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

Sir:

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

In contrast to the exclusive formation of the cyclization product 2 from 3,3-dimethyl-2(3H)-oxepinone (1), the sensitized photolysis [1 equiv of  $\beta$ -acetonaphthone ( $\beta$ -AN), ether, room temperature, a 500-W high-pressure mercury arc lamp through Pyrex] of 3-methyl-3-phenyl-2(3H)-oxepinone (3),<sup>2b</sup> 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.<sup>6,7</sup> 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(5H)-furanone (9), which was identified with the authentic sample.<sup>8</sup> 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),<sup>10</sup> the appearance of the cyclopropane ring <sup>13</sup>C signals of 5 at higher field than those of 4,<sup>11</sup> the observed NOE enhancement between the aromatic protons (ortho) and HA (17%) and H<sub>B</sub> (7%) in 4, and the chemical shift values of the ester methyl protons ( $\delta$  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<sub>2</sub>Cl<sub>2</sub>, 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

Scheme I



Scheme II



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.<sup>13</sup>

As indicated in Scheme I, 3-phenyl-2(3H)-oxepinone (16)<sup>2d,14</sup> 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(3H)-oxepinones examined.<sup>15</sup> and that the sensitized photolytic pathway (triplet) in 2(3H)-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- $\pi$ -methane rearrangement<sup>16</sup> (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,<sup>4a</sup> yields the observed rearrangement products.<sup>17</sup> 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.

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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.<sup>1</sup> We wish to





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				Yield %	
Entry	Cu reagent	lodide	Biaryl	NMR <sup>a</sup>	isolated <sup>b</sup>
1	la	1b	5a	60	44
2	2a	2b	5b	65	59
3	la	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 <sup>c</sup>

<sup>a</sup> Aldehyde proton integrated against benzaldehyde standard. <sup>b</sup> Crystallized yields.<sup>4</sup> <sup>c</sup> Isolated as oxazoline-imine.

report a method for the homogeneous, chemospecific coupling of ortho-halogenated arylimines at ambient temperature<sup>2</sup> as illustrated in Scheme I.

The biarvl 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.<sup>3</sup>



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<sup>5</sup>) can be produced. While nickel(0) biscyclooctadiene,<sup>6</sup> nickel(0) tetrakistriphenylphosphine,<sup>7</sup> and nickel(0) tristriphenylphosphine<sup>8</sup> have been utilized to couple aryl halides, halides flanked by two ortho-substituents fail to dimerize.<sup>7,8</sup> 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,<sup>9</sup> which depend upon initial formation of the biaryl system.