of benzyl alcohols were analyzed by VPC, using a 3-mm i.d. glass column (1.8 m) containing 0.1% FFAP on carbon-coated beads with nitrogen as the carrier gas at 110 °C.

**Acknowledgment.** We are grateful to the Consiglio Nazionale delle Ricerche, C.N.R., for financial support. We also thank Professor Lennart Eberson for making available material to us prior to publication.

**Registry No.** 1, 536-50-5; 2, 768-59-2; 3, 4170-90-5; 4, 50849-01-9; 5, 39126-11-9; *p*-methylacetophenone, 122-00-9; *p*-bromoethylbenzene, 1585-07-5; *p*-ethylbenzoic acid, 586-76-5; $Co(OAc)_3$, 917-69-1; $Mn(OAc)_3$, 993-02-2; $(NH_4)_2Ce(NO_3)_6$, 16774-21-3.

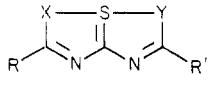
## Reactivity and Synthesis of the 1,6-Dioxa-6a$\lambda^4$-thia-3,4-diazapentalene System[1]

John O. Gardner

*Syntex Research, Palo Alto, California 94304*

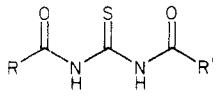
*Received March 13, 1980*

Recent reports[2,3] of the preparation of 2,5-diaryl-1,6-dioxa-6a$\lambda^4$-thia-3,4-diazapentalenes by aroylation of 5-amino-1,2,3,4-thiatriazole have made this interesting heteropentalene system readily available for study. In addition, the authors point out that compounds such as 1 may be converted into di- and trithia derivatives 2 and 3 by treatment with phosphorus pentasulfide.



| | R | R′ | X | Y |
|---|---|---|---|---|
| 1 | Ph | Ph | O | O |
| 2 | Ph | Ph | S | O |
| 3 | Ph | Ph | S | S |
| 4 | $CH_3$ | $CH_3$ | O | O |
| 5 | Ph | $CH_3$ | O | O |

We recently had occasion to react 1 with $P_2S_5$ in dioxane, hoping to obtain 2 as the major product. For this reason, the reaction was done at ca. 90 °C rather than at reflux. A mixture of 2 and 3 plus an unexpected third product which proved to be 1,3-dibenzoylthiourea (6) was produced. Indeed when the reaction was done at 70 °C, 6 was the sole product, isolated in 91% yield.



| | R | R′ |
|---|---|---|
| 6 | Ph | Ph |
| 7 | $CH_3$ | $CH_3$ |
| 8 | Ph | $CH_3$ |

The mechanism of this reduction is not clear but apparently is not due to small amounts of hydrogen sulfide associated with the $P_2S_5$ since bubbling $H_2S$ through a dioxane solution of 1, with and without added sulfur, at temperatures from 50 °C to reflux gave no reaction. Further, attempts to effect the reduction with sodium borohydride gave complex mixtures with only traces of 6. There are reports of phosphorus pentasulfide acting as a reducing agent to convert sulfoxides[4] and sulfilimines[5] to the corresponding sulfides. These authors propose a four-centered mechanism to transfer the sulfoxide oxygen to phosphorus with formation of $P_4O_4S_6$, the sulfide, and elemental sulfur, possibly via the thiosulfoxide. A completely analogous mechanism is obviously not operating in the present example since the transfer of a heteratom is not involved. However, it is likely that elemental sulfur is produced during the reaction along with a phosphorus sulfide containing a reduced percentage of sulfur. No attempt has been made to isolate or identify these by-products.

Since the formation and reduction of 1 can be done very easily and in high yield, this sequence represents a useful synthesis of symmetrical 1,3-diaroylthioureas. It is interesting to note that 1,3-dibenzoyl-2-thiourea has not been previously reported.

The reduction of 1 to 6 suggested the reverse process, namely, an oxidation, as a synthetic method to 1. This proved to be possible by using bromine as an oxidizing agent to instantly convert 6 into 1 in 73% yield. For the synthesis of symmetrical diaryl compounds such as 1, the reaction of aroyl chlorides with 5-amino-1,2,3,4-thiatriazoles is most convenient since the acid chlorides are more readily available than the thioureas. However, in the case of unsymmetrically substituted compounds, or those with alkyl substituents, the thiatriazole method is reported to fail.[2] 1,3-Diacetyl-[6] (7) and 1-acetyl-3-benzoyl-2-thioureas[7] (8) were smoothly converted into 4 and 5, respectively, by bromine oxidation to test the oxidative cyclization method in these instances. The oxidative cyclizations were carried out at room temperature by adding 1 equiv of bromine dropwise to a chloroform solution of the thiourea containing 2 equiv of triethylamine.

### Experimental Section

Melting points were determined in open capillaries and are uncorrected. NMR spectra were measured at 60 MHz in $CDCl_3$. Mass spectra were determined with a Varian-MAT $CH_4$ spectrometer. Percolations were done with Merck silica gel 60. Microanalyses were performed by the analytical department of Syntex Research. Anhydrous magnesium sulfate was used to dry all organic solutions.

**Reaction of 1 with $P_2S_5$ at 90 °C.** A mixture of 5 g (18 mmol) of 1[2,3] and 10 g (45 mmol) of $P_2S_5$ in 200 mL of dioxane was stirred under $N_2$ at 90 °C for 1 h. The reaction mixture was cooled and filtered, and the filtrate evaporated. The residue was passed through a pad of silica gel. Elution with 20% hexane/$CH_2Cl_2$ afforded an orange substance which crystallized from toluene to give 0.8 g (16%) of 3: mp 207.5–209.0 °C (lit.[3] mp 208–209 °C); mass spectrum, *m/e* 314 ($M^+$).

Elution with $CH_2Cl_2$ gave an essentially colorless material which crystallized from EtOH to yield 0.6 g (12%) of 2: mp 152–154 °C (lit.[3] mp 152–153 °C); mass spectrum, *m/e* 298 ($M^+$).

Elution with 1% MeOH/$CH_2Cl_2$ gave material which crystallized from EtOH to give 1 g (20%) of 6 as yellow needles: mp 166–169 °C; NMR $\delta$ 7.4–7.7 (3 H, m), 7.9–8.1 (2 H, m); mass spectrum, *m/e* 284 ($M^+$). Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85; S, 11.28. Found: C, 62.98; H, 4.32; N, 9.73; S, 11.15.

**Reaction of 1 with $P_2S_5$ at 70 °C.** A mixture of 0.5 g (1.8 mmol) of 1[2,3] in 20 mL of dioxane with 1 g (4.5 mmol) of $P_2S_5$ was stirred under $N_2$ in an oil bath at 70 °C for 1.5 h. The reaction mixture was cooled and filtered and the filtrate evaporated. The residue was passed through a pad of silica gel with $CH_2Cl_2$ and

(1) Contribution No. 559 from the Institute of Organic Chemistry, Syntex Research, Palo Alto, CA.
(2) R. J. S. Beer and I. Hart, *J. Chem. Soc., Chem. Commun.*, 143 (1977).
(3) G. L'abbé, G. Verhelst, and G. Vermeulen, *Angew. Chem., Int. Ed. Engl.*, 16, 403 (1977).
(4) I. W. J. Still, S. K. Hasan, and K. Turnbull, *Can. J. Chem.*, 56, 1423 (1978).
(5) I. W. J. Still and K. Turnbull, *Synthesis*, 540 (1978).
(6) E. F. Kohman, *J. Am. Chem. Soc.*, 37, 2130 (1915).
(7) A. E. Dixon and J. Taylor, *J. Chem. Soc.*, 117, 720 (1920).

0022-3263/80/1945-3909$01.00/0 

the product crystallized from EtOH to give 0.45 g (91%) of **6** identical with material described above.

**Oxidation of 6 to 2,5-Diphenyl-1,6-dioxa-6aλ⁴-thia-3,4-diazapentalene (1). General Method.** To a solution of 0.284 g (1 mmol) of **6** in 10 mL of $CHCl_3$ containing 0.3 mL (2 mmol) of triethylamine at room temperature was added dropwise 2 mL of a 0.5 N solution of $Br_2$ in $CHCl_3$. The $Br_2$ color immediately discharged, and after the addition was complete the solvent was removed and the residue partitioned between $H_2O$ and $CH_2Cl_2$. The organic layer was dried and passed through a pad of silica gel and the product crystallized from acetone to give 200 mg (73%) of **1**: mp 193.5–194.0 °C (lit. mp 195–197 °C,[3] 189–190 °C[2]); mass spectrum, *m/e* 282 ($M^+$).

**2,5-Dimethyl-1,6-dioxa-6aλ⁴-thia-3,4-diazapentalene (4).** In an analogous manner to the preparation of **1** from **6**, 1.6 g of **7**[6] gave 0.9 g (58%) of **4** crystallized from $CH_2Cl_2$/hexane. The material was difficult to crystallize, and TLC showed the liquors to contain essentially pure **4**: mp 57.5–59.5 °C; NMR δ 2.63 (s); mass spectrum, *m/e* 158 ($M^+$). Anal. Calcd for $C_5H_6N_2O_2S$: C, 37.97; H, 3.82; N, 17.71; S, 20.27. Found: C, 37.91; H, 3.86; N, 17.63; S, 19.92.

**2-Methyl-5-phenyl-1,6-dioxa-6aλ⁴-thia-3,4-diazapentalene (5).** In an analogous manner to the preparation of **1** from **6**, 0.22 g of **8**[7] gave 0.09 g (41%) of **5** crystallized from $Et_2O$/hexane: mp 102.5–103.5 °C; NMR δ 2.63 (3 H, s), 7.4–7.7 (3 H, m), 8.3–8.5 (2 H, m); mass spectrum, *m/e* 220 ($M^+$). Anal. Calcd for $C_{10}H_8N_2O_2S$: C, 54.53; H, 3.66; N, 12.72; S, 14.56. Found: C, 54.39; H, 3.33; N, 12.36; S, 14.11.

**Registry No.** **1**, 62302-08-3; **2**, 62337-60-4; **3**, 17280-68-1; **4**, 74346-71-7; **5**, 74346-72-8; **6**, 74346-73-9; **7**, 4984-27-4; **8**, 74346-74-0.

# Reactions of Polyarylated Carbinols. 6.[1a] Kinetics of the Thermal [1,5] Sigmatropic Phenyl and Para-Substituted-Phenyl Rearrangements in 3,4-Bis[*p*-substituted-phenyl]-1,2,5-triphenyl-2,4-cyclopentadien-1-ols and 1-[*p*-Substituted-phenyl]-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ols

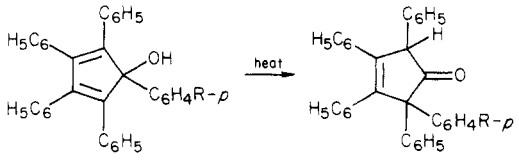
Guy B. Oldaker III, Thomas A. Perfetti, and Michael A. Ogliaruso*

*Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

*Received April 9, 1980*

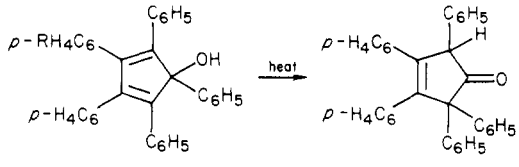
During our continuing research on 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol[1b] and its derivatives,[2] we became interested in using this system to establish the limits for electronic-effect involvement in its thermal [1,5] sigmatropic phenyl rearrangement. This interest stemmed from the meager data that has accompanied theoretical predictions of the electronic effects involved in neutral [1,5] sigmatropic phenyl rearrangements.[3] The pentaphenylcyclopentadienol system is particularly attractive for such a study because it is free from competing shifts of species with migratory aptitudes greater then phenyl;[3,4] thus, this system could be used to establish both the limits of electronic-effect involvement in [1,5] sigmatropic rearrangements and the applicability of using a mechanistic probe of the Hammett type[5] to establish such electronic-effect involvement. In addition, since the cyclopentadiene nucleus is substituted with phenyl groups at all five positions, the opportunity presents itself to probe both at the migration center and on the backbone of the migration framework. To date no investigation has been reported where electronic effects at the migration center of such a rearrangement have been responsive to a Hammett probe.

For these studies two series of compounds were synthesized: the 1-[*p*-substituted-phenyl]-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol series (**1**) and the 3,4-bis-[*p*-substituted-phenyl]-1,2,5-triphenyl-2,4-cyclopentadien-1-ol series (**2**). This paper discusses the results of the investigations of the kinetics of the thermal rearrangements for both these systems to ketones **3** and **4**, respectively.




**1** **3**

R = $OCH_3$, $C(CH_3)_3$, $CH_3$, H, $C_6H_5$, Cl, Br, $CF_3$




**2** **4**

R = $C(CH_3)_3$, $CH_3$, H, Cl, Br

## Experimental Section

**Preparation of Carbinols 1.** These carbinols were prepared in the normal manner[2] by Grignard addition of the appropriate para-substituted phenylmagnesium bromides to tetracyclone.

**Preparation of Carbinols 2.** These carbinols were prepared[2] by Grignard addition of phenylmagnesium bromide to the appropriate 3,4-bis(*p*-substituted-phenyl)-2,5-diphenyl-2,4-cyclopentadien-1-ones.

**Kinetic Runs.** All solvents were of spectral-grade quality and were used without further purification. The kinetic studies of the sigmatropic rearrangements of the polyarylated alcohols were performed as follows. Into a 50-mL, two-necked, round-bottomed flask equipped with a reflux condenser, a serum cap, and a magnetic stirrer was placed 20 mL of tetraethylene glycol, which was then heated to the appropriate temperature (for carbinols **1**, 150, 165, 180, 190, and 200 °C in separate kinetic runs; for carbinols **2**, 180, 190, 200, and 210 °C in separate kinetic runs). The temperature of the reaction mixture was maintained at the temperature reported (±0.2 °C) by means of a thermostatically controlled oil bath. At this point 150 mg of the substituted polyarylated carbinol to be studied was added as a solid all at once to the solvent. While the mixture was stirring, samples of 0.5 mL each were taken at various times by inserting a hypodermic syringe through the serum cap. The samples thus obtained were placed in separate containers and cooled by means of an ice–water bath to room temperature. These samples were then separately injected into a Molecular Separations, Inc., B500, high-performance LC. The mobile phase used was methanol/*n*-hexane (0.01% to 99.99%), flowing at 1.4 mL/min through a 2 ft x 2.1 mm (i.d.) stainless-steel column packed with Vydac absorbant. Peaks were recorded on a 10-mV recorder and the peak heights were used as a measure of concentration.[6] This same procedure was used for all the kinetic investigations.

(1) (a) Part 5: J. G. Mason, A. K. Youssef, and M. A. Ogliaruso, *J. Org. Chem.*, **40**, 3015 (1975). (b) Previous papers in the series referenced in footnote 1a.
(2) T. A. Perfetti and M. A. Ogliaruso, *J. Org. Chem.*, **43**, 884 (1978).
(3) C. W. Spangler, *Chem. Rev.*, **76**, 187 (1976).
(4) W. R. Dolbier, Jr., K. E. Anapolle, L. McCullagh, K. Matsui, J. M. Riemann, and D. Rolison, *J. Org. Chem.*, **44**, 2845 (1979).
(5) I. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, 1970.
(6) D. L. Johnson and R. Stevenson, "Basic Liquid Chromatography", Varian Associates, Inc., Palo Alto, CA, 1978, p 227.

0022-3263/80/1945-3910$01.00/0 