of the solvents in vacuo there was obtained an oil which was directly purified on 50 g of silica gel. Elution with hexane–ether (3:1) gave 333 mg (92%) of pure Michael adduct: bp 105 °C (bath temperature) (15 mmHg); IR ($CCl_4$) 3080, 1700, 1712 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.64–1.00 (m, 4 H). Anal. Calcd for $C_{11}H_{16}O_2$: $M^+$ 180.11503. Found: $M^+$ 180.11523.

**2-Methyl-3-cyclopropylcyclohex-2-enone (3).** A solution of 418 mg (2.2 mmol) of titanium tetrachloride and 312 mg (1.1 mmol) of titanium tetraisopropoxide in 3.0 mL of methylene chloride was added dropwise over a period of 10 min to a solution of 168 mg (2.0 mmol) of ethyl vinyl ketone and 342 mg (2.2 mmol) of silyl enol ether **1** in 8 mL of methylene chloride cooled to −78 °C. Stirring at −78 °C was continued for 45 min. The reaction was quenched with 10% aqueous potassium carbonate solution and the resulting diketone was extracted with methylene chloride. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The resulting crude diketone was chromatographed on 40 g of silica gel. Elution with hexane–ether (3:1) gave 221 mg (66%) of diketone **2**: bp 75 °C (bath temperature) (16 mm Hg); IR ($CCl_4$) 3088, 1712, 1698 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.7–2.2 (m, 6 H), 2.1–1.5 (m, 3 H), 1.01 (t, 3 H, $J$ = 7 Hz), 1.0–0.7 (m, 4 H).

The above diketone (160 mg, 0.95 mmol) was treated with potassium hydroxide (84 mg, 1.5 mmol) in 4.0 mL of methanol for 16 h at room temperature. The reaction mixture was quenched by the addition of a saturated ammonium chloride solution and the product was extracted with ether. The combined ethereal extracts were washed with brine, dried ($MgSO_4$), and evaporated in vacuo. Chromatography of the crude product on 20 g of silica gel afforded 120 mg (84%) of crystalline enone **3**: mp 35 °C (lit.[2a] mp 36–37 °C); IR ($CCl_4$) 3080, 1665, 1616 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.83 (s, 3 H), 0.6–0.9 (m, 4 H).

**3-Cyclopropyl-5,5-dimethylcyclohex-2-enone (5).** A solution of 625 mg (3.33 mmol) of titanium tetrachloride in 6.0 mL of methylene chloride was added dropwise over a period of 15 min to a cooled (−78 °C) solution of 300 mg (3.06 mmol) of mesityl oxide and 520 mg (3.33 mmol) of silyl enol ether **1** in 15 mL of methylene chloride. After an additional 30 min at −78 °C, the reaction was quenched by the addition of a 10% aqueous potassium carbonate solution. Extraction with chloroform followed by drying ($MgSO_4$) afforded 700 mg of crude diketone which was chromatographed on silica gel. Elution with ether–hexane (1:1) gave 508 mg (93%) of pure 1,5-diketone **4**: bp 90 °C (bath temperature ) (15 mmHg); IR ($CHCl_3$) 1710, 1695 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.71 (s, 2 H), 2.57 (s, 2 H), 2.02 (s, 3 H), 1.60 (m, 1 H), 1.08 (s, 6 H), 0.82 (m, 4 H).

The above diketone (300 mg, 1.6 mmol) was treated with 108 mg (2.0 mmol) of potassium hydroxide in 2.0 mL of methanol at room temperature for 8 h. The reaction was quenched with saturated aqueous ammonium chloride solution and worked up as described above. Purification of the crude enone on silica gel gave 250 mg (93%) of pure **5**: bp 70 °C (bath temperature) (15 mmHg); IR ($CCl_4$) 3080, 1665, 1621 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.78 (bs, 1 H), 2.2–2.0 (m, 4 H), 1.45 (m, 1 H), 1.08 (s, 6 H), 1.0–0.6 (m, 4 H).

**2-Methyl-3-cyclopropylcyclopent-2-enone (6).** A solution of 418 mg (2.2 mmol) of titanium tetrachloride and 312 mg (1.1 mmol) of titanium tetraisopropoxide in 3.0 mL of methylene chloride was added slowly (10 min) to a cooled (−78 °C) solution of 202 mg (2.0 mmol) of 2-nitro-1-butene and 342 mg (2.2 mmol) of 1-trimethylsilyloxy-1-cyclopropylethylene in 7.0 mL of methylene chloride. After 1.5 h at −78 °C, 2.0 mL of water was added and the temperature of the reaction was gradually raised to 40 °C. The reaction mixture was refluxed for 5 h. The reaction was diluted with water and the product isolated by extraction with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave crude diketone which was chromatographed on silica gel. Elution with hexane–ether (4:1) gave 194 mg (63%) of pure cyclopropyl 3-oxopentyl ketone: bp 65 °C (bath temperature) (16 mmHg); IR ($CCl_4$) 3085, 1718, 1700 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.9–2.2 (m, 6 H), 1.91 (m, 1 H), 1.1–0.6 (m, 4 H), 1.03 (t, 3 H, $J$ = 7 Hz). Anal. Calcd for $C_9H_{14}O_2$: $M^+$ 154.09938. Found: $M^+$ 154.09912.

A solution of the above diketone (100 mg, 0.71 mmol) in 1.0 mL of dry benzene was added to a solution of potassium *tert*-butoxide in *tert*-butyl alcohol [prepared from 39 mg (1.0 mmol) of potassium in 2.0 mL of *tert*-butyl alcohol]. After 15 min the reaction was quenched by addition of aqueous ammonium chloride. The product was isolated by extraction with ether. The combined ether extracts were dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo gave the crude product, which was directly chromatographed on 15 g of silica gel. Elution with hexane–ether (4:1) afforded 80 mg (82%) of pure cyclopentenone **6**[2a,3] as an oil: bp 60 °C (bath temperature) (16 mmHg); IR ($CCl_4$) 3095, 1695, 1635 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.75–1.20 (m, 4 H), 1.75 (bs, 3 H), 1.80–2.30 (m, 5 H). Anal. Calcd for $C_9H_{12}O$: $M^+$ 136.08882. Found: $M^+$ 136.08866.

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**Registry No.**—**1**, 42161-96-6; **2**, 66270-49-3; **3**, 61765-56-8; **4**, 66270-50-6; **5**, 66270-51-7; **6**, 59939-09-2; cyclopropyl methyl ketone, 765-43-5; chlorotrimethylsilane, 75-77-4; cyclohexenone, 930-68-7; cyclopropyl (3-oxocyclohexyl)methyl ketone, 66270-52-8; ethyl vinyl ketone, 1629-58-9; mesityl oxide, 141-79-7; 2-nitro-1-butene, 2783-12-2; cyclopropyl 3-oxopentyl ketone, 66270-53-9.

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# Reaction of Triarylvinyl Bromides with Lithium Aluminum Hydride[1]

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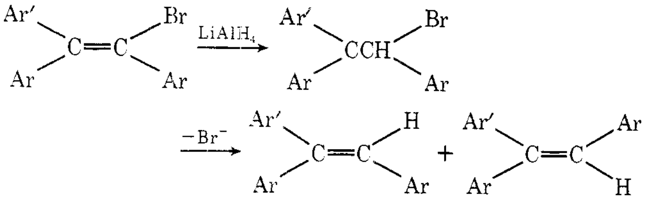
Theoretical calculations have shown that the direct $S_N2$ displacement at a vinylic carbon is energetically unfavorable[2] and it has been pointed out in a recent review[3] that such a reaction has so far not been observed. Where an inversion component in solvolytic displacements with vinylic systems has been observed, the intervention of an ion pair with shielding effects rather than a backside $S_N2$ displacement is suggested as the mechanism.[4] In an early study on $LiAlH_4$ reductions, Trevoy and Brown[5] proposed a general mechanism for the reaction involving a nucleophilic attack on carbon by complex hydride ions. Among the reactions reported by Trevoy and Brown was the conversion of $\beta$-bromostyrene to styrene, and if the proposed mechanism applies, this would constitute a direct displacement on a vinylic carbon. In the present work, the reactions of $LiAlH_4$ with a number of triarylvinyl bromides were studied in order to obtain some mechanistic information on this reaction.

The triarylvinyl bromides used in the present study included triphenylvinyl, tri-*p*-tolylvinyl, tri-*p*-anisylvinyl, *cis*-2-phenyl-1,2-di-*p*-tolylvinyl, and *cis*-1,2-di-*p*-anisyl-2-phenylvinyl bromides (**1**, **2**, **3**, *cis*-**4**, and *cis*-**5**, respectively). These were available from earlier studies in this laboratory on degenerate rearrangements in triarylvinyl cations generated from solvolyses with these bromides as substrates.[6] Treatment of **1**,[6a,b] **2**,[6e] and **3**[6c] with an excess of $LiAlH_4$ in ether gave the corresponding triphenylethylene (**6**), tri-*p*-tolylethylene (**7**), and tri-*p*-anisylethylene (**8**), respectively, and these results are in agreement with expectations from the reported conversion of β-bromostyrene to styrene.[5] A similar treatment with *cis*-**4** or *cis*-**5** gave an essentially 1:1 mixture of the cis and trans olefins, *cis*- and *trans*-1-phenyl-1,2-di-*p*-tolylethylene (*cis*- and *trans*-**9**) from *cis*-**4** and *cis*- and *trans*-1,2-di-*p*-anisyl-1-phenylethylene (*cis*- and *trans*-**10**) from *cis*-**5**. Identification of the olefinic products in all of these reactions was made by comparison of their $^1$H NMR spectra with known spectral data or with those of authentic samples prepared from dehydration of the corresponding 1,1,2-triarylethanols[6] by treatment with $H_3PO_4$.[7]

The formation of a mixture of *cis*- and *trans*-**9** from *cis*-**4** and *cis*- and *trans*-**10** from *cis*-**5** definitely eliminated a direct backside displacement as the mechanism for the $LiAlH_4$ reduction of triarylvinyl bromides, thus giving further confirmation to earlier conclusions that the $S_N2$ reaction at vinylic carbon is energetically unfavorable. The observed results, however, may be reasonably explained by an addition–elimination route[8] as shown below.



## Experimental Section

**Reaction of Triarylvinyl Bromide with $LiAlH_4$.** A solution of 200 mg of triarylvinyl bromide **1**, **2**, **3**, *cis*-**4**, or *cis*-**5** in 25 mL of anhydrous ether was placed in a round-bottom flask fitted with a reflux condenser. $LiAlH_4$ (1.0 g) was added in small portions over a period of about 10 min. The mixture was then refluxed for 12 h and cooled in an ice bath and the excess $LiAlH_4$ was destroyed by the slow addition of 50 mL of $H_2O$ The ether layer was separated and the aqueous layer was extracted with ether (3 × 50 mL). The combined ether solution was dried over $MgSO_4$ and the ether was removed, giving a residual triarylethylene in yields ranging from 50–65%. The mass spectrum of each product showed the expected molecular ion for the triarylethylene and the absence of any unreacted triarylvinyl bromide.

From bromides **1**, **2**, and **3**, the products triphenylethylene (**6**), tri-*p*-tolylethylene (**7**), and tri-*p*-anisylethylene (**8**), respectively, were crystallized from $CH_3OH$. Olefin **6** melted at 67–68 °C (lit.[9] mp 67–68 °C) and showed an $^1$H NMR spectrum identical with that reported previously for an authentic sample of **6**.[9] Olefin **7** melted at 113–114 °C (lit.[10] mp 114 °C): $^1$H NMR ($CDCl_3$) δ 2.25, 2.34, 2.37 ($CH_3$, 3 s), 6.8–7.2 (aromatic + C=CH, m). This spectrum was the same as that of an authentic sample of **7** prepared from the $H_3PO_4$ dehydration[7] of 1,1,2-tri-*p*-tolylethanol.[6e] Olefin **8** melted at 100–101 °C (lit.[7] mp 100–101 °C): $^1$H NMR ($CDCl_3$) δ 3.74, 3.80, 3.83 ($CH_3O$, 3 s), 6.6–7.3 (aromatic + C=CH, m). These spectral absorptions were essentially the same as those reported for **8** by Rappoport et al.[11] and were identical with the spectrum of **8** prepared from dehydration[7] of 1,1,2-tri-*p*-anisylethanol.[6c]

The product from *cis*-**5** was an oil. It was identified as a mixture of *cis*- and *trans*-1,2-di-*p*-anisyl-1-phenylethylene (*cis*- and *trans*-**10**) since its $^1$H NMR spectrum showed four $CH_3O$ singlets at ($CDCl_3$) δ 3.69, 3.77 (for *trans*-**10**), and 3.71 and 3.80 (for *cis*-**10**), with the aromatic and vinyl protons at δ 6.5–7.3. The four $CH_3O$ absorptions observed were essentially the same as those for *cis*-**10** and *trans*-**10** reported by Rappoport and Apeloig.[12] 1-Phenyl-1,2-di-*p*-tolylethylene (**9**) (stereochemistry not specified) has been prepared as an oil, bp 182–183 °C (0.01 Torr).[13] In the present work, the product from *cis*-**4** was also an oil. Its $^1$H NMR spectrum showed three singlets in the $CH_3$ region at ($CDCl_3$) δ 2.22 (6 H), 2.30 (3 H), and 2.34 (3 H) while the aromatic and vinyl protons absorbed at δ 6.8–7.3. These data indicated that the olefinic product from *cis*-**4** was a mixture of *cis*- and *trans*-**9**, with the $CH_3$ absorptions at δ 2.22 and 2.30 for *trans*-**9** and at δ 2.22 and 2.34 for *cis*-**9**.

**Registry No.**—**1**, 1607-57-4; **2**, 66184-02-9; **3**, 25354-46-5; *cis*-**4**, 64833-13-2; *cis*-**5**, 26326-64-7; **6**, 58-72-0; **7**, 6629-83-0; **8**, 7109-27-5; *cis*-**9**, 66184-01-8; *trans*-**9**, 66184-00-7; *cis*-**10**, 26326-61-4; *trans*-**10**, 15789-91-0.

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## The Triphenylmethyl Radical: Equilibrium Measurements and the Reaction with Thiophenol[1]

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Rate constants for hydrogen atom transfer reactions to organic free radicals are usually determined only by rather complex methods with considerable uncertainties. However, an incidental observation during a study of the isotope effect for the reaction of thiophenol with the triphenylmethyl radical (the trityl radical) led to an order of magnitude estimation of the rate constant. That is, the color of the radical was not instantaneously discharged upon mixing the reagents at 0 °C.[4] It was clear that a careful measurement could yield a more precise value.

At the same time, it was clear that the determination of the rate constant required values for the equilibrium constant. In order to use the earlier isotope effect work, it was necessary to use toluene as the solvent. Previous determinations had been made in benzene and other solvents, but not toluene.[5] Depending upon the method of measurement, there was also an uncertainty of a factor of 2.[5] The availability of an apparatus that would allow us to handle and accurately dispense volumes of air and moisture-sensitive solutions prompted us to remeasure the dissociation constant in toluene by spectrophotometric methods, as originally done by Ziegler.[5] The discrepancy between spectrophotometric and magnetic measurements has now been resolved.[1] It arose primarily from the diamagnetic susceptibility of the dimer. Subsequently, the same apparatus was used to measure the rate of reaction of the trityl radical with thiophenol.

**Dissociation of 1-Diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene.** The measurements were made at the 516-nm maximum absorbance of the trityl radical. At this wavelength the dimer does not significantly absorb, so the absorbance in the 1-cm cell used is

$$A = \epsilon(\mathrm{R}\cdot) \qquad (1)$$

0022-3263/78/1943-2722$01.00/0