

Semibenzene Formation During the Acylation of Resonance Stabilized Anions

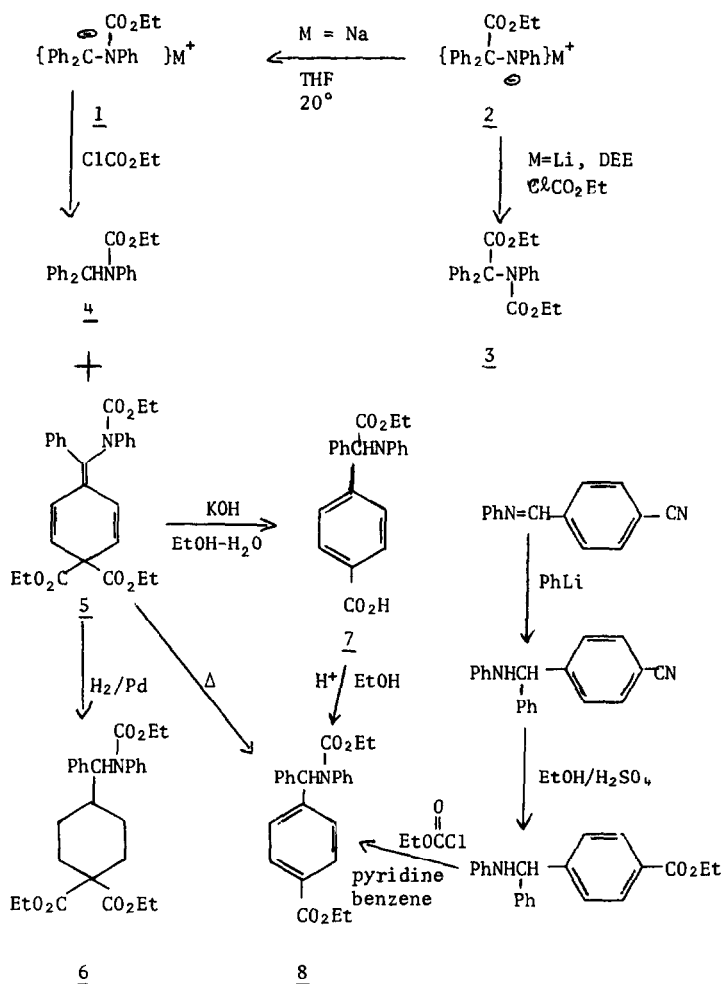
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(Received in USA 8 September 1972; received in UK for publication 17 April 1973)

The facile formation of the functionally substituted benzhydryl anion 1 by rearrangement of 2 has been reported <sup>1</sup> earlier. The accessibility of 1 prompted an investigation of the chemical consequences of resonance delocalization <sup>2</sup> of the anionic charge in 1, the stabilizing influence of which must contribute much of the driving force for the rearrangement of 2 to 1. Such delocalization leads to the formation of ring substituted products during functionalization of these delocalized anions with bulky reagents. As specific examples, the reaction of the trityl anion with triphenylsilyl chloride <sup>3</sup>, benzaldehyde <sup>4</sup>, or benzophenone <sup>5</sup> can be cited.

In this report we describe an example in which only ring substitution occurs, the ultimate consequence of which is the efficient formation of a semibenzene (methylene-2,5-cyclohexadiene) derivative. Treatment of the anion 1 (M = Na<sup>+</sup>, tetrahydrofuran (THF) as solvent) with ethyl chloroformate did not product any detectable amount of the expected product 3, (see Scheme 1). Instead a mixture of ethyl N-diphenylmethyl-N-phenylcarbamate <sup>6</sup>, 4, and an unknown compound containing three carbethoxy groups was obtained and separated by column chromatography.

The latter compound was the semibenzene derivative 5, 1-( $\alpha$ -(N-carbethoxyanilino) benzyli-dene)-4,4-dicarbethoxy-2,5-cyclohexadiene <sup>7</sup>. This identification was based on the nmr spectrum which showed four vinyl protons in the 6.0 - 7.0 $\delta$  region and two identical carbethoxy groups. In addition the uv spectrum showed a strong absorption at 310 nm ( $\epsilon = 2.03 \times 10^4$ ) analogous to that reported by Winstein <sup>8</sup> for a semibenzene derivative. Finally, 5 rapidly reacted with three moles of hydrogen at 20<sup>o</sup> (Pd catalyst) to form 6. In this last compound <sup>9</sup>, the band at 310 nm had disappeared and the benzylic proton appeared as a doublet.

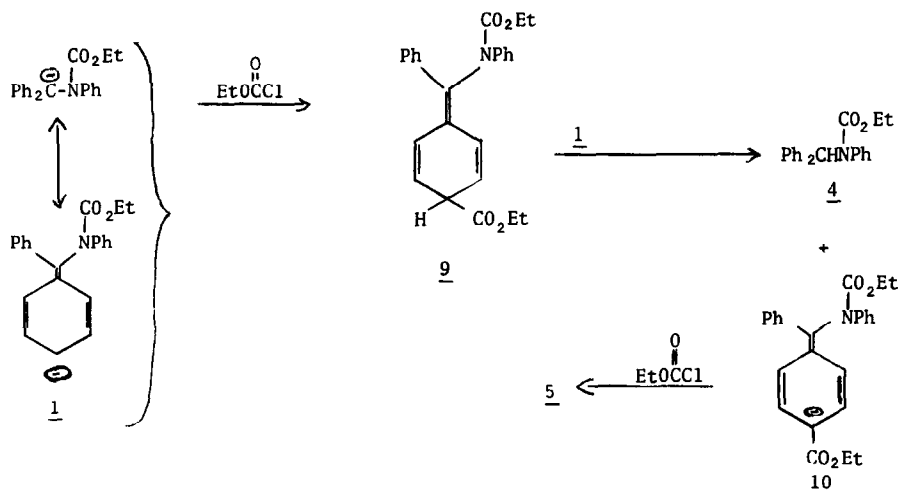


Scheme 1

In further reactions, **5** underwent basic hydrolysis with the loss of one carboxy group to **7**<sup>9</sup> and on thermolysis **5** was converted to **8**<sup>9</sup>. Both **7** and **8** were synthesized<sup>9,10</sup> as shown in Scheme 1 to confirm their structure as well as to provide further support for structure **5**.

Reaction of **1** with the acylating agent must generate a cyclohexadiene intermediate **9** as the primary product. Indeed, quenching a reacting mixture after a brief reaction at  $-60^\circ$  provided

a 66% yield of 4 and a 19% yield of 8, the expected rearrangement product of 9. As the acylation reaction is normally carried out, 9 is formed in the presence of a strong base 1 and proton transfer of the labile allylic proton activated by the introduced carbethoxy group can be expected to occur forming 4 and the anion 10. Reaction of 10 with the acylating agent forms the observed product 5.



It cannot be thermodynamic instability of the C,N-dicarbethoxy compound 3 which controls the course of the reaction. Indeed 3 can be prepared<sup>11</sup> by treating 2 (M = Li, solvent diethyl ether (DEE)) with ethyl chloroformate. It should be stressed that in this reaction, 3 is formed by acylation at the amine anionic center of 2. As Stuart-Briegleb models show, this center is more accessible than the benzydrylic carbanionic center of 1 which is markedly hindered by the three groups attached to it. A high activation energy must exist for the attack by the acylating agent at the benzydrylic carbon. Therefore reaction of the acylating agent at the para position is kinetically favored.

Considering the somewhat laborious synthesis generally used for semibenzene derivatives<sup>12</sup>, this preparation has obvious synthetic utility. Additionally, it is interesting that ring acylation occurs with such efficiency. We are presently evaluating the influence of the substituted amino group<sup>13</sup> of 1 in this reaction by examining the behavior of related simpler anions.

References

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6. Identical to an authentic sample both spectroscopically and by mixture mp. The procedure involved treating the dianion of benzophenone anil <sup>1</sup> with one mole of ethyl chloroformate, allowing the rearrangement to occur, then adding a second mole of ethyl chloroformate at -60°. Beginning with .01 mole of benzophenone anil, .0043 mole (86%) of 4 and .0044 mole (88%) of 5 were isolated. Yields are based on 2 {1} → 4 + 5.
7. nmr (CDCl<sub>3</sub>) 1.10 and 1.22 (two t, 9, J=7 and 8Hz resp., CH<sub>3</sub>CH<sub>2</sub>), 4.17 and 4.24 (two q, 6, J= 7 and 8Hz resp., CH<sub>3</sub>CH<sub>2</sub>), 6.1-6.4 (m,2), 6.67 and 6.87 (two s,2) (vinyl Hs), 7.1-7.5 (m, 10, aromatic H).
8. R. Heck, P.S. Magee and S. Winstein, Tetra. Letters, 2033 (1964).
9. Satisfactory analytical and spectral data for these compounds were obtained.
10. The reaction using phenyl lithium provided a low yield of the indicated product. The major product arose by the addition of 2 moles of the organometallic reagent.
11. mp 109 - 111°, yield 59%. Anal. Calcd. for C<sub>22</sub>H<sub>25</sub>O<sub>4</sub>N: C, 74.42; H, 6.25; N, 3.47. Found : C 74.65; H, 6.22; N, 3.46. ir (KBr) 1690, 1730 cm<sup>-1</sup>. uv, λ max (ε), 257 (880), 312 (280). nmr(CDCl<sub>3</sub>) δ, 1.08 and 1.38 (two t, J = 7Hz, 6, CH<sub>3</sub>CH<sub>2</sub>), 4.09 and 4.43 (two q, J = 7Hz, 4, CH<sub>3</sub>CH<sub>2</sub>), 6.9 - 7.5 (m,15, aromatic).
12. Present syntheses rely on the addition of Grignards to 2,5-cyclohexadienones and dehydration of the addition products. See for example, B. Miller and K.-H. Lei, J. Amer. Chem. Soc., 94, 3472 (1972); A.J. Waring, Cyclohexadienones in Advances in Alicyclic Chemistry, vol 1, p. 129, ed. H. Hart and G.J. Karabatsos, Academic Press (1966).
13. To date, we have been unable to observe any ring acylation of the trityl anion by ethyl chloroformate.