

*Anal.* Calcd for  $C_{17}H_{16}O_3$ : C, 75.53; H, 6.71. Found: C, 75.60; H, 6.48.

**C.** 1-(4-Biphenyloxy)-3-methyl-3-buten-2-one (4).—Band 3 afforded 1.8 g of material which, on recrystallization from methanol, gave 1.23 g of 4, mp 79–82°. The analytical sample of 4 was crystallized from methanol and had mp 81–82.5°; nmr ( $CDCl_3$ )  $\delta$  6.77–7.60 (m, 9), 6.02 (m, 1, A portion of  $AMX_3$  pattern for isopropenyl), 5.83 (m, 1 M portion of the  $AMX_3$  pattern), 4.97 (s, 2,  $OCH_2CO$ ), 1.90 (m, 3,  $X_3$  portion of the  $AMX_3$  pattern); mass spectrum (70 eV) 252 ( $M^+$ ), 183 ( $C_6H_5C_6H_4O=CH_2^+$ ), and other ions at 169, 153, 152, 83, and 69.

*Anal.* Calcd for  $C_{17}H_{16}O_2$ : C, 80.92; H, 6.39. Found: C, 81.00; H, 6.54.

**D.** 3-(4-Biphenyloxy)-1-methoxy-3-methyl-2-butanone (6).—Band 4 afforded 0.8 g of material which was recrystallized from methanol to give 0.25 g of 6, mp 93–94°. The analytical sample of 6 was crystallized from methanol and had mp 94–95°; nmr ( $CDCl_3$ )  $\delta$  4.55 (s, 2,  $OCH_2CO$ ), 3.42 (s, 3,  $OCH_3$ ), 1.52 [s, 6,  $C(CH_3)_2$ ]; mass spectrum (70 eV) 284 ( $M^+$ ), 211 [ $C_6H_5C_6H_4O=C(CH_3)_2^+$ ], and other ions at 170, 153, 152 and 45. High resolution peak matching at mass 211 for this product showed a single ion at  $m/e$  211.1116 (calcd for  $C_{15}H_{15}O$ : 211.1123).

*Anal.* Calcd for  $C_{18}H_{20}O_3$ : C, 76.03; H, 7.09. Found: C, 76.12; H, 7.18.

1-(4-Biphenyloxy)-3-methyl-3-buten-2-one (4).—To a mixture of 20 g 1 and 300 ml of tetrahydrofuran at 0° was added a solution of 1 ml of 70% perchloric acid in 25 ml of tetrahydrofuran. The mixture was stirred at room temperature for 2 hr at which time 2 ml of pyridine was added and the mixture was concentrated *in vacuo*. An ethereal solution of the residue was washed with dilute acid, dilute base, and water and then dried. The crude product was chromatographed in a column prepared by wet packing 2 kg of silica gel (E. Merck) with 15% ethyl acetate in cyclohexane. Elution of the column with the same solvent and concentration of appropriate fractions (as determined by thin layer chromatography) gave material which, on recrystallization from methanol, yielded 8.4 g of product 4, mp 80.5–82°, identical with this substance described above.

1-(4-Biphenyloxy)-3-methyl-2-butanone.—A mixture of 100 mg of 4, 50 ml of tetrahydrofuran, and 100 mg of 10% palladium on carbon was shaken in a Parr hydrogenation apparatus at an initial hydrogen pressure of 15 psi. After the hydrogen uptake ceased (1 hr), the catalyst was removed by filtration and the filtrate concentrated *in vacuo*. The residue was crystallized from methanol and gave 72 mg of 1-(4-biphenyloxy)-3-methyl-2-butanone: mp 62–63°; nmr ( $CDCl_3$ )  $\delta$  4.62 (s, 2,  $OCH_2CO$ ), 2.93 (septuplet, 1,  $J = 7$  Hz, A portion of  $AX_6$  pattern for isopropyl), 1.13 (d, 6,  $J = 7$  Hz,  $X_6$  portion of the  $AX_6$  pattern); mass spectrum (70 eV) 254 ( $M^+$ ), 183 ( $C_6H_5C_6H_4OCH_2^+$ ), and other ions at 153, 152, 71 and 43.

*Anal.* Calcd for  $C_{17}H_{18}O_3$ : C, 80.28; H, 7.13. Found: C, 80.44; H, 6.91.

**Acknowledgment.**—Appreciation is expressed to our analytical section for elementary analyses and especially to L. Baczynskyj, M. F. Grostic, L. M. Humphrey, and R. J. Wnuk for mass spectral measurements and helpful discussions.

**Registry No.**—1, 41507-63-5; 4, 41507-64-6; 5, 41507-65-7; 6, 41507-66-8; 2-(4-biphenyloxy)-2-methylpropionyl chloride, 4878-10-8; diazomethane, 334-88-3; methyl 2-(4-biphenyloxy)-2-methylpropionate, 41507-68-0; 1-(4-biphenyloxy)-3-methyl-2-butanone, 41507-69-1.

### Dehydrobromination by *N*-Phenylbenzamidinium

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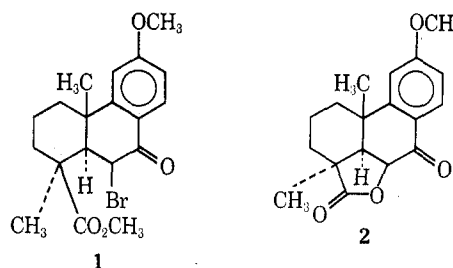
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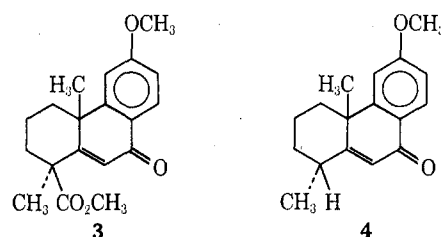
In connection with the synthesis of diterpenoid intermediates an improved yield of lactone 2 from bromo

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ketone 1 was required. The transformation of bromo ketone 1 to a mixture of lactone 2 (47% yield) and ester 3 (40% yield) by refluxing in collidine has been previously reported<sup>2</sup> along with the observation that treatment of bromo ketone 1 with sodium methoxide yields only elimination product 3. The suggestion was offered that a major factor in the contrasting behavior of sodium methoxide and collidine might be the steric requirements of the bases for proton abstraction.<sup>2</sup> Thus we initiated an investigation into the improvement of the yield of lactone 2 by utilizing a variety of bases<sup>3,4</sup> that have greater steric requirements than collidine. As a result of this study, we now wish to report that the base *N*-phenylbenzamidinium is useful for inducement of dehydrobromination.



Reaction of bromo ketone 1 with 3.5 equiv of *N*-phenylbenzamidinium in 25 equiv of *o*-xylene at reflux (148°) for 3 hr gave product 3 in 91% yield in the form of a white, crystalline solid, mp 175–177°. The infrared spectrum showed absorptions at 1725, 1645, 1600, and 1575  $cm^{-1}$  for the ester,  $\alpha,\beta$ -unsaturated ketone, and aromatic functional groups. The nmr spectrum exhibited resonance signals for singlets at  $\delta$  1.56 and 1.76 for the two tertiary methyl groups, singlets at  $\delta$  4.33 and 4.58 for the two methoxy groups, a singlet at  $\delta$  7.71 for the vinylic proton, a multiplet at  $\delta$  8.15 for the C-13 and C-14 protons, and a doublet ( $J = 8$  Hz) at  $\delta$  9.58 for the C-11 proton. Neither lactone 2 nor decarboxymethoxylation product 4 were found in the reaction mixture.



The same reaction could be effected in approximately the same yield under milder conditions. Reaction of bromo ketone 1 with 3.5 equiv of *N*-phenylbenzamidinium in 35 equiv of benzene at reflux (83°) for 48 hr gave product 3 in 90.5% yield.

Significantly, *N*-phenylbenzamidinium gives much higher yields of 3 than the stronger base sodium methoxide<sup>2</sup> and without the concomitant *O*-alkyl cleavage

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(3) D. H. Miles and E. J. Parish, *Tetrahedron Lett.*, 3987 (1972).

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reported<sup>3,4</sup> for dehydrohalogenating agents<sup>5-9</sup> 1,5-diazabicyclo[5.4.0]undecene-5 (DBU) and 1,5-diazabicyclo[4.3.0]nonene-5 (DBN).

The generality of the dehydrobrominating reagent is demonstrated by the application of *N*-phenylbenzamidine to the two bromides 1-bromoheptane and bromocyclohexane. A mixture of 3.5 equiv of *N*-phenylbenzamidine and 1 equiv of the appropriate bromide was dissolved in 25 equiv of *o*-xylene and refluxed (148°) for 8 hr. The resulting olefins were obtained in 98% yield by glc analysis and were identical by ir, nmr, and glc comparison with authentic samples.

Attempts to bring about dehydrochlorination with *N*-phenylbenzamidine gave poor yields of products. Thus *N*-phenylbenzamidine is a relatively mild and selective dehydrobrominating agent.

### Experimental Section

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained using a Jeolco minimar spectrometer. Tetramethylsilane was used as an internal standard. Infrared spectra were obtained using a Perkin-Elmer Model 137 G spectrophotometer. Gas-liquid chromatography (glc) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. A glass column (6 ft × 0.25 in. o.d.) bent in a U shape and packed with 3% SE-30 on 100/120 mesh GCQ at a column temperature of 270 or 60° with a helium flow rate of 90 ml/min was used for all glc analyses.

**Dehydrobromination of Bromo Ketone 1 in *o*-Xylene.**—Bromo ketone 1 (250 mg, 0.63 mmol) was added to a solution of *N*-phenylbenzamidine (412 mg, 2.22 mmol) and 1.87 ml of *o*-xylene. The reaction solution was refluxed (148°) for 3 hr. The ether extract of the acidified (5% HCl) reaction mixture was washed with 5% aqueous sodium carbonate and water, dried over anhydrous sulfate, and evaporated *in vacuo*. Crystallization of the residue from aqueous methanol solution yielded 181 mg (91%) of the crystalline solid **3**: mp 175–177° (lit.<sup>2</sup> mp 173–175°);  $\lambda_{\text{max}}^{\text{KB}} 1725, 1645, 1600, 1575 \text{ cm}^{-1}$ ;  $\delta$  nmr (CHCl<sub>3</sub>) 1.56 (3 H), 1.76 (3 H), 4.33 (3 H), 4.58 (3 H), 7.71 (1 H), 8.15 (2 H, multiplet), 9.58 (1 H, d, *J* = 8 Hz). *Anal.* Calcd for C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>: C, 72.50; H, 7.01. Found: C, 72.86; H, 7.14.

**Dehydrobromination of Bromo Ketone 1 in Benzene.**—Bromo ketone 1 (250 mg, 0.63 mmol) was added to a solution of *N*-phenylbenzamidine (412 mg, 2.22 mmol) and 2.05 ml of benzene which was refluxed (83°) for 48 hr. Following work-up in the manner described above, crystallization from aqueous methanol yielded 180 mg (90.5%) of the crystalline solid **3**, mp 175–177°.

**General Procedure for Dehydrobromination.** 1-Bromoheptane and Bromocyclohexane.—A mixture of *N*-phenylbenzamidine (996 mg, 5.37 mmol) and 1.53 mmol of the appropriate bromide was dissolved in 4.58 ml of *o*-xylene and refluxed at 148° for 8 hr. The usual work-up of the ether extract of the acidified reaction mixture yielded the corresponding olefin (98% glc) which was identical by ir, nmr, and glc comparison with authentic samples.

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**Registry No.**—1, 37931-64-9; **3**, 37931-65-0; *N*-phenylbenzamidine, 1527-91-9.

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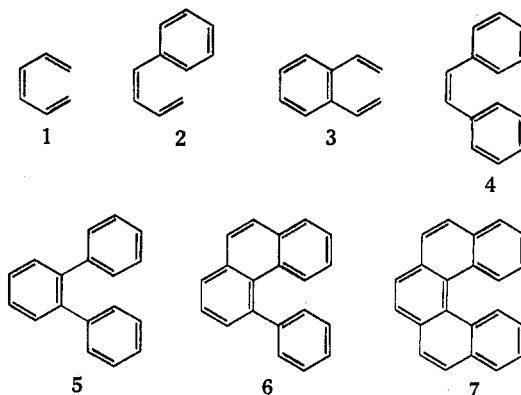
## The Photochemistry of 2-Vinylbiphenyl and 4-Vinylphenanthrene<sup>1</sup>

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The photochemistry of hexatriene (1) and the related compounds, 1-phenyl-1,3-butadiene (2), 1,2-divinylbenzene (3), stilbene (4), *o*-terphenyl (5), 4-phenylphenanthrene (6), and dibenzo[*c,g*]phenanthrene (7),



whose structures may be considered as possessing a disguised hexatriene system, have been investigated.<sup>2</sup> In these compounds the hexatriene system gradually loses its separate identity by successive fusion of benzene rings. We now wish to report some observations on the photochemistry of the other two members of this series: 2-vinylbiphenyl (**8**) and 4-vinylphenanthrene (**12**).

The relative ease of photocyclization of hexatriene analogs has been related to the sum of the free-valence indices in the first excited state,  $\Sigma F^*$ , at the two positions which become bonded during the cyclization.<sup>3,4</sup> Generally, photocyclization is only observed if  $\Sigma F^* > 1.0$ . The photocyclization of both **8** and **12** at the two positions indicated as a and b should be very favorable since  $\Sigma F^*$  is 1.63 and 1.48 for **8** and **12**, respectively. These values are calculated for planar molecules in the usual way and are based on the HMO approximation.

Irradiation of a benzene solution of **8** for 1 hr, in the presence of atmospheric oxygen (aerobic irradiation), gave complete conversion to 9,10-dihydrophenanthrene (**10**); there was no evidence of the formation of phen-

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