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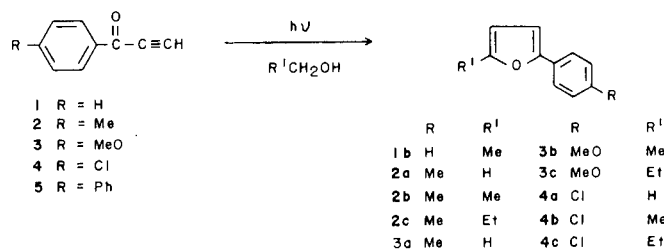
The photochemical reactions of  $\alpha,\beta$ -acetylenic ketones have been examined. Irradiation of 1-*p*-substituted phenyl-2-propyn-1-ones **2-4** in primary alcohols gave 2,5-disubstituted furans **2a-4c**. The formation of furans can be explained in terms of cyclization, followed by dehydration of the 1:1-adduct of acetylenic ketone and alcohol, which was formed initially by hydrogen atom abstraction from alcohol by the excited acetylenic ketone. Irradiation of 1-*p*-tolyl-2-propyn-1-one (**2**) in ethanol- $d_1$  yielded 2-methyl-5-*p*-tolylfuran (**2b**) containing no deuterium. This result was consistent with a mechanism that involves hydrogen atom abstraction from alcohol by the carbon of triple bond rather than abstraction by carbonyl oxygen.

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We previously reported that the photochemical formation of 2-methyl-5-phenylfuran (**1b**) from 1-phenyl-2-propyn-1-one (**1**) and ethanol involved  $\alpha$ -hydrogen atom abstraction of ethanol by the excited **1** [1]. However, the question, which the initial site of hydrogen abstraction could be either carbonyl oxygen or acetylenic carbon, remained. Büchi and Feairheller [2] reported ethyl propiolate underwent photochemical addition of solvent to yield the 1:1-adduct at  $\beta$ -carbon of propiolate *via* hydrogen abstraction by carbonyl oxygen. On the other hand, photochemical reduction of methyl 4,4-dimethyl-2-pentynoate to methyl 4,4-dimethyl-2-pentenoate *via* hydrogen abstraction mechanism by the carbon of triple bond was reported by Stubblefield and Wilson [3]. We have investigated the photochemical reactions of 1-*p*-substituted phenyl-2-propyn-1-one **2-5** in order to provide the scope [4] of this reaction and resolve the question about the initial site of hydrogen abstraction in the formation of furans and here we wish to report these results.

1-*p*-Tolyl- (**2**) and 1-*p*-anisyl-2-propyn-1-one (**3**) were prepared by Jones oxidation of the corresponding propargyl alcohol derived from sodium acetylide and aldehyde [5]. 1-(4-Chlorophenyl)- (**4**) and 1-biphenyl-2-propyn-1-one (**5**) were also prepared by Jones oxidation of propargyl alcohol, which were obtained by the reaction of the corresponding arylaldehyde and ethynylmagnesium bromide [6].

When a solution of 1-*p*-tolyl-2-propyn-1-one (**2**) in benzene was irradiated through a Pyrex filter with a high-pressure mercury lamp under argon, no change was observed and the starting material **2** was recovered quantitatively. Meanwhile, irradiation of  $\alpha,\beta$ -acetylenic ketones **2-4** in primary alcohol such as methanol, ethanol, and propanol under the same conditions as described above for 8 hours gave 2,5-disubstituted furans **2a-4c**. The structure of photoproducts **2a-4c** was determined on the basis of elemental and physicl data. Characteristically, the signals of the furan ring protons for photoproducts **2b-c**, **3b-c**, and **4b-c** in  $^1\text{H}$ -nmr spectra showed at  $\delta$  5.95-6.02 (1H) and



6.38-6.51 (1H), suggesting the furan was 2,5-disubstituted [7] and those of photoproducts **2a**, **3a**, and **4a** showed at  $\delta$  6.39-6.55 (2H), and 7.35-7.43 (1H), suggesting the furan was 2-substituted [7]. On the other hand, when a solution of 1-biphenyl-2-propyn-1-one (**5**) in ethanol was irradiated, no photoproduct could be obtained and acetylenic ketone

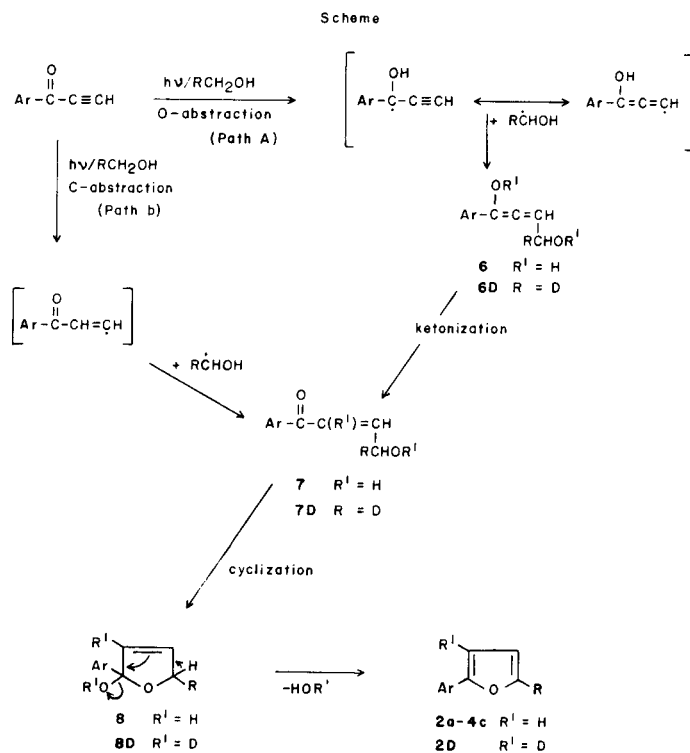


Table 1.

The Yield and Physical Properties of 2,5-Disubstituted Furans **2a-4c**.

| Yield [a]     | mp (°C)<br>[bp (°C/mmHg)]           | IR (CHCl <sub>3</sub> )<br>(cm <sup>-1</sup> ) | <sup>1</sup> H-NMR (CDCl <sub>3</sub> )<br>(δ)   | <sup>13</sup> C-NMR (CDCl <sub>3</sub> )<br>(δ)  |
|---------------|-------------------------------------|--|--|--|
| <b>2a</b>     | 8<br>[90-91/2]<br>lit [8] 56/0.5    | 1610, 1510                                     | 2.33 (s, 3H), 6.39-6.45 (m, 1H), 6.54 (d, 1H, J = 3.9 Hz), 7.15 (d, 2H, J = 8.3 Hz), 7.39-7.43 (m, 1H), 7.55 (d, 2H, J = 8.3 Hz)                       | 21.2 (q), 100.3 (d), 104.2 (d), 111.5 (d), 123.8 (d), 129.3 (d), 137.1 (s), 143.8 (s), 154.2 (s)                     |
| <b>2b</b>     | 16<br>[98-99/2]<br>lit [9] 65/0.005 | 1605, 1500                                     | 2.29 (s, 6H), 5.95-5.99 (m, 1H), 6.42 (d, 1H, J = 3.4 Hz), 7.09 (d, 2H, J = 8.3 Hz), 7.49 (d, 2H, J = 8.3 Hz)  | 13.5 (q), 21.1 (q), 105.0 (d), 107.5 (d), 123.2 (d), 128.6 (s), 129.2 (d), 136.3 (s), 151.3 (s), 152.5 (s)           |
| <b>2c</b> [b] | 19<br>[122-123/2]                   | 1600, 1500                                     | 1.24 (t, 3H), 2.29 (s, 3H), 2.67 (q, 2H), 5.95-6.02 (m, 1H), 6.43 (d, 1H, J = 3.4 Hz), 7.09 (d, 2H, J = 8.3 Hz), 7.50 (d, 2H, J = 8.3 Hz)              | 12.2 (q), 21.1 (q), 21.5 (t), 104.9 (d), 105.9 (d), 123.4 (d), 128.7 (s), 129.3 (d), 136.4 (s), 152.4 (s), 157.1 (s) |
| <b>3a</b>     | 9<br>50-51<br>lit [8] 51.5          | 1610, 1505                                     | 3.81 (s, 3H), 6.40-6.53 (m, 2H), 6.91 (d, 2H, J = 8.8 Hz), 7.35-7.42 (m, 1H), 7.59 (d, 2H, J = 8.8 Hz)   | 55.3 (q), 103.3 (d), 111.5 (d), 114.1 (d), 124.1 (s), 125.2 (d), 141.3 (d), 154.0 (s), 159.0 (s)                     |
| <b>3b</b>     | 12<br>41-42<br>lit [9] 45-46        | 1615, 1495<br>820                              | 2.34 (s, 3H), 3.81 (s, 3H), 6.01 (br s, 1H), 6.38 (d, 1H, J = 3.1 Hz), 6.88 (d, 2H, J = 8.8 Hz), 7.55 (d, 2H, J = 8.8 Hz)                              | 13.7 (q), 55.3 (q), 104.2 (d), 107.4 (d), 114.0 (d), 124.4 (s), 124.7 (d), 151.5 (s), 152.3 (s), 158.6 (s)           |
| <b>3c</b> [c] | 7<br>114/2                          | 1610, 1490<br>820                              | 1.26 (t, 3H), 2.69 (q, 2H), 3.78 (s, 3H), 6.01 (dt, 1H, J = 1.0, 3.4 Hz), 6.39 (d, 1H, J = 3.4 Hz), 6.87 (d, 2H, J = 8.8 Hz), 7.54 (d, 2H, J = 8.8 Hz) | 12.3 (q), 21.5 (t), 55.2 (q), 103.9 (d), 105.9 (d), 114.0 (d), 124.4 (s), 124.7 (d), 152.1 (s), 156.8 (s), 158.5 (s) |
| <b>4a</b>     | 5<br>65-66                          | 1590, 1500                                     | 6.43 (m, 1H), 6.62 (d, 1H, J = 3.4 Hz), 7.17-7.64 (m, 5H)  | 105.4 (d), 111.7 (d), 124.9 (d), 128.8 (d), 129.4 (s), 132.9 (s), 142.3 (d), 152.3 (s)                               |
| <b>4b</b>     | 14<br>55-56<br>lit [9] 59-61        | 1585, 1480                                     | 2.23 (d, 1H, J = 1.0 Hz), 6.02 (dt, 1H, J = 1.0, 3.4 Hz), 6.48 (d, 1H, J = 3.4 Hz), 7.23-7.56 (m, 4H)  | 13.6 (q), 106.3 (d), 107.9 (d), 124.5 (d), 128.8 (d), 129.7 (s), 132.2 (s), 151.2 (s), 152.3 (s)                     |
| <b>4c</b> [d] | 11<br>31                            | 1590, 1480,<br>815                             | 1.27 (t, 3H), 2.70 (q, 2H), 6.00-6.06 (m, 1H), 6.51 (d, 1H, J = 2.9 Hz), 7.22-7.66 (m, 4H)   | 12.2 (q), 21.5 (t), 106.1 (d), 106.2 (d), 124.5 (d), 128.7 (d), 129.7 (s), 132.2 (s), 151.1 (s), 157.9 (s)           |

[a] Isolate Yield. [b] *Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O: C, 83.77; H, 7.62. Found: C, 83.83; H, 7.57. [c] *Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: C, 77.20; H, 6.97. Found: C, 76.94; H, 6.94. [d] *Anal.* Calcd. for C<sub>12</sub>H<sub>11</sub>ClO: C, 69.76; H, 5.36. Found: C, 69.73; H, 5.36.

**5** was recovered in nearly quantitatively. The effect of the substituent at *para*-position of benzene ring was not recognized except phenyl group. When 1-*p*-tolyl-2-propyn-1-one (**2**) was irradiated in ethanol containing triplet sensitizer such as *m*-methoxyacetophenone ( $E_T = 72.4$  kcal/mol), thioxanthone ( $E_T = 65-66$  kcal/mol) and acetone ( $E_T = 79-82$  kcal/mol), the yield of the furan **2b** was almost the same as in direct irradiation. In the same way, irradiation of acetylenic ketone **2** in ethanol containing piperylene ( $E_T = 59.2$  kcal/mol) as triplet quencher was carried out and no photoproduct could be detected. From these results, it can be concluded that the formation of the furan **2b** involves the triplet excited state of acetylenic ketone **2**. The mechanism for the formation of furan involved  $\alpha$ -hydrogen atom abstraction of primary alcohol by the triplet excited state of acetylenic ketone. However, the initial site of hydrogen abstraction can be either carbonyl oxygen or carbon of triple bond as shown in Scheme. In oxygen abstraction mechanism (path A), the C-C bonded 1:1-adduct **7** of acetylenic ketone and alcohol through hydroxy allene intermediate **6**, which formed initially by  $\alpha$ -hydrogen atom abstraction of alcohol by carbonyl oxygen of acetylenic ketone, gives the final product by cyclization and subsequent dehydration. In the carbon abstraction mechanism (path B), the C-C bonded 1:1-adduct **7**, which arises *via*

$\alpha$ -hydrogen atom abstraction of alcohol by acetylenic carbon, gives the same final product. In order to resolve this question about initial site of hydrogen abstraction, the irradiation of acetylenic ketone **2** in ethanol-d<sub>1</sub> was carried out. If the oxygen abstraction mechanism was followed, the expected product would be 2-methyl-5-*p*-tolylfuran-3d (**2bD**). The product **2bD** would be formed *via* hydroxy allene intermediate **6D**, which gives the 1:1-adduct **7D** on ketonization in the deuterated solvent. The alternative path would be expected to produce the furan containing no deuterium. Irradiation of acetylenic ketone **2** in ethanol-d<sub>1</sub> under the same conditions gave the furan **2b**, in which no deuterium was contained. This fact supported that the furan **2b** was formed by carbon abstraction mechanism as shown in Scheme. Consequently, the photochemical formation of the furan proceeds by hydrogen atom abstraction of acetylenic carbon.

## EXPERIMENTAL

Melting and boiling points are uncorrected. Melting points were measured with a Yanaco micro-melting point apparatus (MJ-3) and boiling points were measured with Büchi Kugelrohr (KR-3) apparatus. The uv spectra were recorded on a Shimadzu UV-365 spectrophotometer. The ir spectra were determined with JASCO IRA-1 spectrophotometer. The <sup>1</sup>H-nmr and <sup>13</sup>C-nmr spectra were run on a JEOL FX-90Q spectrome-

ter (90 MHz) in deuteriochloroform with tetramethylsilane as internal standard. A Ushio 450-W high-pressure mercury lamp was used as an irradiation source. Silica gel (Merk, Kieselgel 60 for flash chromatography) was used for column chromatography.

#### Starting Materials.

1-*p*-Substituted phenyl-2-propyn-1-ones **2** and **3** were prepared according to the method previously described in the literature [5] and compounds **4** and **5** were prepared by modification of the method described in the literature [6].

#### 1-*p*-Tolyl-2-propyn-1-one (**2**).

This compound had mp 41-42°; uv (ethanol) ( $\epsilon$ ): 272 nm ( $4.3 \times 10^4$ ); ir (chloroform): 3290, 2085, 1640, and 1600  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$ :  $\delta$  2.44 (s, 3H), 3.41 (s, 1H), 7.28 (d, 2H,  $J = 8.3$  Hz), and 8.05 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C-nmr}$ :  $\delta$  21.8 (q), 80.3 (d), 80.4 (s), 129.4 (d), 129.9 (d), 134.0 (s), 147.5 (s), and 177.0 (s).

#### 1-*p*-Anisyl-2-propyn-1-one (**3**).

This compound had mp 80°; uv (ethanol) ( $\epsilon$ ): 221 ( $1.08 \times 10^4$ ) and 303 nm ( $1.80 \times 10^4$ ); ir (chloroform): 3240, 2075, 1635, and 1590  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$ :  $\delta$  3.40 (s, 1H), 3.88 (s, 3H), 6.95 (d, 2H,  $J = 9.2$  Hz), and 8.12 (d, 2H,  $J = 9.2$  Hz);  $^{13}\text{C-nmr}$ :  $\delta$  55.6 (q), 80.0 (d), 80.4 (s), 113.9 (d), 129.6 (s), 132.1 (d), 164.7 (s), and 175.8 (s).

#### 1-(4-Chlorophenyl)-2-propyn-1-one (**4**).

This compound had mp 68-69°; uv (ethanol) ( $\epsilon$ ): 216 ( $1.09 \times 10^4$ ) and 270 nm ( $1.26 \times 10^4$ ); ir (chloroform): 3290, 2090, 1640, and 1600  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$ :  $\delta$  3.49 (s, 1H), 7.45 (d, 2H,  $J = 8.3$  Hz), and 8.09 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C-nmr}$ :  $\delta$  79.9 (s), 81.3 (d), 129.0 (d), 130.9 (d), 134.5 (s), 141.2 (s), and 175.9 (s).

#### 1-Biphenyl-2-propyn-1-one (**5**).

This compound had mp 108-109°; uv (ethanol) ( $\epsilon$ ): 221 ( $1.24 \times 10^4$ ) and 305 nm ( $2.09 \times 10^4$ ); ir (chloroform): 3290, 2085, 1640, and 1595  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$ :  $\delta$  3.44 (s, 1H), 7.34-7.89 (m, 7H), and 8.21 (d, 2H,  $J = 8.8$  Hz);  $^{13}\text{C-nmr}$ :  $\delta$  80.4 (s), 80.7 (d), 127.2 (d), 127.6 (d), 128.5 (d), 129.9 (d), 130.2 (d), 135.0 (s), 139.5 (s), 147.1 (s), and 176.8 (s).

Anal. Calcd. for  $\text{C}_{15}\text{H}_{10}\text{O}$ : C, 87.35; H, 4.88. Found: C, 87.02; H, 5.01.

#### General Procedure for the Photoreaction of $\alpha,\beta$ -Acetylenic Ketones **2-5**.

A solution of  $\alpha,\beta$ -acetylenic ketone (300 mg) in alcohol (50 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (450 W) under argon at room temperature for 8 hours. After removal of the solvent, the residual oil was chromatographed with benzene-hexane (1:1) as eluent on a silica gel column to give the corresponding 2,5-disubstituted furans **2a-4c**. Prolonged irradiation resulted in polymerization. The yield and physical properties of photoproducts **2a-4c** were summarized in Table 1. Sensitization and Quenching of 1-*p*-Tolyl-2-propyn-1-one (**2**).

*m*-Methoxyacetophenone, thioxanthone, and acetone were used as sensitizer and piperylene was used as a quencher.

#### Sensitization.

A solution of  $\alpha,\beta$ -acetylenic ketone **2** (50 mg) and a sensitizer (in such a ratio that the sensitizer absorbs the incident light more than 95%) in ethanol (10 ml) was irradiated at 313 nm (for *m*-methoxyacetophenone) or 366 nm (for thioxanthone and acetone) under argon with merry-go-round photoreactor. The yield of 2-methyl-5-*p*-tolylfuran (**2b**) thus produced was determined by  $^1\text{H-nmr}$  spectrometer using piperanal as standard after removal of the solvent. The 313 nm light was isolated with a filter solution containing 0.002 mol/l potassium chromate in 5% aqueous sodium carbonate and the 366 nm light was isolated with a filter solution containing 0.04 mole/l naphthalene in methanol.

#### Quenching.

A solution of  $\alpha,\beta$ -acetylenic ketone **2** (50 mg) and a large excess of piperylene (240 mg) in ethanol (10 ml) was irradiated under the same conditions. No detectable formation of 2-methyl-5-*p*-tolylfuran (**2b**) was observed and acetylenic ketone **2** was quantitatively recovered.

#### Irradiation of 1-*p*-Tolyl-2-propyn-1-one (**2**) in Ethanol- $d_1$ .

A solution of the compound **2** (200 mg) in ethanol- $d_1$  (20 ml) was irradiated under the same conditions. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene-hexane (1:1) as eluent to yield 2-methyl-5-*p*-tolylfuran (**2b**), which contained no deuterium, in 11% yield.

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