through Celite, $NaBH_4$ (200 mg) was added little by little to the filtrate with stirring at room temperature, and the mixture was stirred for a further 1 h at the same temperature. The solvent was distilled off and the residue was dissolved in $CHCl_3$. The solution was washed with water, dried (Na_2SO_4), and evaporated to give a pale yellowish solid which was subjected to PLC. The major band was then extracted with CH_2Cl_2 and the extracts were evaporated to dryness (26 mg, 70%). The resulting solid residue (mp 133-134 °C) was found to be identical with an authentic sample of (±)-corydaline (mp 133-134 °C; lit.[19] mp 135 °C).

Attempted Phenylation of Isatin 1c.[10] A refluxing dioxane solution of "istin" **1c** (100 mg, 0.25 mmol) was treated with in situ generated benzyne **2a** as described in method A. Usual workup yielded 90 mg of starting material.

Preparation of Anthranilic Acid 6d[18] from 3,4-Dimethoxyaniline. To a solution of 4.34 g (28.4 mmol) of 3,4-dimethoxyaniline in 120 mL of dry THF was added 6.8 g (31.2 mmol) of di-*tert*-butyl pyrocarbonate all at once. The resulting solution was refluxed for 2 h. After cooling, the solvent was stripped off and the solid residue crystallized from hexane (5.05 g, 74% yield) as colorless needles: mp 87-89 °C; IR (KBr) 3350, 1700 cm^{-1}; UV (EtOH) λ_{max} 240 (log ϵ 4.18), 284 (3.63); ^1H NMR ($CDCl_3$) δ 7.15 (d, 1 H, J = 1.3 Hz), 6.75 (br s, 2 H), 3.87 (s, 3 H), 3.84 (s, 3 H), 1.51 (s, 9 H); mass spectrum, m/e 253 (relative intensity) (17, M^+), 197 (61), 57 (100).

The previous *tert*-butyl carbamate (2 g, 8.2 mmol) dissolved in dry THF (20 mL) at 0 °C was treated with 11.2 mL (20.1 mmol) of a 1.81 M solution of *tert*-butyllithium at -78 °C. Stirring at -78 °C was continued for 15 min and then for 2 h at -20 °C. The resulting yellow solution was transferred via canula, under an argon atmosphere, to a slurry of CO_2 (excess) in THF (75 mL) cooled at -78 °C. The mixture was then stirred while slowly reaching room temperature, and 2 h further at this temperature. Ether (150 mL) was added and the solution washed with 5% aqueous $NaHCO_3$ 3 times. The basic aqueous solution was then acidified with citric acid and extracted with ether. Once washed with water and dried (anhydrous Na_2SO_4), the ethereal solution was evaporated to dryness leaving a crude solid (2.2 g, 95% yield) mixture of protected anthranilics acids which was subjected to final deprotection without further purification. This was achieved by treating a THF solution of the above mixture with concentrated HCl (40 mL) at room temperature overnight. Careful basification (10% NaOH) to neutrality was followed by extraction subjected to open column chromatography (silica gel, CH_2Cl_2). Pure anthranilic acid **6d** was eluted first and obtained (61%) as crystalline material from ethanol, mp 98-99 °C (lit.[18] mp 98.8-100 °C). Spectroscopic data are identical with that described.[18]

Registry No. **1a**, 102421-38-5; **1b**, 102421-39-6; **3a**, 64938-92-7; **3b**, 102421-40-9; **4a**, 15495-36-0; **4b**, 102421-41-0; **4c**, 58471-28-6; **4d**, 102421-42-1; **6a**, 118-92-3; **6b**, 53600-33-2; **6c**, 5701-87-1; **6d**, 5653-51-0; ClC(O)C(O)Cl, 79-37-8; 1-methyl-3,4-dihydroisoquinoline, 2412-58-0; 1-ethyl-3,4-dihydroisoquinoline, 41173-70-0; (±)-corydaline, 6018-35-5; 3,4-dimethoxyaniline, 6315-89-5; *N*-(*tert*-butoxycarbonyl)-3,4-dimethyoxybenzenamine, 102421-43-2; benzenediazonium-2-carboxylate, 1608-42-0.

2,7-Diphenyloxepin

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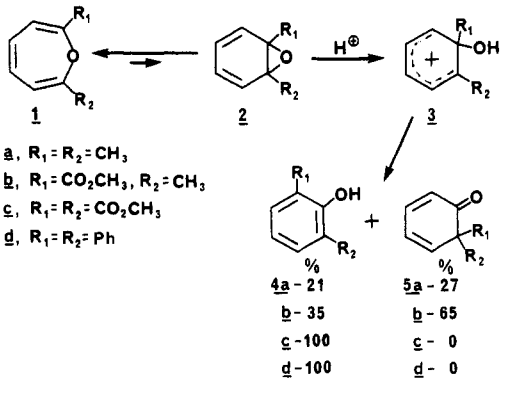
A synthesis of 2,7-diphenyloxepin (**1d**) is described. Acid-catalyzed isomerization of **1d** gives 2,6-diphenylphenol (**4d**) in quantitative yield. X-ray crystal structure analysis indicates that oxepin **1d** exists in a boat conformation in the solid state.

Oxepin valence tautomer **1** is more stable than oxide valence tautomer **2** in 1,2-disubstituted arene 1,2-oxides.[1] With few exceptions sufficient **2** is present in solution to observe acid-catalyzed isomerization via the NIH shift pathway, which involves migration of R_1 of cation **3** to either adjacent carbon atom with ultimate formation of **4** and/or **5** (Scheme I). Although the factors that determine the direction of substituent migration are not fully understood, the product ratios (**4**/**5**) from acid-catalyzed isomerization of 1,2-disubstituted arene 1,2-oxides such as **2a**,[2,3] **2b**,[4] and **2c**[4] support the expectation that substituent migration to the adjacent carbon atom with the higher

Scheme I

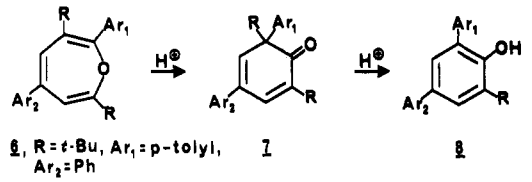


degree of carbonium ion character ought to be the favored pathway. Under appropriate reaction conditions, further isomerization of **5b** (migration of CO_2CH_3) to a 2,3-disubstituted phenol is observed.[4] The acid-catalyzed isomerization of **1a** affords 2,3-dimethylphenol (2%) and

(1) For a recent review of arene oxides-oxepines, see: Boyd, D. R.; Jerina, D. M. In *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley-Interscience: New York, 1984; Part 3, Vol. 42, pp 197-282.
(2) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385-401.
(3) Kaubisch, N.; Daly, J. W.; Jerina, D. W. *Biochemistry* **1972**, *11*, 3080-3088.
(4) Boyd, D. R.; Berchtold, G. A. *J. Am. Chem. Soc.* **1979**, *101*, 2470-2474.

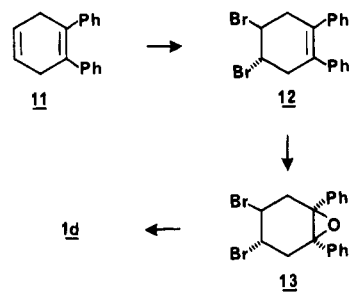
0022-3263/86/1951-2784$01.50/0

Scheme II



6, R = t-Bu, Ar1 = p-tolyl, Ar2 = Ph 7 8

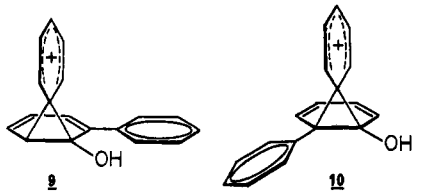
Scheme III



3,4-dimethylphenol in addition to **4a** and **5a**.[2,3]

Rieker and co-workers have shown that 3,7-di-*tert*-butyl-2,5-diaryloxepins such as **6** (Scheme II) undergo acid-catalyzed aromatization by aryl migration to dienone **7** and subsequent loss of isobutylene to afford **8**.[2,3] Previous studies on the related acid-catalyzed rearrangement of 4,4-disubstituted cyclohexadienones[5] have indicated that the phenyl group has a greater migratory aptitude than either a methyl or a carboalkoxy group.

The acid-catalyzed isomerization of 2,7-diphenyloxepin (**1d**) was of interest to establish the effect of the phenyl substituent (R_2 of cation **3d**) on the direction of phenyl (R_1) migration by the NIH shift pathway. The expected phenonium ion intermediate for **3d** → **4d** is **9** and that for **3d** → **5d** is **10**. It is not possible to predict the favored pathway of phenyl migration on the basis of electronic and steric factors.



Described below are the synthesis, acid-catalyzed isomerization, and x-ray structure data of **1d**.

The synthesis of **1d** is outlined in Scheme III. Bromination of 1,2-diphenyl-1,4-cyclohexadiene (**11**)[7] gave only regioisomer **12**. Oxidation of **12** with 3,5-dinitroperbenzoic acid (3,5-DNPBA)[8] in CH_2Cl_2 gave **13** in 52% yield after recrystallization. Base-catalyzed elimination of HBr from **13** with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in tetrahydrofuran (THF) at 0 °C afforded **1d** in 72% yield as a stable, yellow-orange crystalline substance.

The time required for complete isomerization of **1d** varied dramatically with the acidity of the reaction medium: 1:20 trifluoroacetic acid (TFA)–CH_2Cl_2, 10–15 min; 1:1 THF–H_2O (pH 0), 148 h; 1:1 THF–H_2O (pH 1.1), 60 days. No reaction of **1d** was observed over a period of 6 months in 1:1 THF–H_2O (pH 7). The sole product from

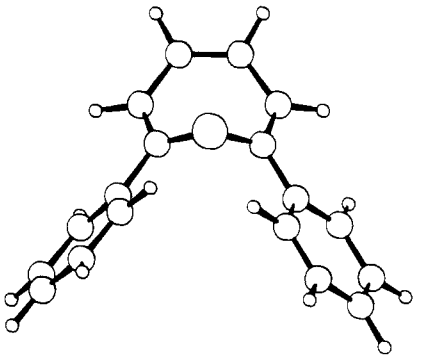


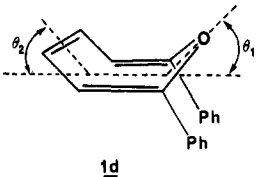
Figure 1. End view of **1d**.

acid-catalyzed isomerization of **1d** was 2,6-diphenylphenol (**4d**) which was characterized by comparison with an authentic sample (see Experimental Section). Dienone **5d** was not observed as a reaction product. In view of the considerable migratory aptitude of the phenyl ring[5] it was expected that **5d** would readily undergo further acid-catalyzed isomerization to 2,3-diphenylphenol (**14**), and thus a sample of **14** was prepared. Comparison of the ^1H NMR and ^{13}C NMR spectra of the crude isomerization product from **1d** with the corresponding spectra of **4d** and **14** established the complete absence of **14**. These observations confirm that the isomerization of **1d** occurs only by NIH shift of the phenyl group via phenonium ion **9**. Involvement of phenonium ion **9** provides an unusual example of isomerization of an arene oxide to a norcaradiene intermediate.

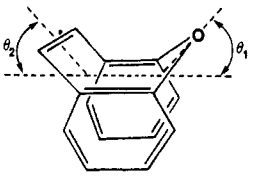
In view of the remarkable stability of oxepin **1d** and its availability in suitable crystalline form, an X-ray crystallographic analysis was carried out (see Experimental Section).

The asymmetric unit contains two independent molecules, each of which adopts a boat conformation with no significant differences in dihedral angles for molecule 1 and molecule 2 (θ_1 = 61.2° and 60.9°, θ_2 = 24.8° and 24.4°, respectively). The molecular structure is shown in Figure 1.

These conformations for the oxepin rings may be compared with those from (i) the only previous X-ray analysis of a monocyclic oxepin, namely the asymmetric tetrasubstituted oxepin **6**[9] (θ_1 = 62.4°, θ_2 = 29.3°) and (ii) the symmetric tricyclic dibenz[*b*,*f*]oxepin **15**[10] (θ_1 = 57°, θ_2 = 24°). These latter values suggest a more "shallow" boat accompanying the higher degree of conjugation in **15**.



1d



15

Regarding the orientation of the phenyl groups in **1d**, molecular mechanics calculations predict a preferred conformation, on steric grounds, in which each phenyl ring would be almost perpendicular to the adjacent O—C=C plane. Conjugation on the other hand, would favor coplanarity. In fact bond lengths in **1d** show little evidence of conjugation and therefore the actual orientations of the phenyl groups (twisted by +22.7° and −26.7° for molecule

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1, +33.0° and −18.9° for molecule 2, with respect to the adjacent C=C bond of the oxepin ring) seem likely to be determined predominantly by crystal packing forces.

Experimental Section[11]

1,2-Diphenyl-*trans*-4,5-dibromocyclohexene (12). A solution of 11 (6.57 g, 28.3 mmol) in $CH_2Cl_2/CHCl_3$ (1:1, 150 mL) was cooled to −78 °C under N_2. Bromine (4.52 g, 28.3 mmol) dissolved in $CH_2Cl_2/CHCl_3$ (1:1, 50 mL) was added dropwise over 30 min to the solution of diene. After the addition was complete the solution was allowed to warm to room temperature. The solution was washed with one 100-mL portion of 10% aqueous Na_2SO_3, three 100-mL portions of saturated aqueous NaCl solution, and dried ($MgSO_4$). Evaporation of solvent under reduced pressure gave 11.09 g (100%) of **12** as a yellow-brown oil. Preparative TLC (silica gel, 9:1 *n*-hexane–ethyl acetate) provided an analytical sample as a colorless oil: IR (CCl_4) 1600, 1495, 1450, 1420, 1220, 760, 700 cm^{-1}; UV (hexane) λ_{max} 256 nm (ϵ 8500); ^1H NMR δ 6.9–7.2 (10 H, m), 4.69–4.72 (2 H, m), 3.57–3.65 (2 H, dm, J = 17.2 Hz), 2.99–3.07 (2 H, dm, J = 17.2 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 141.6, 130.2, 128.9, 127.9, 126.4, 48.9, 37.6; MS, m/z 394 (12), 392 (24), 390 (13), 231 (58), 230 (100), 229 (72), 228 (49). Exact mass calcd for $C_{18}H_{16}{}^{79}Br_2$, $C_{18}H_{16}{}^{79}Br^{81}Br$, $C_{18}H_{16}{}^{81}Br_2$: 389.9618, 391.9598, 393.9578. Found: 389.9623, 391.9596, 393.9575.

1,6-Diphenyl-*trans*-3,4-dibromo-7-oxabicyclo[4.1.0]heptane (13). A solution of **12** (11.0 g, 28.3 mmol) in CH_2Cl_2 (125 mL) was cooled to 0 °C, and a solution of 3,5-DNPBA[8] (6.80 g, 28.3 mmol) in CH_2Cl_2 (250 mL) was added dropwise over 30 min. After the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 2 h. The solution was washed with two 200-mL portions of 10% aqueous Na_2SO_3 solution, three 200-mL portions of saturated aqueous $NaHCO_3$ solution, and three 200-mL portions of saturated aqueous NaCl and dried (K_2CO_3). Solvent was removed under reduced pressure to afford 10.4 g (90%) of **13** as a thick brown mass. Two crystallizations from ethyl ether provided 6.0 g (52%) of **13** as off-white prisms: mp 106.0–106.5 °C; IR (CCl_4) 1600, 1550, 1500, 1450, 1420 cm^{-1}; UV (hexane) λ_{max} 201 (ϵ 22 600), 245 (440), 253 (465) 258 (485), 263 nm (345); ^1H NMR (60 MHz, $CDCl_3$) δ 6.9–7.4 (10 H, m), 4.5–4.9 (2 H, m), 3.1–3.6 (2 H, dm, J = 18 Hz), 2.6–3.0 (2 H, dm, J = 18 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 138.9, 138.4, 127.9, 127.4, 127.3, 126.7, 67.1, 66.1, 49.8, 44.6, 39.2, 38.2; MS, m/z 410 (0.06), 408 (0.13), 406 (0.07), 105 (100), 77 (59).

2,7-Diphenyloxepin (1d). A solution of **13** (5.50 g, 13.5 mmol) in anhydrous THF (110 mL) was cooled to 0 °C under N_2, and DBN (5.02 g 40.4 mmol) was added by syringe over 15 min. The mixture was allowed to warm to room temperature over 4.5 h. The mixture was diluted with ether and filtered to remove DBN salts. The ether solution was washed with four 200-mL portions of aqueous phosphate buffer (pH 7.0) and three 200-mL portions of saturated aqueous NaCl solution and dried (K_2CO_3). Evaporation of solvent under reduced pressure gave 2.37 g (72%) of **1d** as orange-yellow crystals. Four recrystallizations from *n*-hexane gave **1d** with a constant melting point: mp 100.5–101.0 °C; IR (CCl_4) 1630, 1600, 1570, 1540, 1490, 1450 cm^{-1}; UV (hexane) λ_{max} 253 (ϵ 17 100), 259 (25 500), 266 (30 900), 358 (5440), (C_2H_5OH) 205 (29 900), 263 (35 500), 352 nm (6650); ^1H NMR δ 7.69 (4 H, dd, J = 8.3, 2.0 Hz), 7.2–7.3 (6 H, m), 6.4 (2 H, m), 6.3 (2 H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 150.7, 135.1, 128.9, 128.6, 128.1, 126.3, 113.5; MS, m/z 247 (3), 246 (15), 144 (16), 115 (28), 105 (100), 104 (15), 77 (74), 76 (16). Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.85; H, 5.76.

Isomerization of 1d. Method A. To a solution of **1d** (9.80 mg) in $CDCl_3$ (0.5 mL) was added TFA (0.025 mL). The reaction was followed by ^1H NMR and was complete after 10–15 min at room temperature. Solvent was removed under high vacuum. Purification by recrystallization from *n*-hexane or by preparative TLC (silica gel, 9:1 *n*-hexane–ethyl acetate) gave pure **4d**.

Method B. Oxepin **1d** (10 mg) was dissolved in 1:1 THF–H_2O in which the pH of the aqueous portion was 0.0 (HCl), 1.1 (HCl), or 7.0 (phosphate buffer), and the solution was kept at room temperature. When the isomerization was complete (pH 0.0, 148 h; pH 1.1, 60 days; pH 7.0, no reaction after 6 months), the mixture was diluted with ether. The aqueous layer was extracted with ether, and the combined ether extracts were washed three times with saturated, aqueous NaCl solution and dried ($MgSO_4$). Solvent was removed under reduced pressure, and the resulting solid was purified as described in method A.

All acid-catalyzed isomerizations resulted in quantitative conversion to **4d**: mp 101.0–101.5 °C (lit.[12] mp 101 °C), a mixture mp with authentic **4d** was not depressed; the IR, UV, ^1H NMR, ^{13}C NMR, and mass spectra were identical with those of authentic **4d**.

2,6-Diphenylphenol (4d). A solution of Br_2 (1.96 g, 12.3 mmol) in CCl_4 (20 mL) was added dropwise over 30 min to a solution of *cis*-2,6-diphenylcyclohexanone[13] (1.50 g, 6.00 mmol) and PBr_3 (3 drops) in CCl_4 (30 mL) at room temperature. After the addition was complete, the reaction mixture was stirred for 1.5 h. The mixture was washed with two 50-mL portions of 10% aqueous Na_2SO_3 solution, 50 mL of saturated, aqueous $NaHCO_3$ solution, and two 50-mL portions of saturated, aqueous NaCl solution and dried ($MgSO_4$). Solvent was removed under reduced pressure to give 2.46 g of dibromide as a colorless oil. The dibromide was dissolved in anhydrous THF (50 mL), and the solution was cooled to 0 °C under N_2. DBN (2.23 g, 18.0 mmol) was added dropwise over 3 min. The mixture was warmed to room temperature over 2 h, during which time a heavy precipitate formed. The mixture was diluted with 1 N HCl (25 mL) and extracted with five 50-mL portions of ether. The combined ether extracts were washed with three 50-mL portions of saturated, aqueous NaCl solution and dried ($MgSO_4$). Removal of solvent under reduced pressure gave an oil that solidified under high vacuum. Two recrystallizations from *n*-hexane gave 589 mg (40%) of **4d**: mp 101.0–101.5 °C; IR (CCl_4) 3550, 1600, 1550, 1500, 1470, 1460, 1420 cm^{-1}; UV (C_2H_5OH) λ_{max} 206 (ϵ 38 100), 237 (26 300), 294 nm (5100); ^1H NMR δ 7.6–7.0 (13 H, m), 4.50 (1 H, s); ^{13}C NMR (76.9 MHz, $CDCl_3$) δ 149.2, 137.5, 129.8, 129.2, 128.7, 127.5, 120.6; MS, m/z (relative intensity) 247 (19), 246 (100), 245 (23), 215 (24), 202 (27), 139 (15), 115 (29).

2,3-Diphenylphenol (14). A mixture of *trans*-5,6-diphenylcyclohex-2-en-1-one[14] (176 mg, 0.707 mmol), *N*-bromosuccinimide (126 mg, 0.707 mmol), and AIBN (5 mg) in CCl_4 (5 mL) was heated under reflux for 23 h. The reaction was cooled, and succinimide was removed by filtration. The filtrate was washed with two 25-mL portions of 10% aqueous Na_2SO_3 solution, two 25-mL portions of saturated, aqueous $NaHCO_3$ solution, and two 25-mL portions of saturated, aqueous NaCl solution and dried ($MgSO_4$). Solvent was removed under reduced pressure to give 223 mg of bromides as a yellow oil. The bromide mixture was dissolved in benzene and DBN (212 mg, 1.71 mmol) was added dropwise over 10 min. The mixture was stirred at room temperature for 19 h and at reflux for 1 h. The mixture was washed with three 50-mL portions of 1 N HCl and two 50-mL portions of saturated, aqueous NaCl solution and dried ($MgSO_4$). Evaporation of solvent gave an oil that solidified on standing. Two recrystallizations from *n*-hexane gave 126 mg (72%) of **14**: mp 102.0–102.5 °C (lit.[14] mp 99.0–99.5, 101.5–102.0 °C); ^1H NMR (270 MHz, $CDCl_3$) δ 7.36–7.00 (13 H, m), 5.13 (1 H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 153.0, 141.1, 135.0, 131.0, 129.6, 129.0, 128.8, 127.8, 127.6, 126.4, 122.4, 114.5.

X-ray Data for 1d: $C_{18}H_{14}O$, M_r 246.3, monoclinic, a = 11.656 (5) Å, b = 13.694 (9) Å, c = 17.025 (2) Å, β = 100.8 (1)°, U = 2669 Å^3, D_c = 1.23 g cm^{-3}, space group $P2_1/n$, λ(Mo Kα) = 0.71069 Å, μ = 0.4 cm^{-1}, Z = 8, F(000) = 1040.

The lattice was characterized by preliminary photographic analysis and showed the asymmetric unit to contain two independent molecules. A crystal of dimensions 0.54 × 0.42 × 0.31 mm was mounted with the unique axis (b) coincident with the rotation axis (ω) of a Stoe STADI-2 two-circle diffractometer. Using monochromated Mo Kα radiation and the background–ω

(11) High-resolution mass spectra were provided by the facility supported by National Institutes of Health Grant RR00317 (principal investigator Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Unless otherwise indicated, ^1H NMR spectra were obtained in $CDCl_3$ at 250 or 270 MHz.

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scan–background technique, 2158 unique intensity data were recorded within the range $0 \leq 2\theta \leq 50°$. The 1784 reflections with $I \geq 3\sigma(I)$ were considered to be observed and were used in the subsequent analysis and refinement after correction for Lorentz and polarization effects. The structure was solved by the direct methods of MULTAN-80[15] and was refined by least squares with SHELX-76.[16] Hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H = 1.08 Å) with a common isotropic thermal parameter which refined to a final value of $U = 0.099$ (4) Å^2. Full-matrix refinement with anisotropic thermal parameters for non-hydrogen atoms yielded a final conventional R value of 0.056, with $R_w = 0.072$. The weighting scheme adopted was

$$W = 1.00/(\sigma^2(F_o) + 0.037155(F_o)^2).$$

A final difference Fourier synthesis showed no peak >0.1 eÅ^{-3} (see supplementary material).

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM 26388) for financial support.

Registry No. **1d**, 102342-18-7; **4d**, 2432-11-3; **11**, 17351-29-0; **12**, 102367-83-9; **13**, 102342-19-8; **14**, 93654-94-5; *cis*-2,6-diphenylcyclohexanone, 20834-02-0; *trans*-5,6-diphenylcyclohex-2-en-1-one, 70238-90-3.

Supplementary Material Available: Lists of atomic coordinates, thermal parameters, bond distances and angles, and torsion angles for **1d** (8 pages). Ordering information is given on any current masthead page.

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Reactions of Uracils. 10.[1,2] Novel Michael Adducts of Uracils and New Synthesis of Imidazo[5,1-*f*][1,2,4]triazines

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Upon treatment with ethyl propiolate (**2a**), cyanoacetylene (**2b**), and tetracyanoethylene (**5**) the 6-[(triphenylphosphoranylidene)amino]uracil **1** undergoes Michael addition to afford the 5-adducts **4a,b** and **8**. However, with diethyl azodicarboxylate Michael attack and then heterocyclic transformation occur to give the 6-(diaminomethylene)-1,2,4-triazine-1,2-dicarboxylate **11**, which can be cyclocondensed to the imidazo[5,1-*f*][1,2,4]triazine **12**.

Recently, a novel heterocyclic transformation reaction has been described involving an addition–rearrangement sequence of 6-aminouracils with acetylenedicarboxylates leading to zwitterionic amidinium–pyridinedionates and pyrrolo[3,4-*c*]pyridines.[4]

In continuation of this work we now have studied the reaction of further potential Michael addition[5] partners on 1,3-dimethyl-2,4-dioxo-6-[(triphenylphosphoranylidene)amino]pyrimidine (**1**). From these ethyl propiolate (**2a**), cyanoacetylene (**2b**),[6] and tetracyanoethylene (**5**) give only the Michael adducts **4a,b** and **7**[4,5] as the intermediary carbanion resulting from Michael attack is so basic that prototropy occurs more rapidly than nucleophilic attack at carbon 2; thus, no further transformation step[4] could be observed. From these intermediates **7** stabilizes spontaneously by evolution of HCN to give **8** (Scheme I).[14]

However, diethyl azodicarboxylate shows a behavior similar to the dialkyl acetylenedicarboxylates:[4] instead of forming a final Michael product by prototropy, the terminal basic nitrogen atom attacks the 2-carbonyl group of the uracil moiety. As a consequence, heterocyclic transformation occurs; intermediate **10** stabilizes to 6-[(*N*-methylamino)-(*N*-(triphenylphosphoranylidene)-amino)methylene]-3,5-dioxo-1,2,4-triazine-1,2-dicarboxylate **11**.

Unprotected 6-amino- and 6-hydrazinopyrimidines have been shown by Taylor and Sowinski[7] to react with diethyl azodicarboxylate in refluxing chlorobenzene at 150–160 °C to give the Michael adducts, namely, 5-(1,2-dicarbethoxyhydrazino) derivatives, in a way assumed, such as **13**.[7] However, in the present case, protective and steric effects of the iminophosphorane group in **1** disfavor an arrangement like **13**. Furthermore, the extension of the enaminocarbonyl resonance in **1** by the iminophosphorane rest and the high polarity of the solvent (MeCN)[8] stabilize

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