 1016.

4. See, for example, Z. Horii, M. Tsujiuchi, and T. Momose, Tetrahedron Letters, 1969, 1079.

5. Shortly before the completion of our work, Heller and Strydom reported a selective photocyclization of (EE)-3,4-bisaryl-

methylenedihydro-2(3H)-furanones, but without giving a mention of the possible role of the enone system [H. G. Heller and P. J. Strydom, *J. Chem. Soc., Chem. Commun.*, 1976, 50].

6. A. W. Schrecker, *J. Amer. Chem. Soc.*, 1957, **79**, 3823.
7. The term 'cis' means that the phenyl substituents are located cis to the central carbon-carbon linkage of the butadiene system.
8. R. J. Hart and H. G. Heller, *J. Chem. Soc. Perkin I*, 1972, 1321, and references therein.
9. H. A. Szymanski and R. E. Yelin, "NMR Band Handbook", IFI/Plenum Data Corporation, New York, 1968.
10. Prepared by methylation of cis-cinnamic acid with diazomethane, and the NMR spectrum was obtained for the solution in deuteriochloroform. The cis-acid was prepared in a manner similar to that reported for the p-methoxy analog; see J. Bregman, K. Osaki, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2021.
11. The starting material (V) disappeared after 4 hrs' irradiation. Irradiation through a filter of ordinary glass was also accompanied by formation of VII, but to a somewhat lesser extent.
12. If DABCO is absent, VI and VII are obtained in low yields. For the effect of DABCO as a quencher of singlet oxygen, see R. S. Atkinson, D. R. G. Brimage, R. S. Davidson, and E. Gray, *J. Chem. Soc. Perkin I*, 1973, 960.
13. L. H. Klemm, K. W. Gopinath, D. H. Lee, F. W. Kelly, E. Trod, and T. M. McGuire, *Tetrahedron*, 1966, **22**, 1797.
14. Y. Poirier and N. Lozac'h, *Bull. Soc. Chim. France*, 1966, 1062.
15. The phenyl migration to β-position of the enone system in 4,4-diphenyl-2-cyclohexenones is a well-known feature of $n \rightarrow \pi^*$ excited photorearrangement; see H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, 1968, **90**, 3749.

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