A Novel Photochemical Rearrangement of 3-Phenylated 2(3*H*)-Oxepinones

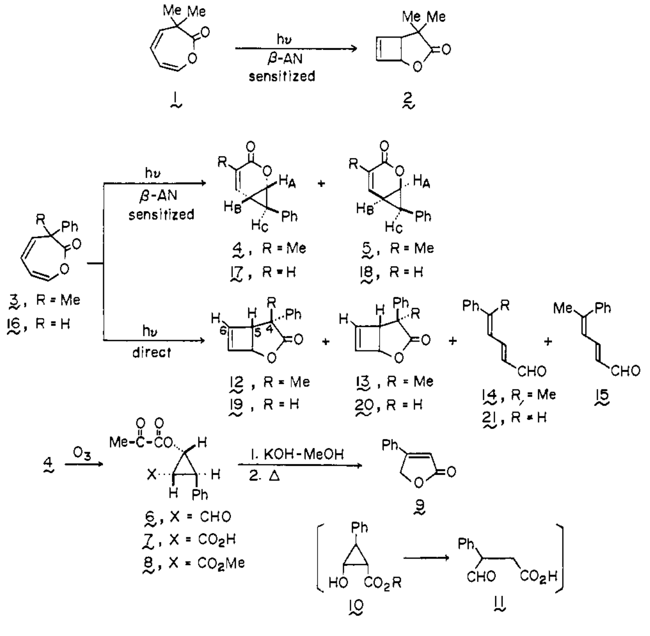
Sir:

Recently attention has been focused on the photochemistry of cyclohepta-3,5-dienones.[1] 2-Oxepinones, the oxygen-hetero analogues of cycloheptadienones, are now readily available by the photooxidation of 6-mono- and 6,6-disubstituted fulvenes.[2] We report a new photochemical rearrangement of 3-phenylated 2(3*H*)-oxepinones into 2-oxabicyclo[4.1.0]hept-4-en-3-one derivatives, a novel example of a valence bond alteration involving the photoinduced 1,4-migration of a phenyl group.[3-5]

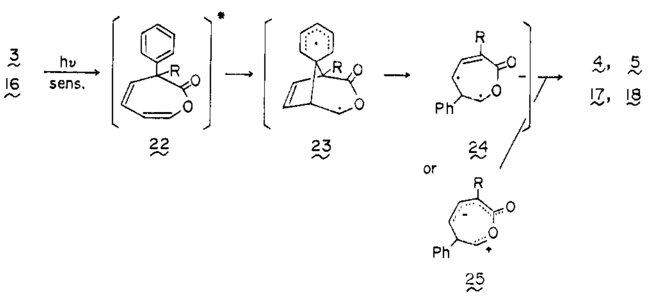
In contrast to the exclusive formation of the cyclization product **2** from 3,3-dimethyl-2(3*H*)-oxepinone (**1**), the sensitized photolysis [1 equiv of β-acetonaphthone (β-AN), ether, room temperature, a 500-W high-pressure mercury arc lamp through Pyrex] of 3-methyl-3-phenyl-2(3*H*)-oxepinone (**3**),[2b] followed by chromatography on silica gel afforded two rearrangement products **4**, mp 85-86 °C, in 65% yield, and **5**, mp 89-90 °C, in 2.5% yield; there was no indication of the presence of the cyclization products (see below). The structure of **4** was assigned on the basis of its spectroscopic properties.[6,7] The spectral properties of **5** were also entirely consistent with a stereoisomer of **4**. As shown in Scheme I, **4** was converted to 4-phenyl-2(5*H*)-furanone (**9**), which was identified with the authentic sample.[8] The formation of **9** is explained by assuming the aldehydic carboxylic acid **11** as the intermediate which would arise from the base-catalyzed ring opening of the cyclopropanol **10**.[9] That the major photorearrangement product of **3** is **4** indicates that a novel photoinduced 1,4-migration of the phenyl group is involved. The coupling constants of the cyclopropane ring protons ($J_{H_AH_B}$ = 6.9, $J_{H_AH_C}$ = 3.4, and $J_{H_BH_C}$ = 4.9 Hz in **4**; $J_{H_AH_B}$ = 6.9, $J_{H_AH_C}$ = 6.9, and $J_{H_BH_C}$ = 10.2 Hz in **5**),[10] the appearance of the cyclopropane ring ^{13}C signals of **5** at higher field than those of **4**,[11] the observed NOE enhancement between the aromatic protons (ortho) and H_A (17%) and H_B (7%) in **4**, and the chemical shift values of the ester methyl protons (δ 3.76 in **8** and 3.53 in the corresponding ester derived from **5**)[12] confirm the assigned configuration of the phenyl groups: exo in **4** and endo in **5** as indicated.

Direct irradiation (CH_2Cl_2, room temperature, 30-W low-pressure mercury lamp) of **3** gave an inseparable mixture of the cyclization products **12** and **13** (44% total) and two geometrically isomeric unsaturated aldehydes **14** (36%) and **15** (20%). The result was similar to the case of the dimethyl derivative **1**, and the rearrangement leading to **4** and **5** did not take place at all. The structures of **14** and **15** were apparent from their spectral properties with reference to the literature values.[13]

Scheme I



Scheme II



As indicated in Scheme I, 3-phenyl-2(3*H*)-oxepinone (**16**)[2d,14] behaves analogously to **3**. Thus, the immediate conclusion which can be drawn is that on direct photolysis (singlet) cyclization and decarbonylation are competitive processes in all 2(3*H*)-oxepinones examined,[15] and that the sensitized photolytic pathway (triplet) in 2(3*H*)-oxepinones is greatly affected by a phenyl substituent at the 3-position. The cyclization of a diene moiety is the essential reaction pathway in the 3-alkyl derivatives, whereas a phenyl group suppresses completely the cyclization by participating in a 1,4-migration process, with concomitant formation of a cyclopropane ring. The phenyl-migrating rearrangement is most rapidly accounted for by the pathway in which the 1,4-bridging step of the excited species **22** leading to **23** and the subsequent cleavage leading to **24** are apparently the etheno (vinylogous) analogue of the first two formal steps of a di-π-methane rearrangement[16] (Scheme II). Recombination of the diradical **24** or of the zwitterionic species **25**, which are the vinylogous analogues of a five-membered lactone postulated by Padwa and Dehm,[4a] yields the observed rearrangement products.[17] The predominant formation of **4** and **17** having an *exo*-phenyl group is presumably attributable to the fact that these are thermodynamically more stable than the endo isomers **5** and **18**.

Further experiments on the reactivities of these oxepinones and the related compounds are in progress.

Acknowledgment. We are grateful to Professor Y. Senda and Mr. J. Ishiyama, Department of Applied Science, Faculty of Engineering, Tohoku University, for measurement of the ^{13}C NMR spectra.

References and Notes

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Zimmerman, H. G. C. Dürr, R. G. Lewis, and S. Bram, *ibid.*, **84**, 4149 (1962); H. E. Zimmerman, H. G. C. Dürr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967).

(5) It has been reported that on direct irradiation the nitrogen-hetero analogues, 1,3-dihydro-2*H*-azepin-2-ones, underwent exclusively cyclization to give 2-azabicyclo[3.2.0]hept-6-en-3-ones: O. L. Chapman and E. D. Hoganson, *J. Am. Chem. Soc.*, **86**, 498 (1964); L. A. Paquette, *ibid.*, **86**, 500 (1964); H.-D. Becker and K. Gustafsson, *Tetrahedron Lett.*, 1705 (1976).

(6) All new compounds except **6**, **8**, and **18** in this communication gave satisfactory elemental analyses. Compounds **6** and **8** decomposed partially during purification by vacuum distillation or TLC on silica gel. Compound **18** was homogeneous on TLC, but still contained a trace of impurities as detected by NMR.

(7) IR ($CHCl_3$) 1718 (sh), 1707, and 1142 cm^{-1}; UV (EtOH) λ_{max} 225 (ϵ 8200) and 264 nm (ϵ 5200); ^1H NMR (100 MHz, C_6D_6) δ 1.31 (ddd, 1 H, $J = 6.9$, 5.5, and 4.9 Hz), 1.58 (dd, 1 H, $J = 4.9$ and 3.4 Hz), 1.77 (finely splitted s, 3 H), 4.06 (dd, 1 H, $J = 6.9$ and 3.4 Hz), 6.26 (finely splitted d, 1 H, $J = 5.5$ Hz), 6.54–6.70 (m, 2 H), and 6.98–7.12 (m, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) 17.35 (q), 22.26 (d), 33.91 (d), 64.00 (d), 123.76 (s), 125.71 (d), 126.74 (d), 128.68 (d), 137.54 (s), 142.09 (d), and 161.87 ppm (s).

(8) G. W. Perold and H. K. L. Hundt, *J. Chem. Soc.*, 1924 (1966).

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(12) G. L. Krueger, F. Kaplan, M. Orchin, and W. H. Faul, *Tetrahedron Lett.*, 3979 (1965).

(13) W. Skorianetz and G. Ohloff, *Helv. Chim. Acta*, **58**, 1272 (1975).

(14) Compound **16**, the original product formed by the photooxidation of 6-phenylfulvene, is unstable in solutions and isomerizes easily to the stable fully conjugated isomer. Hence, the sample separated from the photooxidation mixture by chromatography was immediately subjected to photolysis at low temperature.

(15) It was reported that decarbonylation is the main reaction pathway in the photochemical transformation of enol lactones: A. Yogev and Y. Mazur, *J. Am. Chem. Soc.*, **87**, 3520 (1965); C. D. Gutsche and B. A. M. Oude-Alink, *ibid.*, **90**, 5855 (1968); O. L. Chapman and C. L. McIntosh, *Chem. Commun.*, 383 (1971); B. A. M. Oude-Alink, A. W. K. Chan, and C. D. Gutsche, *J. Org. Chem.*, **38**, 1993 (1973); A. Padwa, D. Dehm, T. Oine, and G. A. Lee, *J. Am. Chem. Soc.*, **97**, 1837 (1975).

(16) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973). See also ref 4a.

(17) This ring-forming step is formally a cycloheptatriene → norcaradiene type transfomation.

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The Chemospecific, Homogeneous, Ambient Temperature Ullmann Coupling of *o*-Haloarylimines

Sir:

The classical Ullmann reaction allows for the coupling of aryl halides to form biaryls at elevated temperatures (100-250 °C). In the case of unsymmetrical couplings, three products (AA, AB, BB) are formed in varying amounts.[1] We wish to report a method for the homogeneous, chemospecific coupling of ortho-halogenated arylimines at ambient temperature[2] as illustrated in Scheme I.

Scheme I

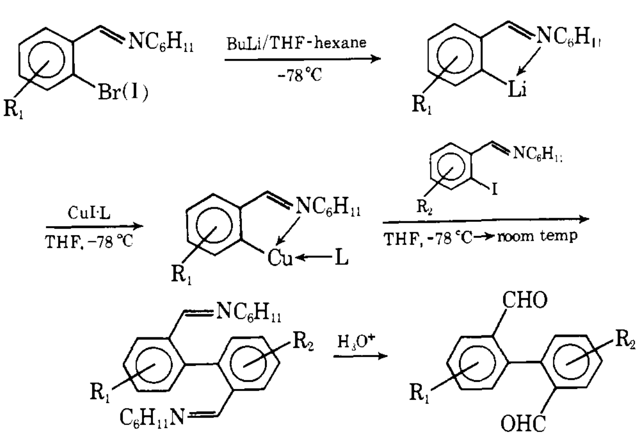
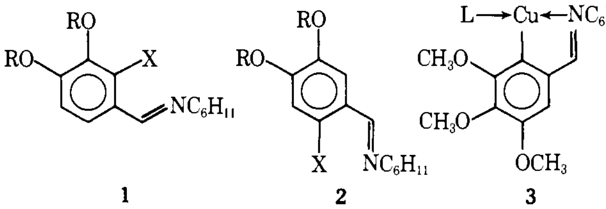


Table I

Entry	Cu reagent	Iodide	Biaryl	Yield % NMR[a]	Yield % isolated[b]
1	1a	1b	5a	60	44
2	2a	2b	5b	65	59
3	1a	2b	5c	70	54
4	2a	1b	5c	86	58
5	2c	2d	5d	—	62
6	3	2b	5e	77	63
7	4	2b	6	—	54[c]

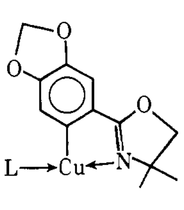
[a] Aldehyde proton integrated against benzaldehyde standard. [b] Crystallized yields.[4] [c] Isolated as oxazoline-imine.

The biaryl formed in each case is determined by the position of the halogen atom in each of the starting imines and is formed by the union of the preformed copper reagent and the aryl iodide. The specific couplings which were investigated are listed in Table I.[3]

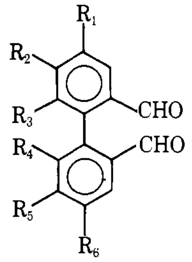


1 **2** **3**

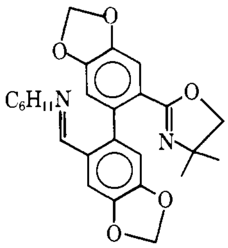
a, R = $-CH_2-$; X = Cu←L
b, R = $-CH_2-$; X = I
c, R = CH_3; X = Cu←L
d, R = CH_3; X = I



4



5



6

a, $R_1 = R_6 = H$; $R_2,R_3 = R_4,R_5 = OCH_2O$
b, $R_3 = R_4 = H$; $R_1,R_2 = R_5,R_6 = OCH_2O$
c, $R_1 = R_4 = H$; $R_2,R_3 = R_5,R_6 = OCH_2O$
d, $R_3 = R_4 = H$; $R_1 = R_2 = R_5 = R_6 = OCH_3$
e, $R_3 = H$; $R_1,R_2 = OCH_2O$; $R_4 = R_5 = R_6 = OCH_3$

The sequence has the advantage over traditional Ullmann conditions in that (a) the reaction can be conducted homogeneously at ambient temperature; (b) both symmetrical and unsymmetrical dimers can be produced; (c) unsymmetrical biaryls can be prepared in either of two modes (Table I, entries 3 and 4); (d) both biaryl aldehydes and oxazolines (latent ester or carboxylic acid[5]) can be produced. While nickel(0) biscyclooctadiene,[6] nickel(0) tetrakistriphenylphosphine,[7] and nickel(0) tristriphenylphosphine[8] have been utilized to couple aryl halides, halides flanked by two ortho-substituents fail to dimerize.[7,8] Entry 6 reveals that this effect is not significant in this reaction, a fact of critical importance in synthetic approaches to the antileukemic biaryls, steganacin **7a** and steganagin **7b**,[9] which depend upon initial formation of the biaryl system.