The Thermal Rearrangement of α-Phenylazo-β-benzoyloxystilbene

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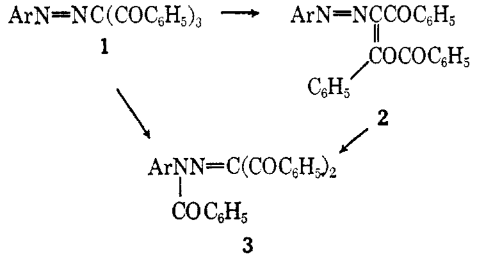
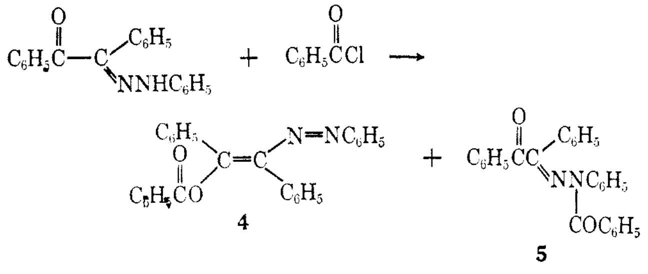
Curtin and co-workers[1] have studied the rearrangements of arylazotribenzoylmethanes (1) to the azo esters (2) and benzoylphenylhydrazones (3) (Scheme I).

Scheme I



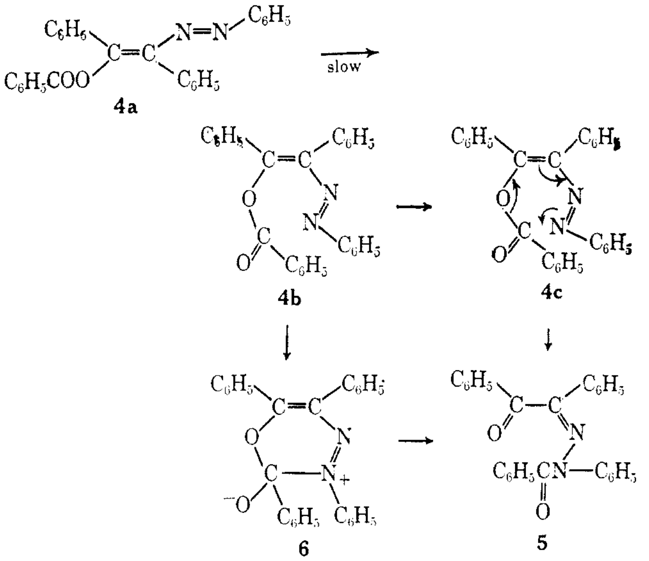
In connection with other work, we have obtained, by treating benzil monophenylhydrazone with benzoyl chloride in pyridine at room temperature for 3 days, a red compound (4) which melts at 140–141° and colorless benzil benzoylphenylhydrazone (5) which melts at 175–176° (Scheme II). Compound **5** is a known compound[2] which can be prepared from benzil and N,N-benzoylphenylhydrazine. Compound **4** can be separated from **5** by its greater solubility in ether and can be further purified by thin layer chromatography. The structure of **4** was assigned on the basis of its method of preparation, analysis, ultraviolet spectrum, and infrared spectrum. Interpretation of the spectra follows quite closely that of Curtin and Poutsma[1a] for **2**. The structure of **4** is further corroborated by its rearrangement in solution, as a melt, or in the solid state to **5**. The analogy to the rearrangement of **2** to **3** is apparent. Compound **4** appears to be an easily accessible simple model for studying the enol benzoate rearrangement. The solid-state rearrangement takes place at about 100° over a period of days. A shiny red crystal of **4** retains its shape but becomes opaque and very pale yellow. In a melt, at temperatures over 140°, the rearrangement, indicated by loss of color and resolidification, occurs in several minutes. Preliminary studies of the rearrangement in ethylene glycol monomethyl ether solution at 101.5 ± 0.1° give a first-order rate constant of $1.11 \times 10^{-4}\ \text{sec}^{-1}$.

Scheme II



The rearrangement of **4** to **5** appears to require a six-membered transition state (**4c**) or intermediate (**6**). We favor[1c] a *trans* structure (**4a**) for **4** with the rearrangement requiring a rate-determining conversion of **4a** to the *cis* isomer (**4b**) and subsequent fast rearrangement (Scheme III). The cyclic mechanism for the formation of **5** would demand the *cis* configuration around the carbon–nitrogen double bond of **5**. Unlike **3**, which yields benzanilide in good yield when it is eluted through a column of chromatographic alumina,[3] **5** will yield only benzil phenylhydrazone. The N,N cleavage which **3** undergoes is analogous to the reaction of benzil monoxime esters[4] with dilute base, which has been shown to proceed only when the carbonyl function and the leaving group on nitrogen are *trans*. The *cis* isomers undergo ester hydrolysis instead. It appears that **5** exists in the *cis* form which precludes N,N cleavage and that, indeed, the base-catalyzed hydrolysis observed may be aided by participation of the neighboring carbonyl group. We are investigating the rearrangement of **4** to **5** and the base-catalyzed cleavage of **5** further.

Scheme III



Experimental Section

α-Phenylazo-β-benzoyloxystilbene (4).—A solution of 1 g of benzil phenylhydrazone in 10 ml of dry pyridine was treated with 1.5 ml of benzoyl chloride. The yellow solution turned orange, orange-red, and then red. After standing at room temperature for 3 days, the mixture was treated with 50 ml of ether and washed six times with 30 ml of water. As the pyridine was washed out, 0.30 g of colorless **5**, mp 172–174°, separated. After filtration, the ether solution was dried over anhydrous magnesium sulfate, filtered, and taken to dryness below room temperature. The red oil residue was treated with 5 ml of 95% ethanol and refrigerated to yield 0.65 g of red crystals which melted at 134–139°, turned colorless when maintained at that temperature, solidified, and then melted at 172–174°. Compound **4** could be

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(1) (a) D. Y. Curtin and M. L. Poutsma, *J. Am. Chem. Soc.*, **84**, 4887, 4892 (1962); (b) R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *ibid.*, **88**, 4637 (1966); (c) D. Y. Curtin and L. L. Miller, *ibid.*, **89**, 637 (1967).

(2) K. Auwers and A. Bennecke, *Ann. Chem.*, **378**, 243 (1910).

(3) D. Y. Curtin and C. S. Russell, *J. Am. Chem. Soc.*, **73**, 5450 (1951).

(4) (a) R. Barnes and A. Blatt, *ibid.*, **57**, 1330 (1935); (b) A. Hassner and N. A. Wentworth, *Chem. Commun.*, **44** (1965), and references cited.

purified by streaking an ether solution on Eastman chromagram sheet and using benzene–hexane (90:10) as the solvent system. Compound **4** appeared as an orange band with R_f 0.85. Compound **5** was a colorless band, visible under ultraviolet light, with R_f 0.077. Shiny red crystals of **4** melted at 140–141° when the sample was placed in the Mel-Temp melting point apparatus at 120° and heated 2 deg/min. The infrared spectrum of a KBr disk showed a maximum at 1745 cm^{-1}. The ultraviolet–visible spectrum in $HOCH_2CH_2OCH_3$ showed maxima at 449 mμ (ε 513), 348 (346–350) (1.98×10^4), 238 (2.48×10^4), and a shoulder at 255 (1.89×10^4).

Anal. Calcd for $C_{27}O_{20}O_2N_2$: C, 80.19; H, 4.95; N, 6.93. Found: C, 80.06; H, 4.98; N, 7.27.

Preliminary studies of the rearrangement at 101.5 ± 0.1° in $HOCH_2CH_2OCH_3$ were followed by changes in absorption at 350 mμ. Light absorption of **4** [4] and **5** [5] at this wavelength followed Beer's law. The absorption of light by **4** and **5** (ϵ_5^{350} 1.43×10^4) at this wavelength was additive. The expression for [4] was $\epsilon_4^{350}[4] + \epsilon_5^{350}[C_0 - [4]] = OD_{obsd}$. The first-order rate constant was estimated to be 1.11×10^{-4} sec^{-1}. The rearrangement product was shown to be identical with **5** by a mixture melting point and similarity in the spectrum.

Registry No.—**4a**, 13144-85-9; **5**, 13144-86-0.

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Retention of Configuration in Nucleophilic Vinylic Halide Substitution. II. Stereospecific Preparation of Vinylarsines

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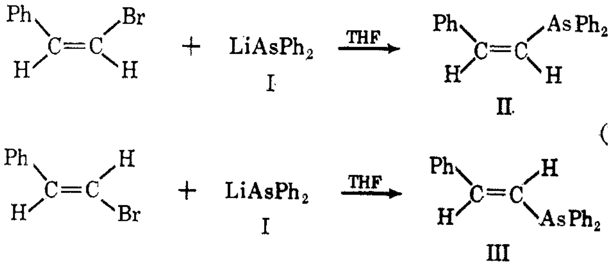
In a study of nucleophilic vinylic halide substitution, we have reported the stereospecific replacement of bromine in the β-bromostyrenes by lithium diphenylphosphide.[2,3] This reaction was shown to occur with retention of configuration leading to the production of stereochemically pure β-styryldiphenylphosphines, having the same configuration as the starting halide.[3]

Extension of this work has shown that lithium diphenylarsenide (I) also reacts in the same manner to give stereochemically pure β-styryldiphenylarsines, retaining the configuration of the starting halide (eq 1).



(1)

Reaction of the β-bromostyrenes with the mixture of lithium diphenylarsenide and phenyllithium, obtained by the lithium cleavage of triphenylarsine, led to a complex mixture of products.

We have described a convenient preparation of phenyllithium free tetrahydrofuran (THF) solutions of lithium diphenylphosphide from triphenylphosphine and lithium.[4] In an analogous manner, a tetrahydrofuran solution of I was prepared from triphenylarsine and lithium metal, followed by treatment with an equimolar amount of *t*-butyl chloride (eq 2).

$$\begin{gathered} Ph_3As + 2Li \xrightarrow{\text{THF}} \underset{\text{I}}{Ph_2AsLi} + PhLi \\ PhLi + (CH_3)_3CCl \xrightarrow{\text{THF}} PhH + (CH_3)_2C{=}CH_2 + LiCl \end{gathered} \qquad (2)$$

The reaction of I with *cis*-β-bromostyrene gave *cis*-β-styryldiphenylarsine (II), isolated in 61% yield, mp 91–92°.

The reaction of I with commercial *trans*-β-bromostyrene gave *trans*-β-styryldiphenylarsine (III), isolated in 70% yield, bp 187–189° (0.25 mm).

Reaction of excess I with either II or III caused no isomerization, nor addition to give phenylethylenebis(diphenylarsine). Complete isomerization of II to III occurred with a small amount of PCl_5 in refluxing benzene after 10 hr, as shown by gas chromatographic analysis.

The 60-Mc nuclear magnetic resonance (nmr) spectrum of II in $DCCl_3$ solution shows a phenyl complex at τ 2.65 and one-half of the AB vinyl proton signal at τ 3.36 (J = 12 cps). The other half of this vinyl signal is hidden under the phenyl complex as indicated by the relative ratios of 16:1. The spectrum of III shows only a complex centered at τ 2.70. The coupling constants for vinyl proton signals found by Cullen, *et al.*,[5] for $Me_2AsCH{=}CHCF_3$ were J_{cis} = 13 cps and J_{trans} = 18 cps. Comparison of these values with the coupling constant (J = 12 cps) found for II indicate it to be the *cis* isomer.

The stereochemical purity of the β-styryldiphenylarsines was verified by gas chromatographic analysis on a $^1/_8$ in. × 4 ft, 3% SE 30 column at 200°. Neither II nor III isomerized under these conditions. The reaction of I with pure *cis*-β-bromostyrene gave only II. Reaction of I with commercial *trans*-β-bromostyrene (containing 10% of the *cis* isomer) gave II and III in a ratio of 1:10.

Although other nucleophilic vinylic halide substitutions with retention of configuration are known,[2,3,6–9] this is the first instance where a metalloorgano arsenide has been the nucleophile.

Experimental Section

General Procedure.—All reactions, unless otherwise stated, were run under nitrogen in a dry, three-neck, 500-ml flask fitted with dropping funnel, gas inlet tube, condenser, gas outlet tube, and magnetic stirrer. Proton nmr spectra were taken on a Varian nmr spectrometer, Model A-60, using a tetramethylsilane standard (τ 10.0). All of the gas–liquid partition chromatography was done on a Microtech Model DSS instrument, having a flame ionization detector, using a $^1/_8$ in. × 4 or 10 ft column (3% SE

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(1) NASA fellow, 1965–1968.

(2) A. M. Aguiar and Donald Daigle, *J. Org. Chem.*, **30**, 2826 (1965).

(3) A. M. Aguiar and Donald Daigle, *ibid.*, 3527 (1965).

(4) A. M. Aguiar, J. Beisler, and A. Mills, *ibid.*, **27**, 1001 (1962).

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