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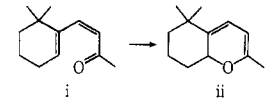

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Acylation of Vicinal Dianions. Formation of Products by Rearrangement and Proton Transfer

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The acylation of the vicinal dianions **1** and **20**, respectively derived by reductive metalation of benzophenone anil and *N*-(*p*-cyanobenzal)aniline, was examined in detail with ethyl chloroformate as the acylating agent. In the case of **1**, dimethylcarbamoyl chloride was used as well. In addition to the expected acylation at the benzylic and amine anionic sites, additional products were formed by rearrangement of the acyl group and/or proton transfer. In the case of **1**, these reactions, under certain conditions, led to triacylated semibenzene derivatives as a major product. Reaction of **20** was more complicated since the reaction products consisted of mono-, di- and triacylated derivatives. The reaction was studied by generating the individual monoanions formed as intermediates in the reaction. Proton transfer was more dominant in this reaction although migration of a carbethoxy group again occurred.

Ethyl chloroformate is a useful reagent for characterizing and functionalizing anionic species. Recently, in studies of two vicinal dianions,[1,2] some interesting deviations from the anticipated acylation were noted. This report describes these reactions which involved acyl group migration and/or proton transfer and outlines some of the factors affecting the extent of the side reactions.

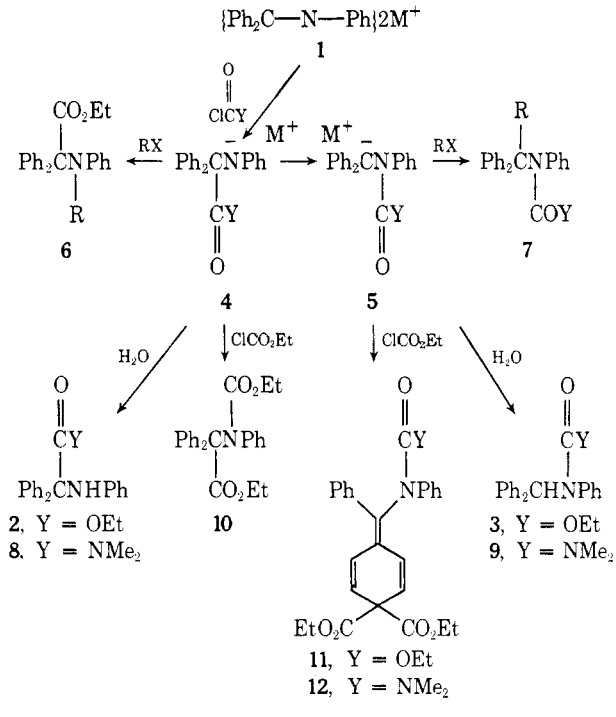
Scheme I summarizes our earlier observations with ethyl chloroformate and the vicinal dianion **1** derived from benzophenone anil. Thus rearrangement of the initially formed anion **4** (Y = OEt) to **5** (Y = OEt) occurred as clearly indicated by the characterizing reactions of **4** and **5** shown in Scheme I.

This rearrangement proceeded with even greater facility with dimethylcarbamoyl chloride[3] as acylating agent. Indeed, the unrearranged anion **4** (Y = NMe_2) could only be detected under reaction conditions unfavorable to rearrangement (*i.e.*, diethyl ether as solvent, lithium as counterion).

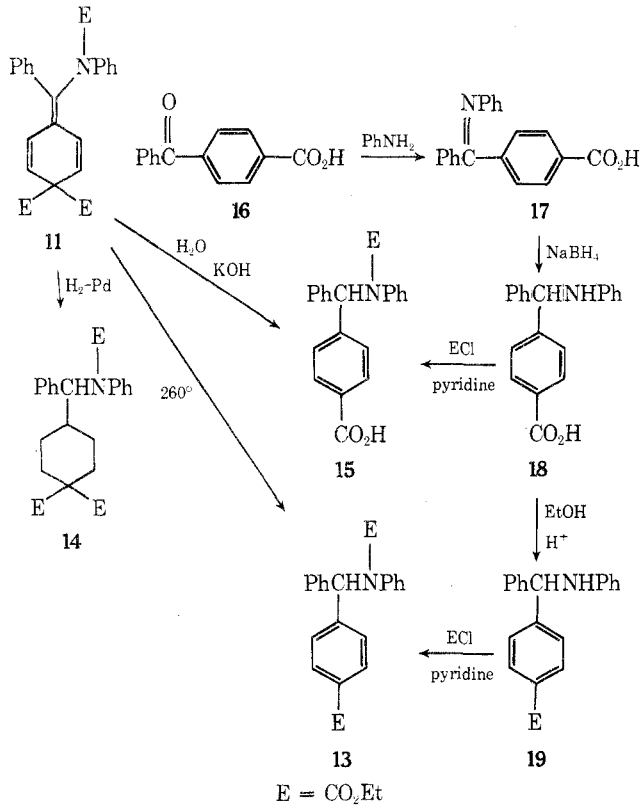
Proton transfer was observed[1] during further acylation of the rearranged monoacylated anion **5** to produce the semibenzene derivative **11**. Again this same reaction occurred with dimethylcarbamoyl chloride to give **12**. In the case of **11** both spectral and chemical evidence supported the proposed structure (see Scheme II and Experimental Section), while structure **12** was based on the presence of four vinyl protons in the 5.8–6.8 region of the nmr spectrum and on the strong absorption band in the 320–340-nm region of the uv spectrum.[4]

The availability of a second vicinal dianion **20** derived from *N*-(*p*-cyanobenzal)aniline[2] prompted a comparison of its behavior toward ethyl chloroformate with that of **1**. This reaction proved quite complex. With 1 equiv of acylating agent both mono- and diacylated products **21** and **23** were isolated (see Scheme III). With 2 equiv, the additional N-monoacylated product **22**, a second diacylated derivative **24** and a triacylated compound **25** were also formed. The relative amounts of these products varied somewhat with reaction temperature (see Table I).

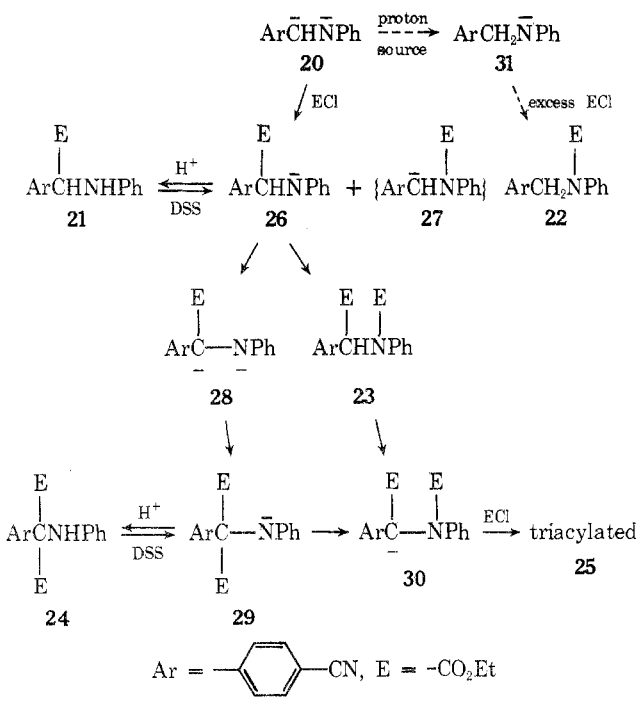
Scheme I
Acylation of the Benzophenone Anil Dianion



Scheme II
Proof of Structure for the Semibenzene Product



Scheme III
Acylation of Vicinal Dianion 20

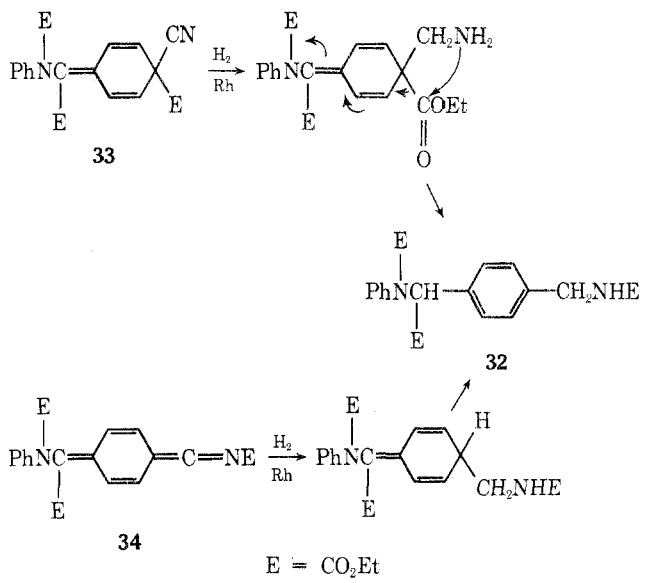


In order to analyze this behavior, the individual monoanionic species **26, 27, 29, 30,** presumed present in the reacting system, were generated by treating the corresponding protonated compounds with the disodium–stilbene (DSS) complex, followed by acylation with ethyl chloroformate of the anion in order to determine its behavior under the reaction conditions used in acylating dianion **20.** This approach failed to produce anion **27** from **22**—instead 4,4′-dicyanobibenzyl[6] was formed. The results are summarized in Table II and outlined below.

The anion **30** (from the C,N-diacylated compound **23** and DSS) produced the triacylated species **25** on acylation. Slow protonation of **30** by the solvent evidently occurred, since delaying the acylation for 16 hr produced only the starting material **23.** Rearrangement of the anion **29** (from the C,C-diacylated derivative **24** and DSS) occurred and only the C,N-diacylated product **23** was isolated after 16 hr. At shorter reaction times, acylation produced the triacylated species **25** indicating the intermediacy of anion **30** in the rearrangement.

Acylation of the anion **26** or **28** (from the C-acylated compound **21** and DSS) produced both the C,C-diacylated and the N-acylated compounds **24** and **22.** The latter product arose by acylation of the N-(*p*-cyanobenzyl)aniline which itself was formed by a reductive cleavage of **21** by DSS. Quenching of the anionic species showed this cleavage to account for about 30% of the reaction. Since no **23** was detected, the anion **29** was absent.

Isolation of the triacylated compound **25** was complicated by its thermal sensitivity[7] and column chromatography failed to give completely pure material. Thermal decomposition of **25** produced **24**; hydrogenation of **25** (2 mol of hydrogen reacted) gave a compound identified as **32** on the basis of its spectra and its synthesis (see Experimental Section). Two structures **33** and **34** are reasonable for the triacylated compound. Structure **33** is suggested by analogy



with the semibenzene product formed from the benzophenone anil dianion **1** and hydrogenation of the nitrile group followed by rearrangement provides **32.** In the case of **34,** hydrogenation followed by a proton shift produces **32.** Neither structure is completely satisfactory—**32** because a strained cyclic transition state must be proposed for the rearrangement and **34** because of the absence of a ketenimine band in the ir spectrum.

Discussion

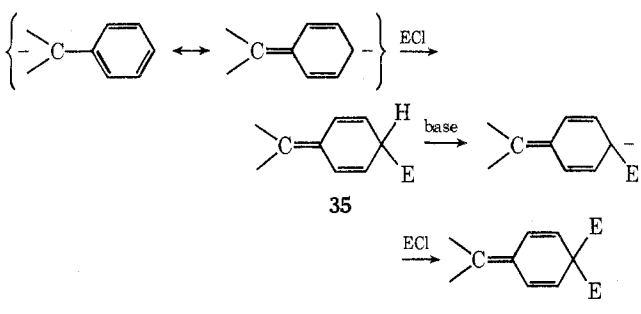
Of the two anionic centers in the vicinal dianions **1** and **20,** the carbanionic one is the more reactive. This is clearly evident in the acylation of **1** but is less obvious in the case of **20.** Here N-monoacylation (*i.e.*, **22**) is observed in significant quantities in reactions 3 and 4 (Table I). However, after acylation at the carbanionic center of **20,** the product **26** now contains a labile proton and can be transformed by a base to **28.** The base is, of course, the initial dianion **20**

and protonation of this produces **31** and/or the amine, *N*-(*p*-cyanobenzyl)aniline, which becomes the source of the *N*-monoacylated compound **22.** Note that the amount of **22** in reaction 3 closely approximates the amount of the *N*-(*p*-cyanobenzyl)aniline in reactions 1 and 2. The much lower temperature of reaction 4 retards proton transfer and the yield of **22** is less than in reaction 3.

Only in the presence of 2 equiv of ethyl chloroformate are reaction products observed which are clearly characteristic of proton transfer. Thus the anions **28** and **30,** formed by proton transfer, manifest themselves as the diacylated product **24** and the triacylated product **25.** In this regard, the amount of **24** in reaction 3 is of the same order of magnitude as the C-monoacylated product **21** of reaction 1. The difference between these values (9%) probably is due to rearrangement of **24** (through **29**) to **30.** Note that the sum of products **23** and **25** (both derived from **30**) in reaction 3 closely approximates the sum of the C,N-diacylated product **23** in reaction 1 plus the 9% difference.

A lower reaction temperature surpresses proton transfer but does not eliminate it. (Changing the counterion to lithium does not eliminate proton transfer insofar as the formation of **25** is concerned. Material balance was incomplete in these experiments; so the results are not discussed in detail.) Note the smaller amount of triacylated product **25** in reaction 4 compared to reaction 3 although the sum of **23** and **25** is equivalent in both reactions. The lower temperature also favors monoacylation over diacylation (reaction 2 *vs.* 1) and this larger amount of **21** (and its anion **28**) is reflected in the larger amount of **21** and **24** in reaction 4 compared to reaction 3. Again the combined amounts of **21** and **24** in reaction 4 approximates the amount of **21** in reaction 2.

In the case of the dianion **1,** proton transfer is observed only after acylation occurs in the ring as shown in the partial formulas. Rapid quenching of the reaction shortly after the addition of the second equivalent of ethyl chloroformate produced a complex mixture which included the *p*-carbethoxy derivative **13** arising by rearrangement of **35** during isolation.



Delocalization of the anionic charge into the aromatic ringe[8] accounts for the ring acylation of monoanions **5** and **30.** In the case of **5,** it would appear that steric crowding at the benzhydrylic anionic site sufficiently inhibits acylation that ring acylation predominates. The C,N-diacylated compound **10** can be obtained by acylation of the unrearranged monoanion **4** (Y = OEt) but in this case the second acyl group is introduced at the less crowded amine anionic center. Similar considerations apply to the monoanions formed on acylation of the dianion **20.** Thus the steric crowding present in **30** causes acylation to occur at more remote locations producing **25.** However, the less crowded benzylic anion **28** yields the "normal" product **24** on further acylation.

Rearrangement of the acylated anions is slow relative to acylation or proton transfer. Although the C,C-diacylated compound **24** is observed to rearrange at room temperature *via* **29** to the C,N-diacylated species **23, 24** is a product of the acylation of **20** with 2 equiv of ethyl chloroformate. Thus neutralization of the reaction medium occurs faster than the rearrangement.

The driving force for the rearrangement is the formation of a more stable anion.[9] In the case of **4,** a benzhydrylic anion (*i.e.,* **5**) is generated while with **29** the rearrangement produces **30,** a benzylic anion additionally stabilized by the carbethoxy group. The rearrangement also appears dependent upon the degree of association of the ion pair with loose ion pairs favoring rearrangement. Thus the polarity of the solvent affects the reaction, rearrangement occurring much more rapidly in the more basic solvent THF.[10] Similarly, the lithium cation with its greater Lewis acidity than that of sodium[11] slows the rearrangement markedly because of its tight association with the amine anionic center.

Experimental Section

Melting points, measured in a Mel-Temp apparatus, are uncorrected. Infrared spectra were recorded on a Beckman IR-10 in KBr pellets unless otherwise indicated. Nmr spectra were recorded on a Varian T-60 spectrometer in $CDCl_3$; chemical shifts are reported in δ units downfield from internal tetramethylsilane.

Reaction products were isolated by diluting the reaction mixture with water, ether extracting, drying the extract with magnesium sulfate, and removing the solvent on a rotary evaporator. Column chromatography of the crude products was performed on 0.05–0.20-mm silica gel using hexane–25% benzene as solvent except where otherwise specified.

The preparation of dianion[12] **1** from benzophenone anil and dianion[2] **20** from *N*-(*p*-cyanobenzal)aniline has been described.

Acylation of Benzophenone Anil Dianion 1 without Rearrangement. Preparation of 2, 6, 8 and 10. The dianion **1** (M = Na, 0.01 mol) in THF was cooled to −75° and treated with 1.1 g (0.01 mol) of ethyl chloroformate. The color faded from deep red to pink over a 15-min period and was then quenched with methanol. Isolation of the reaction products (2.97 g) followed by chromatography gave 2.8 g (79% yield) of ethyl *N*,2,2-triphenylglycinate, **2.** Recrystallization from ethanol gave an analytical sample: mp 111–113°; nmr 0.97 (t, J = 8 Hz, 3, CH_3), 4.14 (q, J = 8 Hz, 2, CH_2), 5.2 (broad s, 1, NH), 6.3–7.7 (m, 15, aromatics); ir (KBr) 3420 (NH), 1735 (C=O), 1600, 1500, 750, 690 (aromatic), 1240, 1180 (ester C—O) cm^{-1}.

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.

The above experiment was repeated except that the reaction mixture was treated with 1.4 g (0.01 mol) of methyl iodide prior to the methanol quench. The crude reaction product (3.3 g) was recrystallized from ethanol to give 2.48 g (72% yield) of ethyl *N*-methyl-*N*,2,2-triphenylglycine, **6** (R = Me): mp 84–85.5°; nmr 1.0 (t, J = 8 Hz, 3, CH_3), 2.88 (s, 3, NCH_3), 4.13 (q, J = 8 Hz, 2, CH_2), 6.5–7.6 (m, 15, aromatics); ir (film) 2830 (NCH_3), 1735 (C=O), 1600, 1500, 750 and 700 (aromatic CH), 1220 (ester C—O) cm^{-1}.

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.

The dianion **1** (M = Li, 0.01 mol) in THF was treated with 1.2 g (0.01 mol) of dimethylcarbamoyl chloride at −78°, allowed to react for 1 hr, and quenched with ethanol, and the isolated crude product was recrystallized from ethanol to give 1.38 g (42% yield) of **8**: mp 219–220°; nmr 2.83 (s, 6, NMe_2), 5.0 (broad s, 1, NH), 6.5–7.6 (m, 15, aromatics); ir (KBr) 3400 (NH), 1640 (C=O), 750, 740, 690 (aromatic) cm^{-1}.

Anal. calcd for $C_{22}H_{22}N_2O$: C, 79.96; H, 6.71; N, 8.48. Found: C, 79.80; H, 6.67; N, 8.29.

In the case of **1** (M = Na) similar results were obtained provided quenching occurred after a 15-min reaction at −78°.

The dianion **1** (M = Li, 0.01 mol) in DEE was cooled to −78°, treated with 1.1 g (0.01 mol) of ethyl chloroformate, and allowed to warm to 20° for 15 hr. It was then recooled to −78° and treated with a second 1.1-g amount (0.01 mol) of ethyl chloroformate. After warming the mixture to 20° for 9 hr, the crude product (3.6 g) was isolated. Chromatography gave 2.4 g (60%) of ethyl *N*-carbethoxy-*N*,2,2-triphenylglycinate, **10,** mp 106–108°. Two recrystallizations from pentane gave an analytical sample: mp 109–111°;

nmr 1.08 (t, J = 7 Hz, 3, CH_3), 1.40 (t, J = 7 Hz, 3, CH_3), 4.12 (q, J = 7 Hz, 2, CH_2), 4.45 (q, J = 7 Hz, 2, CH_2), 7.0–7.4 (m, 15 aromatics); ir (KBr) 1730 and 1700 (C=O), 1600, 1500, 750, 700 (aromatics), 1230 (broad, ester C—O) cm^{-1}.

Anal. Calcd for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47. Found: C, 74.65; H, 6.22: N, 3.46.

Acylation of the Benzophenone Anil Dianion, 1, with Ethyl Chloroformate and with Rearrangement. Preparation of 3, 7 (Y = OEt) and 11. The dianion 1 (M = Na, 0.01 mol) in THF was cooled to −75°, and ethyl chloroformate (1.1 g, 0.01 mol) was added. After 15 min the solution was allowed to warm to 20° (solution became dark red) and stand for 12 hr (solution A).

Quenching of solution A with methanol, isolation of the crude product (2.94 g), and chromatography with benzene–25% hexane gave 0.4 g of a benzhydrylaniline–benzophenone anil mixture followed by 2.0 g (61% yield) of crude *N*-carbethoxy-*N*-benzhydrylaniline, **3**, 57–60°. Recrystallization from pentane gave an analytical sample: mp 59–61°; nmr 1.1 (t, J = 7 Hz, 3, CH_3), 4.17 (q, J = 7 Hz, 2, CH_2), 6.71 (s, 1, CH), 6.9–7.3 (m, 15, aromatic H); ir (KBr) 1700 (C=O), 1300 (broad, C—O), 760, 720, 700, 680 (aromatic CH) cm^{-1}.

Anal. Calcd for $C_{22}H_{21}O_2N$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.88; H, 6.26; N, 4.06.

Solution A was treated with 1.4 g (0.01 mol) of methyl iodide at −78°. After warming and isolating the crude product (3.3 g), chromatography using benzene −25% hexane gave 2.6 g (75% yield) of crude **7** (R = CH_3, Y = OEt). Recrystallization from pentane gave an analytical sample: mp 88–91°; nmr 0.92 (t, J = 7 Hz, 3, CH_2CH_3), 1.73 (s, 3, CH_3), 3.91 (q, J = 7 Hz, 2, CH_2CH_3), 7.1–7.6 (m, 15, aromatic H); ir (KBr) 1710 (C=O), 1600, 1490, 760, 700 (aromatic CH) cm^{-1}.

Anal. Calcd for $C_{23}H_{23}O_2N$: C, 79.97; H, 6.71; N, 4.06. Found: C, 79.85; H, 6.69; N, 3.90.

Solution A was treated at −78° with 1.3 g (0.01 mol) of benzyl chloride and after 3 hr the reaction product (4.1 g) was isolated. Chromatography of 1 g using benzene 40% hexane gave 0.9 (88%) of **7** (R = $PhCH_2$, Y = OEt), mp 186–190°. An analytical sample was obtained by recrystallization from diethyl ether: mp 188–190°; nmr 0.87 (t, J = 7 Hz, 3, CH_2CH_3), 3.27 (s, 2, CH_2Ph), 3.86 (q, J = 7 Hz, 2, CH_2CH_3), 6.2–7.5 (m, 20, aromatic H).

Anal. Calcd for $C_{29}H_{27}NO_2$: C, 82.63; H, 6.46; N, 3.32. Found: C, 82.79; H, 6.50; N, 3.14.

Solution A was treated at −78° with 1.1 g (0.01 mol) of ethyl chloroformate and allowed to warm to 20°. The crude product (4.0 g) was chromatographed using benzene–25% hexane to give 1.4 g of **3** (42% yield). Continuing the elution with chloroform gave 2.4 g (50% yield) of **11** as a gum. The crude **11** was treated with activated charcoal in hot ethanol and the filtrate was cooled to 10°. After several days, **11** crystallized out (0.65 g): mp 83.5–85°; nmr 1.05 and 1.23 (overlapping t, J = 7 Hz, 9, CH_3), 4.16 and 4.20 (overlapping q, J = 7 Hz, 6, CH_2), 6.0–6.9 (m, 4, vinyl H), 7.0–7.5 (m, 10, aromatic H); ir (KBr) 1730, 1710 (C=O), 1500, 750, 690 (aromatic), 1240 (ester C—O) cm^{-1}; uv (EtOH) λ_{max} 230 (ϵ 1.5 × 10^4), 250 (sh, 1.3 × 10^4), 315 (2.0 × 10^4).

Anal. Calcd for $C_{28}H_{29}NO_6$: C, 70.71; H, 6.15; N, 2.95. Found: C, 70.93; H, 6.38; N, 2.89.

This experiment was repeated but the solution, after treatment with the second equivalent of ethyl chloroformate, was quenched with water after a 15-min reaction. Chromatography gave 2.16 g (65% yield) of **3** and 0.80 g (20% yield) of **13** identified on the basis of its spectral properties. No semibenzene **11** could be detected.

Reaction of the Benzophenone Anil Dianion, 1, with Dimethylcarbamoyl Chloride with Rearrangement. Preparation of 7 (R = Me, Y = NMe_2), 9 and 12. Reactions of the rearranged anion **5** (Y = NMe_2) proceeded in the same manner as that of **5** (Y = OEt). Thus, the reaction product of **1** (M = Na, 0.01 mol) in THF with 1.2 g (0.01 mol) of dimethylcarbamoyl chloride at −78° was allowed to warm to 20° to complete the rearrangement and then recooled to −78° (solution B).

Treatment of the solution B with methanol gave 3.15 g of crude product. Chromatography gave 1.63 g (50% yield) of **9**, mp 105–108°. A second fraction (1.13 g) eluted later which contained **9** and a second unidentified compound. Recrystallization of the crude **9** from hexane gave an analytical sample: mp 107–109°; ir (Nujol) 1670 (C=O, 1500, 1210, 1170, 750, 740, 690 cm^{-1}; nmr 2.73 (s, 6, NMe_2), 6.8–7.4 (m, 16, aromatic and benzylic H's).

Anal. Calcd for $C_{22}H_{22}N_2O$: C, 79.96; H, 6.71; N, 8.48. Found: C, 80.17; H, 6.48; N, 8.52.

Treatment of solution B with 1.4 g (0.01 mol) of methyl iodide and warming to 20° gave 3.2 g of isolated crude product. Chromatography gave 2.15 g (62% yield) of **7** (R = Me, Y = NMe_2), mp 130–145°. An analytical sample was obtained by column chromatography followed by two recrystallizations from hexane–25% benzene: mp 158–159°; ir (Nujol) 1660 (C=O), 1490, 770, 710, 700 (phenyl), 1180 cm^{-1}; nmr 2.30 (s, 3, CH_3),2.73 (s, 6, NMe_2), 6.5–7.6 (m, 15, aromatics).

Anal. Calcd for $C_{23}H_{24}N_2O$: C, 80.20; H, 7.02; N, 8.13. Found: C, 80.37; H, 7.18; N, 8.07.

Treatment of the rearranged anion **5** (Y = NMe_2) at −78° with 1.1 g (0.01 mol) of ethyl chloroformate followed by warming to 20° gave 3.66 g of isolated crude product. Chromatography using benzene gave 1.15 g (35% yield) of **9** followed by 0.9 g (19% yield) of **12.** Purification was effected by rechromatography and recrystallization from hexane–25% benzene: mp 113–115°; nmr 1.23 (t, J = 7 Hz, 6, CH_2CH_3), 2.77 (s, 6, NMe_2), 4.28 (q, J = 7 Hz, 4, CH_2CH_3), 5.9–6.3 (m, 2, vinyl H), 6.7–7.5 (m, 12, vinyl and aromatic H's); ir (Nujol) 1740, 1730 and 1670 (C=O's), 1500, 750, 700 (aromatics), 1250 (ester C—O) cm^{-1}; uv (EtOH) λ_{max} 264 (ϵ 1.74 × 10^4), 337 (1.94 × 10^4) nm.

Anal. Calcd for $C_{28}H_{30}N_2O_5$: C, 70.86; H, 6.37; N, 5.90. Found: C, 71.02; H, 6.51; N, 5.78.

Reactions of the Semibenzene 11. Pyrolysis of 11. The semibenzene **11** (0.75 g) was heated under nitrogen for 0.5 hr at 250°. The dark residue was chromatographed to give 0.5 g of product having nmr and ir spectra identical with thosof **13.**

Hydrolysis of 11. The semibenzene **11** (0.65 g) was dissolved in 50 ml of ethanol, 10 ml of 10% aqueous sodium hydroxide was added, and the mixture was refluxed 0.5 hr. Acidification (aqueous HCl) precipitated 0.4 g of product whose nmr and ir spectra were identical with those of **15.**

Hydrogenation of 11. The semibenzene **11** (0.8 g, 0.0017 mol) was hydrogenated in 20 ml of ethanol with 0.05 g of 5% Pd on charcoal as catalyst. Hydrogen uptake (119 cm^3 at NTP) corresponded to 3 mol/mol of **11.** The crude product, purified by short-path vacuum distillation using a sublimation apparatus, was a clear gum showing no absorption at 310 nm: nmr 1.0–1.4 (m, CH_3) and 1.4–2.6 (m, cyclohexyl H) (combined area 18), 3.9–4.4 (m, 6, CH_2), 5.04 (d, J = 10 Hz, 1, benzylic H), 6.5–7.4 (m, 10, aromatic H); ir (film) 1730 and 1700 (C=O), 1240 (broad, ester C—O, 750, 700 (aromatic) cm^{-1}.

Anal. Calcd for $C_{28}H_{35}NO_6$: C, 70.05; H, 7.38; N, 2.76. Found: C, 69.83; H, 7.33; N, 2.91.

Preparation of *N*-(*p*-Carboxybenzhydryl)aniline, 18. *p*-Benzoylbenzoic acid,[13] **16** (10 g, 0.044 mol), was converted to its corresponding anil **17** by the procedure previously described.[10] This product, mp 139–145°, hydrolyzed rapidly on attempted purification; consequently it was directly reduced. The crude anil, **17** (13 g), was dissolved in 50 ml of 0.2 *N* sodium hydroxide and 0.5 g (0.013 m) of sodium borohydride was added. After 24 hr of stirring, the solution was acidified to precipitate 8 g of crude **18.** Recrystallization from ethanol provided an analytical sample: mp 197–200°; nmr 4.94 (broad s, 2, NH and CO_2H), 5.62 (s, 1, CH), 6.5–7.4 (m, 10, C_6H_5's), 7.56 and 8.15 (AB q, J = 8 Hz, 4, *p*-C_6H_4); ir (KBr) 3360 (NH, OH), 1650 (C=O), 1600, 1530, 750, 700, 680 (aromatic), 1440, 1320, 920 (CO_2H).

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.31; H, 5.86; N, 4.37.

Preparation of *N*-Carbethoxy-*N*-(*p*-carboxybenhydryl)aniline, 15. A mixture of 2 g (0.005 mol) of **18** and ethyl chloroformate (1.1 g, 0.01 mol) in 20 ml of 1:1 benzene–pyridine was refluxed for 6 hr. After removal of the solvent, the product was dissolved in aqueous NaOH, the solution was filtered, and precipitation was done by acidification. Recrystallization from benzene–hexane gave 0.5 g of **15:** mp 149–151°; nmr 1.10 (t, J = 7 Hz, 3, CH_3), 4.21 (q, J = 7 Hz, 2, CH_2), 6.74 (s, 1, CH), 7.0–7.4 (m, 10, C_6H_5's), 7.46 and 8.11 (AB q, J = 8 Hz, 4, *p*-C_6H_4), 10.75 (s, 1, CO_2H); ir (KBr) 3200 (broad, OH), 1690 (C=O) 1600, 1500, 760, 700 (aromatics).

Anal. Calcd for $C_{23}H_{21}NO_4$: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.60; H, 5.48; N, 3.50.

Preparation of *N*-(*p*-Carbethoxybenzhydryl)aniline, 19. Esterification of **18** was effected by refluxing in excess ethanol with sulfuric acid as catalyst. The crude product was purified by recrystallization from ethanol: mp 101–103°; nmr 1.35 (t, J = 7 Hz, 3, CH_3), 4.0 (broad s, 1, NH), 4.38 (q, J = 7 Hz, 2, CH_2), 5.56 (s, 1 CH), 6.5–7.4 (m, 10, C_6H_5's), 7.50 and 8.06 (AB q, J = 8 Hz, 4, *p*-C_6H_4); ir (KBr) 3380 (NH), 1700 (C=O), 1600, 1500, 750, 690 (aromatic), 1270 (broad, ester C—O) cm^{-1}.

Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.74; H, 6.48; N, 4.16.

Table I
Acylation of Dianion 20

Reaction	Temp, °C	Ethyl chloroformate[a]	Amine[c]	Product compn[b] Monoacylated 21	22	Diacylated 23	24	25
1	20	1	35	29	1	36		
2	−78	1	30	40	1	29		
3	20	2		1	29	22	20	28
4	−78	2		11	6	42	24	16

[a] Moles per mole of **20**. [b] Area per cent by vpc. [c] *N*-(*p*-cyanobenzyl)aniline.

Preparation of *N*-Carbethoxy-*N*-(*p*-carbethoxybenzhydryl)aniline, 13. Acylation of **19** was effected in the same manner as used in the conversion of **18** to **15**. The crude **13** was obtained as a gum by short-path distillation at 0.05 mm and 150° using a sublimation apparatus: nmr 1.12 (t, J = 7 Hz) and 1.38 (t, J = 7 Hz, 6, CH_3's), 4.17 and 4.41 (overlapping q, J = 7 Hz, 4, CH_2's), 6.71 (s, 1, CH), 6.9–7.3 (m, C_6H_5's), 7.39 and 8.05 (AB q, *p*-C_6H_4) (total 14); ir (film) 1720 (broad, C=O), 1270 (broad, ester C—O), 1600, 1500, 760, 690 (aromatics) cm^{-1}.

Anal. Calcd. for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47. Found: C, 74.45; H, 6.46; N, 3.21.

General Procedure for the Acylation of Dianion 20. A THF solution of the dianion **20** (M = Na, 0.01 mol) was treated with ethyl chloroformate (0.01 or 0.02 mol) at −78° (or at room temperature). The adduct color changed from deep red to dark green. After stirring for 2 hr at −78°, the reaction mixture was warmed to room temperature overnight. The mixture was diluted with water, and the reaction product isolated by ether extraction.

The ether extracts were analyzed by vpc (flame ionization detectors) using a 5 ft × ⅛ in. column pack with 3% SE-52 on Varaport 30 and 5 ft × ⅛ in. column packed with 3% XE-60 on Varaport 30 at 195° with a helium flow rate of 30–40 cm^3/min, the latter column being necessary to obtain the ratio of the two diacylated products, **23** and **24**. Peaks were identified by "spiking" with authentic samples. The results are summarized in Table I.

Reaction with 1 equiv of Ethyl Chloroformate. Isolation of Ethyl α-Anilino(*p*-cyanophenyl)acetate, 21, and Ethyl α-(*N*-carbethoxy anilino)-*p*-cyanophenylacetate, 23. The standard run was quenched with ethyl chloroformate (1.08 g, 0.01 mol) at −78°. The crude product (2.48 g) was chromatographed and three fractions were collected, the first two being eluted with benzene and the third with chloroform.

The first fraction was distilled to give 0.81 g (33%) of **21** as a pale yellow oil containing some *N*-(*p*-cyanobenzyl)aniline. Two additional distillations gave an analytical sample of **21**, bp 189–192° (0.08 mm).[14]

Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75; N, 10.00. Found: C, 72.63; H, 5.68; N, 9.85.

Reaction with 2 equiv of Ethyl Chloroformate at −78°. Isolation of Diethyl *p*-(Cyanophenyl)anilinomalonate, 24. The above reaction was repeated using 2 equiv of ethyl chloroformate (2.17 g, 0.02 mol) and the crude oil (3.53 g) was chromatographed. The first fraction (1.11 g) eluted with benzene was found to contain two components, **21** and **24**. This fraction was rechromatographed on 60 g of silica gel with benzene as eluent to give as the first component 0.52 g (15%) of **24**. Recrystallization from ethanol gave a white crystalline solid: mp 79–80°; ir (KBr) 3400 (NH), 2980, 1380, 1360 (aliphatic CH), 2220 (CN), 1760 (broad C=O), 1600, 1500 (aromatic C—C), 1020 (–C(=O)O–) cm^{-1}; nmr (D_2O washed) 1.11 (t, 6, J = 7 Hz, CH_3CH_2), 4.22 (q, 4, J = 7 Hz, CH_3CH_2), 6.3–7.4 (m, 5, NC_6H_5), 7.67 and 8.04 (AB q, 4, J_{AB} = 8 Hz, $-C_6H_4CN$).

Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.05; H, 5.64; N, 7.70.

The second component which eluted (0.40 g, 11%) was distilled to give a pale yellow oil, bp 189–192° (0.09 mm). The ir and nmr spectra agreed in all respects with those of **21**.

Continuing the elution of the original silica gel column with chloroform gave a second fraction, 2.10 g. Recrystallization from ethanol afforded 0.65 g (18%) of **23**, mp and mmp 84–85°. Vpc analysis of the filtrate showed the presence of **23** and **25**. Isolation of **25** is described below.

Isolation and Hydrogenation of 25. Preparation of Ethyl α-(*N*-Carbethoxyanilino)-*p*-(*N*-carbethoxyaminomethyl)phenylacetate, 32. The preceding reaction was repeated. A portion of the crude product (2.75 g) was chromatographed with diisopropyl ether as eluent. Two major fractions were collected. The first fraction (0.93 g) which contained a mixture of **21** and **24** was discarded. The second fraction (1.57 g) consisting of **23, 21,** and **25** was rechromatographed with diisopropyl ether as eluent. A center fraction (1.05 g) was collected. Vpc analysis showed 30% of **23** and 70% of **25**; the nmr showed multiplets at 1.0–1.6 (CH_3CH_2), 4.0–4.5 (CH_3CH_2), and 7.1–8.0 (vinyl and aromatic H's) and a singlet at 5.83 (CH of **23**). Correcting the spectrum for the known content of **23** indicated three carbethoxy groups per mole of **25**. This fraction was hydrogenated in ethanol (60 ml) at atmospheric pressure of H_2 at 22° with 5% of rhodium on carbon (0.5 g) for 24 hr, during which time a total of 135 cm^3 of hydrogen was taken up. The crude product was chromatographed with chloroform as eluent. One major fraction (0.6 g), a viscous pale yellow oil of **32**, was collected which had a boiling point higher than 210° at 0.1 mm pressure: ir (film), 3370 (broad NH), 2990, 2950, 1380 (aliphatic CH), 1750, 1700 (broad C=O), 1600, 1500 (aromatic C—C), 1050 and 1030 (–C(=O)O–) cm^{-1}; nmr (D_2O washed) 1.1–1.4 (m, 9, CH_2CH_3), 4.0–4.5 (m, 8, CH_2CH_3 and $C_6H_4CH_2NH$), 5.90 (s, 1, benzylic H), 7.1–7.3 (m, 9, aromatic H).

Anal. Calcd for $C_{23}H_{28}N_2O_6$: C, 64.46; H, 6.59; N, 6.54. Found: C, 64.65; H, 6.45; N, 6.24.

Reaction with 2 equiv of Ethyl Chloroformate at Room Temperature. Isolation of Ethyl *N*-(*p*-Cyanobenzyl)-*N*-phenylcarbamate, 22. The above reaction was repeated at room temperature. The crude product (3.50 g) was chromatographed with benzene as eluent. The first fraction 0.6 g (17.1%) was recrystallized from ethanol to give **22**, mp and mmp 80–81°. The ir and nmr spectra agreed with those of the authentic sample of **22** in all aspects.

Preparation of Ethyl *N*-(*p*-Cyanobenzyl)-*N*-phenylcarbamate, 22. Ethyl chloroformate (0.35 g, 0.0006 mol) was added in one portion to a stirred solution of *N*-(*p*-cyanobenzyl)aniline (0.67 g, 0.0003 mol) in ether (15 ml). The mixture was gently refluxed for 2 hr, washed with aqueous base, dried, and evaporated. The residue after recrystallization from ethanol gave 0.92 g (86% yield) of **22**: mp 81–82.5°; ir (KBr) 2990, 1390, 1370 (aliphatic CH), 2220

Table II
Reactions of Model Anions

Substrate	Anion	Reaction conditions: Time,[a] hr	Reagent	Product compn, %: Monoacylated 21	22	Diacylated 23	24	25
23	**30**	0.5	ECl[b]			37		63
		16	ECl			100		
24	**29**	16	H_2O or ECl			100		
		0.5	ECl	3		32	44	21
21	**26** (**28**)	0.5	ECl	2	18		80	
		16	H_2O	69	(31)[c]			

[a] Time of reaction with DSS. [b] Ethyl chloroformate. [c] *N*-(*p*-Cyanobenzyl)aniline.

(CN), 1700 (C=O), 1600, 1500, (aromatic C—C), 1010, and 1030 (-C(=O)O-) cm^{-1}; nmr 1.22 (t, 3, J = 7 Hz, CH_3CH_2), 4.22 (q, 2, J = 7 Hz, CH_3CH_2), 4.95 (s, 2, CH_2NPh), and 7.0–7.7 (m, 9, aromatic H).

Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75; N, 10.00. Found: C, 72.96; H, 5.85; N, 9.81.

General Procedure for the Reaction of *N*-(*p*-Cyanobenzyl)aniline Derivatives with the Disodium-Stilbene Complex and Ethyl Chloroformate. A THF solution of the disodium-stilbene complex was treated with a solution of an equivalent amount of the selected ester in THF (*ca.* 10 ml) at room temperature. The color changed from deep red of the stilbene complex to pale yellow or colorless immediately. The reaction was stirred and quenched with ethyl chloroformate. After 24 hr of additional stirring, this reaction mixture was diluted with water; the reaction product was isolated and analyzed by vpc using the same conditions as described earlier. The results are summarized in Table II.

Preparation of Ethyl α-(*N*-Carbethoxyanilino)-*p*-(*N*-carbethoxyaminomethyl)phenylacetate, 32. Ethyl α-(*N*-carbethoxyanilino)-*p*-cyanophenylacetate, **23** (0.704 g, 0.002 mol), was hydrogenated in ethanol (65 ml) with 5% rhodium on carbon (0.2 g) as a catalyst at atmospheric pressure of hydrogen for 24 hr, during which time 96 cm^3 of hydrogen was consumed. The crude hydrogenated product was then dissolved in anhydrous ether (20 ml) and ethyl chloroformate (0.216 g, 0.002 mol) was added. After being stirred for 24 hr, the mixture was treated with 3*N* sodium hydroxide (1.0 ml), and the organic product was isolated (0.69 g) and chromatographed with chloroform as eluent. Of the two fractions obtained, the first (0.21 g) contained incompletely hydrogenated material. The second fraction (0.26 g, 30% yield) was a pale yellow oil whose ir and nmr spectra were identical with those of **32** prepared by hydrogenation of the tricarbethoxy compound **25**.

Thermal Decomposition of 25. A small amount of **25** placed in a test tube under nitrogen was heated in a metal block at 260° for 6 hr. The product was analyzed by vpc and found to contain 90% of **23** and 10% of ethyl *N*-(*p*-cyanobenzyl)-*N*-phenylcarbamate, **22**. The latter compound was present in the initial **25** as an impurity.

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Registry No.—**1** (M = Na), 53418-39-6; **1** (M = Li), 53418-40-9; **2**, 33672-87-6; **3**, 7714-87-6; **6** (R = Me), 33672-88-7; **7** (R = CH_3, Y = OEt), 53418-41-0; **7** (R = $PhCH_2$, Y = OEt), 53418-42-1; **7** (R = Me, Y = NMe_2), 53418-43-2; **8**, 53418-44-3; **9**, 53418-45-4; **10**, 42391-89-9; **11**, 42391-85-5; **12**, 53418-46-5; **13**, 42391-88-8; **14**, 42391-86-6; **15**, 42391-87-7; **17**, 53418-47-6; **18**, 53418-48-7; **19**, 42391-91-3; **20** (M = Na), 53418-49-8; **21**, 40577-15-9; **22**, 53418-50-1; **23**, 40577-09-1; **24**, 53418-51-2; **25**, 53418-52-3; **32**, 53418-53-4; ethyl chloroformate, 541-41-3; dimethylcarbamoyl chloride, 79-44-7; *N*-(*p*-cyanobenzyl)aniline, 37812-49-0.

References and Notes

(1) Preliminary reports on some aspects of this study have appeared: (a) J. G. Smith and G. E. F. Simpson, *Tetrahedron Lett.*, 3295 (1971); (b) *ibid.*, 1947 (1973).
(2) J. G. Smith and I. Ho, *J. Org. Chem.*, **38**, 2776 (1973).
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(4) R. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Lett.*, 2033 (1964).
(5) This synthesis is considerably more satisfactory than that reported in our preliminary communication.[1b]
(6) This interesting reaction is presently being investigated.
(7) In vpc analyses, the injection and detector temperatures were 210°; at 260°, **25** was not detected.
(8) See for example (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N.Y., 1965, pp 54–55; (b) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963); (c) R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Commun.*, 117 (1969).
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(13) E. Wertheim, *J. Amer. Chem. Soc.*, **55**, 2540 (1933).
(14) Spectral properties have been reported.[2]

Vinylogous Systems. III. Mass Spectra of Vinylogous Imides[1]

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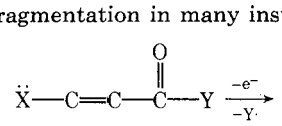
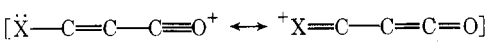
The mass spectra of sixteen acyclic, isocyclic, and heterocyclic vinylogous imides, -(O)CNC=CC(O)-, have been examined. Stereochemical and structural factors strongly influence the preferred fragmentation pathways, with oxazolium and/or isoxazolium fragment ions playing prominent roles in the decomposition of acyclic and isocyclic compounds.

Several reports have appeared concerning the mass spectral fragmentations of vinylogous amides (**1a**),[2-4] esters (**1b**),[3] urethanes (**1c**),[2] and *N*-acylurethanes (**1d**).[5] Loss of Y from the molecular ion of **1** to form the resonance stabilized α,β-unsaturated acylium ion **2** is the major initial fragmentation in many instances, and then **2** usually constitutes the base peak. Radical ions analogous to **2a** are also important intermediates in the fragmentation patterns of uracils.[6,7]



1a, X = R_2N; Y = R
b, X = RO; Y = R
c, X = R_2N; Y = OR
d, X = RC(O)NH; Y = OR



2a, X = R_2N
b, X = RO
c, X = RC(O)NH

The present study of vinylogous imides, β-amido α,β-unsaturated ketones, -(O)CNC=CC(O)-, had two main thrusts. First, we wanted to extend previous results by including compounds of greater stereochemical variety in our work.[8] Second, it seemed likely that the initial fragmentation of the imides would be unique, leading not to ion **2c**,[9] but, if stereochemically permissable, to highly stable oxazolium and/or isoxazolium daughter ions.[10] Earlier work in this laboratory[1,11] made available a number of acyclic, isocyclic, and heterocyclic vinylogous imides. We herewith report the mass spectral results for these compounds.

Experimental Section

Melting points are uncorrected. Mass spectra were obtained on an A.E.I. MS-9 mass spectrometer operating at 70 eV. Samples were introduced *via* a direct insertion probe. The inlet system tem-