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# REARRANGEMENTS DURING THE ACYLATION OF VICINAL DIANIONS

James G. Smith and G. E. F. Simpson
University of Waterloo
Department of Chemistry
Waterloo, Ontario

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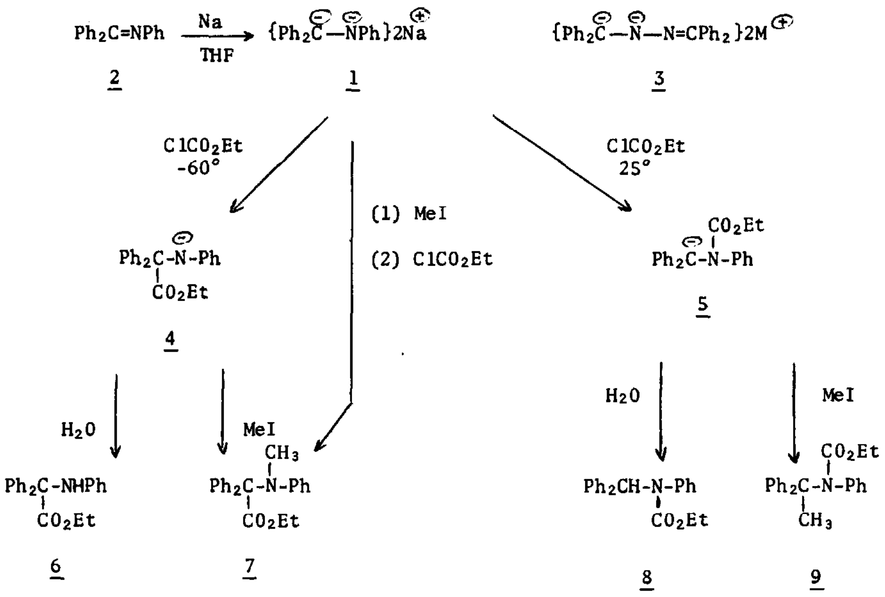
The dianion, 1, derived by the alkali metal reduction of benzophenone anil, 2, possesses two vicinal anionic centers which should differ in nucleophilicity and basicity. On the basis of the dissociation constants of related protonated species (1), one would predict that both the nucleophilicity and basicity of the carbanionic center would exceed that of the amino center by a sizeable factor. Indeed, earlier studies of the alkylation of 1 (2) with methyl iodide have shown that the reaction proceeded stepwise - the first alkyl group was introduced at the benzylic carbon followed by the second at the nitrogen (or dehydrohalogenation and protonation of the nitrogen in the case of secondary halides).

In contrast to this, acylation of vicinal dianions has presented a confused picture. In the case of 1, acylation only at the amino anionic center was detected (2). However, the closely related vicinal dianion derived from benzophenone azine, 3, was found to acylate only at the carbanionic center (3). We wish to report experimental data which resolves these conflicting observations.

Treatment of the dianion 1 (in THF) with one mole of ethyl chloroformate at -60° resulted in a rapid change in colour from a deep purple red to a clear light red. On warming to room temperature, this color deepened over the next several hours to a dark red. Quenching of the light red solution with water gave the ethyl ester of N,2,2-triphenylglycine, 6, (4) while quenching the dark red solution gave ethyl N-diphenylmethyl-N-phenylcarbamate, 8, (6). (see Scheme 1).

That the second anionic center is still active in each of the reactions described, is shown by the following experiments. Addition of one mole of ethyl chloroformate at -60° was followed by one mole of methyl iodide. The isolated product was the ethyl ester of N-methyl-

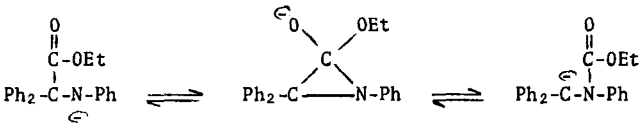


Scheme 1. Acylation Reactions of the Benzophenone Anil Dianion.

N,2,2-triphenylglycine, 7 (7). If the addition of methyl iodide was preceded by a warming period, the product was ethyl N-(1,1-diphenylethyl)-N-phenyl-carbamate, 9, (8). This last compound was also prepared by the addition of one mole of methyl iodide to 1, (carbon alkylation), followed by one mole of ethyl chloroformate.

These experiments establish that acylation (like alkylation) occurs first at the more nucleophilic carbanionic center to produce 4. This product then rearranges on warming to the isomeric anion 5. The rearrangement is quite facile at temperatures above 0°. Acylation of 1 with ethyl chloroformate at 20° or 0° (15 min. reaction time) produced only 8. Warming 4 to -5° for 2 hrs. resulted in a product consisting of 80% 8 and 20% 6.

Migration of acyl groups from a carbon to a nitrogen has been observed elsewhere (9, 10). The simplest intermediate whereby the acyl group is transferred from the carbon to the nitrogen is through a three membered transition state 10 in which the direction of ring opening is dictated by the thermodynamic stability of the two possible monoanions 4 and 5 (11).



4 10 5

With the present results in hand, the behaviour of dianion 3 becomes understandable. Acylation occurs on the carbanionic center but decomposition of the resulting monoanion to diphenyldiazomethane and the anion of ethyl diphenylacetate (3, 12) occurs at a faster rate than rearrangement. Thus only the first stage of acylation is observed.

References:

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4. 85% yield, mp 113-114°; ir (KBr) 3430 (NH), 1730 (C=O) cm$^{-1}$; nmr ($CDCl_3$) δ, 1.0 (t, J=4 Hz, 3, $\underline{H}_3CH_2O$-), 4.15 (q, J=4 Hz, 2, $CH_3C\underline{H}_2O$), 5.2 (s (broad), 1, NH), 6.3-7.7 (m, 15 aromatics); hydrolysis produced N,2,2-triphenylglycine mp 179-182°(reported (5) 178-180°); anal. calcd. for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.54; H, 6.14; N, 4.23.
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6. 82% yield, mp 58-9°; ir (KBr) 1700 (C=O) cm$^{-1}$; nmr ($CDCl_3$) δ, 1.2 (t, J=4 Hz, 3, $C\underline{H}_3CH_2O$-), 4.2 (q, J=4 Hz, 2, $CH_3$-$C\underline{H}_2O$-), 6.7 (s, 1, $Ph_2C\underline{H}$-), 6.8-7.5 (m, 15, aromatics); hydrolysis produced $Ph_2CHNHPh$. Anal. Calcd. for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.88; H, 6.26; N, 4.06.
7. 75% yield, mp 84-5°; ir (KBr) 1740 (C=O) cm$^{-1}$; nmr ($CDCl_3$) δ, 1.0 (t, J=4 Hz, 3, $CH_3C\underline{H}_2O$), 2.9 (s, 3, N-$C\underline{H}_3$), 4.1 (q, J=4 Hz, 2, $CH_3C\underline{H}_2O$), 6.2-7.6 (m, 15, aromatics); Anal. calcd. for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.06. Found: C, 80.19; H, 6.87; N, 4.10.
8. 90% yield, mp 89-90°; ir (KBr) 1710 (C=O) cm$^{-1}$; nmr ($CDCl_3$) δ 0.9 (t, J=3 Hz, 3, $C\underline{H}_3CH_2O$), 1.7 (s, 3, $Ph_2C$-$C\underline{H}_3$); 3.9 (q, J=3 Hz, 2, $CH_3C\underline{H}_2O$), 7.1-7.5 (m, 15, aromatics); Anal. calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.06. Found: C, 79.90; H, 6.78; N, 3.90.
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