Acylation of Vicinal Dianions. Further Observations Concerning Proton Transfer and Rearrangements during Reaction

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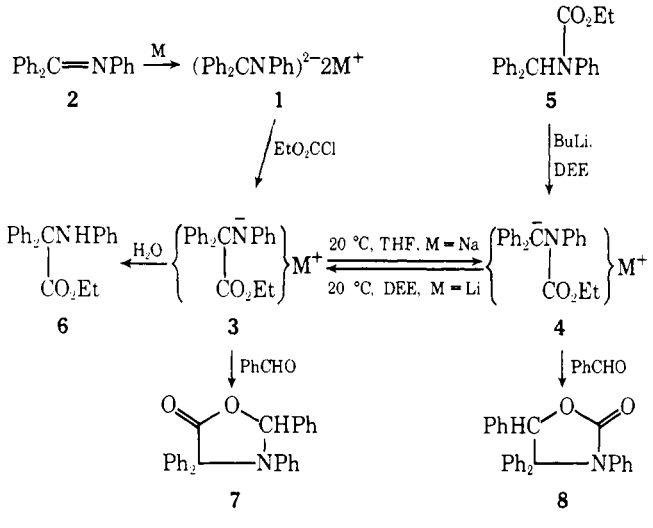
The dianion 1 formed by reducing benzophenone anil with alkali metals is used as a model compound in examining reactions involving acyl chlorides and a series of aliphatic chloro esters. The previously reported C → N rearrangement of an ethoxycarbonyl group derived from ethyl chloroformate is shown to be reversible and dependent on the cation involved. A similar behavior of 2-chloroethyl chloroformate is also described. Successful alkylations of the dianion by ethyl chloroacetate and ethyl 3-chloropropionate are obtained. However, with ethyl 4-chlorobutyrate and with propionyl chloride, enolate anion formation becomes a serious side reaction forming, in the case of the chloro ester, a complex series of products.

The dianionic species, **1**, formed by the reductive metalation of benzophenone anil (**2**) with alkali metals has served as a model compound in studying the chemical behavior of such anions. Recently, it was reported[1] that preferential acylation occurred at the benzhydrylic carbon of 1 to produce the functionalized monoanion **3** (Scheme I). This anion was also

Scheme I. Formation and Reactions of the Ethoxycarbonyl Monoanions



observed[1] to rearrange rapidly in tetrahydrofuran (THF) to the isomeric anion **4** with sodium or potassium as counterion. In contrast, with lithium as counterion and diethyl ether as solvent, no rearrangement of **3** was detected. In the present report further observations on the acylation of **1** with acid chlorides and with esters are described.

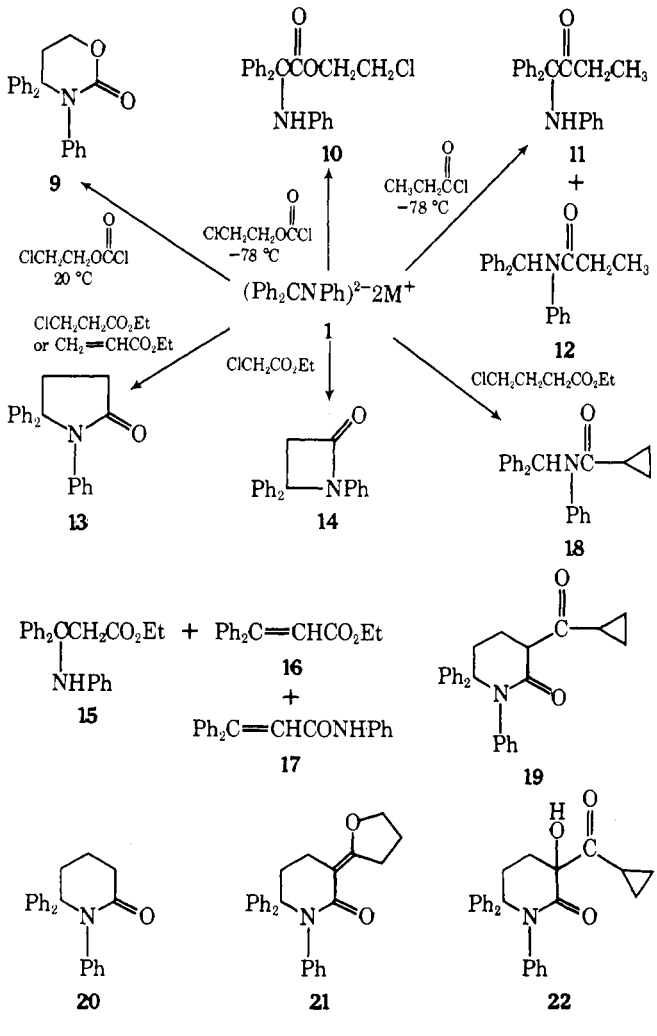
Results and Discussion

The stability of anion **3** (M = Li) in diethyl ether[1] prompted the synthesis of its isomer **4** (M = Li) by deprotonation of ethyl *N*-benzhydryl-*N*-phenylcarbamate (**5**) with *n*-butyllithium. Reaction of the anionic product so formed with benzaldehyde produced **7** rather than the expected cyclic urethane, **8**, which was obtained from benzaldehyde and **4** (M = Na) in THF. The structure **7** was assigned on the basis of an ester carbonyl absorption band in the infrared spectrum and on the hydrolysis of **7** in the presence of 2,4-dinitrophenylhydrazine which produced benzaldehyde 2,4-dinitrophenylhydrazone and α-anilinodiphenylacetic acid. The rearrangement of anion **4** (M = Li) to **3** (M = Li) prior to its reaction with benzaldehyde was confirmed by repeating the reaction of **5** and *n*-butyllithium and protonating the anionic product to give **6**, the rearranged *C*-ethoxycarbonyl compound.

This interesting interconversion of anions **3** and **4**, seemingly dependent on the associated alkali metal cations, prompted an examination of the reactivity of **1** toward bifunctional reagents in which one functional group served as the acylating agent.

With 2-chloroethyl chloroformate it was expected that the cation effect just described might lead to different products. However, with either lithium or sodium as the cation, the same product, 3,4,4-triphenylperhydro-1,3-oxazin-2-one (**9**), (Scheme II) was formed. By quenching the reaction at −78 °C

Scheme II. Reactions with Bifunctional Reagents



after a few minutes, a good yield of 2-chloroethyl α-anilinodiphenylacetate (10) was obtained, establishing again that the initial stage of the reaction was acylation at the benzhydrylic carbon.

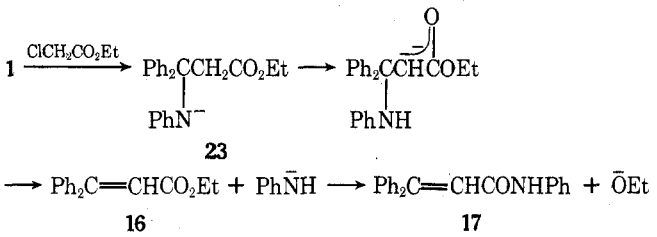
Evidently anions of the type 3 and 4 are in equilibrium. In the case of the reaction with 2-chloroethyl chloroformate, the monoanion analogous to 4 is intramolecularly alkylated by the 2-chloroethyl group forming 9 and is thus removed from the equilibrium. However, the monoanion analogous to 3 undergoes rearrangement faster than it is alkylated.

The successful C-acylation of dianion 1 by 2-chloroethyl chloroformate prompted a similar experiment with propionyl chloride. While a small yield of the C-acylated product 11 was isolated, the chief product was *N*-benzhydryl-*N*-phenylpropionamide (12). Evidently the basicity of the dianion 1 resulted chiefly in proton abstraction from the propionyl chloride by the carbanionic site of 1 forming methylketene.[2] Subsequent reaction of the methylketene produced the observed propionamide.

The ethyl esters of chloroacetic, 3-chloropropionic, and 4-chlorobutyric acid were examined to assess the relative amounts of acylation vs. alkylation. Generally, these reactions were accompanied by enolate anion formation as a complicating side reaction.

The dianion 1 (M = Li) reacted smoothly with ethyl chloroacetate to produce 1,4,4-triphenyl-2-azetidinone (14) in good yield. However, with sodium or potassium as counterions, the reaction was much more complex and proved to be time dependent. At short reaction times and low temperatures, both the β-lactam 14 and the alkylation product 13 were isolated. At longer reaction times, substantial amounts of ethyl 3,3-diphenylacrylate (16) were detected and at still longer reaction times the amount of 16 decreased while *N*,3,3-triphenylacrylamide (17) was isolated.

On the basis of this time-dependent sequence of products, it is suggested that the reactive[3] α-chloro ester rapidly alkylates dianion 1 to produce 23 which is converted to its enolate



anion when sodium or potassium are present as counterions. Cyclization to the β-lactam is prevented and a slow reverse Michael reaction occurs to produce the acrylic ester 16 and, by a slower aminolysis reaction with aniline, the anilide 17 is formed. The success of the reaction with lithium as counterion in forming the β-lactam 14 reflects a slower rate of enolate anion formation relative to acylation at the amine anionic site.

The complete disappearance of the β-lactam 14 which was formed concomitantly with 15 in experiments of short duration is due to base-induced ring opening of 14 to the anilide 17. This reaction was demonstrated to occur with *n*-butyllithium as the base.

Ethyl 3-chloropropionate reacted rapidly with 1 at −78 °C to produce 1,5,5-triphenyl-2-pyrrolidone (13). Dehydrohalogenation followed by a Michael addition to the ethyl acrylate so formed cannot explain the rapidity of the reaction since such a dehydrohalogenation would result in protonation of the benzhydrylic carbon of 1 and prevent formation of the observed product. However, ethyl acrylate did react with the dianion 1 to produce the pyrrolidone 13 showing that Michael addition reactions are possible with such anionic species as 1.

Ethyl 4-chlorobutyrate produced two compounds 18 and 19 in addition to a considerable quantity of *N*-benzhydrylaniline. Identification of 18 was based on its NMR spectrum and by synthesis of an authentic sample. The second compound was assigned structure 19 on the basis of its ir, NMR, and mass spectra. Both the keto and enol forms of 19 were detected by characteristic resonances in the NMR spectrum.

The large amount of *N*-benzhydrylaniline indicated that enolate anion formation was proceeding much faster than alkylation. Intramolecular alkylation of the enolate anion formed from ethyl 4-chlorobutyrate is known to occur rapidly[4] and produce ethyl cyclopropanecarboxylate. By terminating an experiment after a few minutes reaction at −78 °C, the rapid formation of ethyl cyclopropanecarboxylate was demonstrated. In experiments of longer duration, this ester reacted with dianion 1 or its monoprotonated derivative to give 18.

The formation of 19 demonstrated that some alkylation proceeded competitively with enolate anion formation. After cyclization to the piperidone 20 a Claisen condensation with the ethyl cyclopropanecarboxylate generates 19.

In an attempt to reduce the extent of enolate anion formation, the dianion 1 (M = Li) was used. Indeed, the amount of *N*-benzhydrylaniline was reduced and 1,6,6-triphenyl-2-piperidone (20) was isolated as well as the previously isolated 18 and 19. However, the reaction mixture was rather complex with two additional products 21 and 22 being detected. Presumably 21 arose by Claisen condensation of 20 and ethyl 4-chlorobutyrate followed by intramolecular O-alkylation of the enolate anion of this condensation product. The minor product, 22, probably arose by oxidation[5] of the enolate anion of 19 during isolation.

In summary, the results described here indicate that those dianions formed by reductive metalation of azomethines are more versatile synthetically than their hydrocarbon analogues. With reagents containing labile protons, proton transfer is an interfering reaction but some measure of control is available. In particular, with lithium as the counterion and/or with reagents of sufficient reactivity (e.g., ethyl chloroacetate or ethyl 3-chloropropionate) successful reactions are effected. The reversible migration of ethoxycarbonyl groups which has been described earlier and is elaborated upon here is also a reaction with possibilities that bear further exploration.

Experimental Section

Melting points were measured in a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrometer and NMR spectra were recorded on a Varian T-60 spectrometer in deuteriochloroform (unless otherwise specified) with chemical shifts reported in δ units downfield from internal tetramethylsilane. Mass spectra were determined with an AEI MS-30 double beam double focusing mass spectrometer at 70 eV with perfluorokerosene in the reference beam. Vapor phase chromatography (VPC) was performed on a Varian 1520 instrument with flame ionization detectors. Analyses were performed by MHW Laboratories, Garden City, Mich.

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

The preparation of dianion 1 from benzophenone anil has been described[6] elsewhere.

***N*,3,3-Triphenylacrylamide (17)** was prepared by the dehydration[7] of phenyl 3-hydroxy-3,3-diphenylpropionamide, mp 134–135 °C (reported 136–137 °C).

Preparation of 3,4,4,5-Tetraphenyl-1,3-oxazolid-2-one (8). The monoanion 4 (M = Na) was prepared as previously described[1] and treated with 1.1 g (0.01 mol) of benzaldehyde at 20 °C. After 12 h the reaction product (3.7 g) was isolated and chromatographed to give 2.7 g of crude 8 (69%), mp 210–215 °C. Recrystallization from ethanol

gave an analytical sample: mp 216–218 °C; ir (KBr) 1750 (C=O), 1370 (C–O), 1600, 1500, 760, 720, 700, 690 cm^{-1}; NMR δ 6.47 (s, 1, PhC**H**), 6.8–7.8 (m, 20, aromatic H).

Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 82.62; H, 5.32; N, 3.34.

Acylation of **4** with 1.2 g (0.01 mmol) of dimethylcarbamoyl chloride followed by 1.1 g (0.01 mol) of benzaldehyde also produced **8** although in lower yield (25%).

Preparation of 2,3,4,4-Tetraphenyl-1,3-oxazolid-5-one (7). *N*-Ethoxycarbonyl-*N*-benzhydrylaniline (**5**, 207 mg, 0.63 mmol) was dissolved in 40 ml of anhydrous diethyl ether, cooled to −78 °C, and treated with 0.32 ml of a 2 M solution of *n*-butyllithium in hexane (0.64 mmol). After 15 min the yellow solution was warmed to 20 °C whereupon it became reddish brown, and after 3 h, the solution was treated with ethanol. Analysis of the crude product (198 mg) by VPC (10 ft × 0.125 in. column of 3% SE-52 on Chromosorb W at 220 °C) showed this to consist of 7% of the starting material **5** and 93% of the rearrangement product ethyl α-anilinodiphenylacetate (**6**). Crystallization of the crude product from ethanol gave 130 mg (63%) of **6**, mp 111–114 °C, mixture melting point was undepressed.

Treatment of the anion with 75 mg (0.71 mmol) of benzaldehyde dissolved in 1 ml of ether led to slow formation of a precipitate. The crude product was recrystallized from ethanol giving 127 mg (52%) of **7**: mp 131–132 °C dec; ir (KBr) 1790 (C=O), 1610, 1500, 1310, 1200 (broad), 1060, 740, 690 cm^{-1}; NMR δ 6.4–8.0 (m, aromatic H and benzylic).

Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.83; H, 5.42; N, 3.58. Found: C, 82.71; H, 5.43; N, 3.37.

Hydrolysis of 2,3,4,4-Tetraphenyl-1,3-oxazolid-5-one (7). A solution of 200 mg (0.51 mmol) of **7** and 109 mg (0.55 mmol) of 2,4-dinitrophenylhydrazine in 20 ml of ethanol was treated with 0.5 ml of concentrated sulfuric acid and refluxed for 1 h. Within a few minutes a precipitate formed. The mixture was cooled and filtered and the solid washed with ethanol to give 132 mg (93%) of benzaldehyde 2,4-dinitrophenylhydrazone, mp 238–241 °C, mmp with an authentic sample 238–242 °C.

The ethanol filtrate was diluted with water and extracted with ether to give 173 mg of material, mp 160–165 °C. This was dissolved in the minimum amount of benzene and extracted with dilute sodium hydroxide solution; the alkaline extract was acidified and the precipitate filtered off, washed with water, and dried to give 93 mg (60%) of α-anilinodiphenylacetic acid, mp 174–178 °C dec, mmp with an authentic sample 175–177 °C dec,[8] and the ir spectra (KBr) were identical.

Reaction of Dianion 1 with Chloroethyl Chloroformate. Preparation of 3,4,4-Triphenylperhydro-1,3-oxazin-2-one (9) and 2-Chloroethyl α-Anilinodiphenylacetate (10). A solution of **1** (0.01 mol, M = Na) in THF was treated at −78 °C with 1.4 g (0.01 mol) of chloroethyl chloroformate. After warming to 20 °C, the reaction product (2.94 g) was isolated and triturated with ether to give 2.21 g (67%) of **9**, mp 228–232 °C. Recrystallization from benzene gave an analytical sample: mp 230–232 °C; ir (Nujol) 1690 (C=O), 1410, 1300 (C–O), 765, 750, 700 cm^{-1}; NMR δ 2.83 (t, J = 6 Hz, 2) and 4.10 (t, J = 6 Hz, 2) (CH_2CH_2), 6.93 (s, 5, NPh), 7.23 (s, 10, CPh_2).

Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.41; H, 5.84; N, 4.16.

A repetition of this reaction with **1** (0.01 mol, M = Li) gave 2.89 g (88%) of **9**, mp 228–231 °C.

The introduction of 2-chloroethyl chloroformate to the solution of the dianion **1** at −78 °C was accompanied by an immediate color change from opaque dark red to a translucent red orange. If the solution (0.01 mol of **1**, M = Li) after 15 min at −78 °C was treated with 2 ml of water, the crude product (3.73 g) was found to have mp 107–114 °C and differed markedly by TLC from **9**. Recrystallization from 80–100 °C petroleum ether–benzene (4:1) gave 2.62 g of **10**, mp 122–124.5 °C. Concentration of the filtrate to ⅓ volume gave an oil which slowly crystallized. Recrystallization of this from 80–100 °C petroleum ether gave an additional 0.43 g of **10**, mp 120–122 °C (combined yield 83%).

The analytical sample had mp 124–126 °C; ir (Nujol) 3420 (NH), 1740 (C=O), 1600, 1510, 1240, 1170, 750, 690 cm^{-1}; NMR δ 3.33 (t, J = 6 Hz, 2, CH_2Cl), 4.32 (t, J = 6 Hz, 2, CH_2O), 5.2 (broad s, 1, NH), 6.4–7.7 (m, 15, aromatic H); mass spectrum *m/e* (rel intensity) 367 (M^+, ^{37}Cl, 0.6), 365 (M^+, ^{35}Cl, 1.7), 259 (20), 258 (100), 180 (11), 165 (11).

Anal. Calcd for $C_{22}H_{20}O_2NCl$: C, 72.21; H, 5.52; N, 3.83; Cl, 9.69. Found: C, 72.08; H, 5.49; N, 3.82; Cl, 9.87.

Reaction of Dianion 1 with Propionyl Chloride. The dianion **1** (0.01 mol, M = Li) in tetrahydrofuran was treated at −78 °C with 0.93 g (0.01 mol) of propionyl chloride. After 20 min reaction, the solution was treated with 3 ml of methanol, warmed to 20 °C, and the reaction products isolated.

Chromatography of the reaction products (3.12 g) using 1:1 benzene–30–60 °C petroleum ether graded through benzene to 3:1 benzene–diethyl ether gave in order of elution 0.45 g (17%) of *N*-benzhydrylaniline, 0.24 g (8%) of 1-anilino-1,1-diphenyl-2-butanone (**11**), 0.27 g (11%) of benzophenone anil, 0.16 g of an unidentified compound, and 1.36 g (43%) of *N*-benzhydryl-*N*-phenylpropionamide (**12**).

The impure **11** was recrystallized twice from methanol to give an analytical sample: mp 112–113 °C; ir (CCl_4) 3400 (NH), 1720 (C=O), 1605, 1505, 700, 670 cm^{-1}; NMR (CCl_4) δ 0.90 (t, 3, J = 7 Hz, CH_2CH_3), 2.41 (q, 2, J = 7 Hz, CH_2CH_3), 5.78 (s, 1, NH), 6.2–7.7 (m, 15, aromatic H); mass spectrum *m/e* (rel intensity) 259 (20), 258 (100, $M^+ - C_3H_5O$), 180 (15), 165 (10), 77 (62).

Anal. Calcd for $C_{22}H_{21}NO$: C, 83.77; H, 6.71; N, 4.44. Found: C, 84.00; H, 6.81; N, 4.40.

The propionamide **12** was a noncrystallizable viscous oil and was identified by comparison of its spectral properties with those of an authentic sample prepared from *N*-benzhydrylaniline and propionyl chloride: ir (CCl_4) 1670 (C=O), 1600, 1500, 1380, 1250, 700 cm^{-1}; NMR (CCl_4) δ 1.05 (t, 3, J = 8 Hz, CH_2CH_3), 2.03 (q, 2, J = 8 Hz, CH_2CH_3), 6.6–7.4 (m, 16, $CHPh_2$).

Reaction of Dianion 1 with Ethyl 3-Chloropropionate and Ethyl Acrylate. Preparation of 1,5,5-Triphenyl-2-pyrrolidone (13). The dianion **1** (0.01 mol, M = Na) was treated with 1.36 g (0.01 mol) of ethyl 3-chloropropionate at −78 °C whereupon rapid decolorization occurred. The crude product was triturated with ether giving 2.3 g (73%) of the insoluble 1,5,5-triphenyl-2-pyrrolidone (**13**), mp 179–183 °C. An analytical sample, obtained by recrystallization from 80–100 °C petroleum ether, had mp 182.5–184.5 °C; ir (CCl_4) 1710 (C=O), 1500, 1340 (C–N), 690 cm^{-1}; NMR δ 2.53 and 2.77 (two t, J = 5 Hz, 4, CH_2CH_2), 7.07 (s, 5, NPh), 7.1–7.6 (m, 10, CPh_2).

Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.12; H, 6.32; N, 4.29.

A repetition of the above experiment with 1.0 g (0.01 mol) of ethyl acrylate required warming to 20 °C before decolorization was observed. The crude reaction product was thrice recrystallized from 80–100 °C petroleum ether to give 1.2 g of **13** identical with that previously isolated.

Reaction of Dianion 1 with Ethyl Chloroacetate. A. The dianion **1** (0.01 mol, M = Li) was treated with 1.2 g (0.01 mol) of ethyl chloroacetate at −78 °C. After warming to 20 °C, the reaction product (2.56 g) was isolated and chromatographed using benzene as eluent. *N*-Benzhydrylaniline and benzophenone anil eluted first and these were followed by 1.8 g of 1,3,3-triphenyl-2-azetidinone (**14**, 60%), mp 120–124 °C. Recrystallization from ethanol gave an analytical sample: mp 121.5–123 °C; ir (KBr) 1760 (C=O, β-lactam), 1350 (N–C), 1600, 1500, 750, 700, 690 cm^{-1} (aromatics); NMR δ 3.63 (s, 2, CH_2), 7.0–7.5 (m, 15, aromatic H).

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.24; H, 5.73; N, 4.68. Found: C, 84.38; H, 5.86; N, 4.56.

B. The above experiment was repeated with potassium as the counterion. After addition of the ethyl chloroacetate the color of the solution became green and the reaction was immediately quenched with methanol. The crude reaction product was chromatographed to give 0.72 g of *N*-benzhydrylaniline, 1.2 g of benzophenone anil containing 20% of ethyl 3-anilino-3,3-diphenylpropionate (**15**), 0.24 g (7%) of **15**, and 0.36 g (12%) of the β-lactam **14**, mp 123–124 °C after recrystallization from ethanol.

The isolated **15** was recrystallized from ethanol: mp 90–91.5 °C; NMR δ 0.97 (t, J = 7 Hz, 3, CH_3CH_2), 3.53 (s, 2, CH_2CO), 3.87 (q, J = 7 Hz, 2, CH_3CH_2), 4.8 (broad s, 1, NH), 6.3–7.7 (m, 15, aromatic H); ir (CCl_4) 3400 (NH), 1740 (C=O), 1600, 1500, 1210, 1160, 700 cm^{-1}.

Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.96; H, 6.72; N, 4.05. Found: C, 79.78; H, 6.77; N, 4.04.

C. The above reaction was repeated with **1** (0.01 mol, M = Na) and the reaction warmed to 20 °C over a 1-h period before quenching with ethanol. Chromatography of the reaction products using benzene–hexane (10:3) as eluting solvent gave 1.0 g (39%) of *N*-benzhydrylaniline, 1.0 g (40%) of ethyl 3,3-diphenylacrylate (**16**), identified by comparison of its spectral properties with those of an authentic sample,[9] and 0.3 g (24%) of aniline.

D. When the reaction mixture stood at 20 °C for at least 12 h, chromatography gave 1.10 g (42%) of *N*-benzhydrylaniline, 0.24 g (4%) of benzophenone anil, 0.33 g (13%) of ethyl 3,3-diphenylacrylate (**16**), and 1.02 g (34%) of *N*,3,3-triphenylacrylamide (**17**). Recrystallization of the last from ethanol gave material of mp 130–134 °C identical in spectral properties with an authentic sample, mmp 133–134 °C.

Reaction of Dianion 1 with Ethyl 4-Chlorobutyrate. The dianion 1 (0.01 mol, M = Na) in THF was treated at −78 °C with 1.51 g (0.01 mol) of ethyl 4-chlorobutyrate. After 1 h at −78 °C, the mixture was allowed to warm to 20 °C for 20 h. The crude product (3.15 g) was chromatographed using benzene graded to benzene–20% ether as eluting solvent. In order of elution, there were obtained 1.64 g (63%) of *N*-benzhydrylaniline, 1.00 g (30%) of crude *N*-benzhydryl-*N*-phenylcyclopropanecarboxamide (18), and 0.51 g (12%) of crude 19.

The crude amide 18 crystallized on warming in 30–60 °C petroleum ether to give 0.65 g (20%) of 16, mp 74–77 and 95–97 °C.[10] Recrystallization from 30–60 °C petroleum ether gave an analytical sample: mp 75–77 °C; ir (CCl_4) 1660 (C=O), 1500, 1600, 1410, 1140, 700 cm^{-1}; NMR δ 0.4–0.8 (m, 2) and 0.9–1.3 (m, 3, cyclopropyl H), 6.8–7.4 (m, 15, aromatic H); mass spectrum *m/e* (rel intensity) 327 (11, M^+), 168 (16), 167 (100), 152 (11), 77 (13).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.36; H, 6.46; N, 4.24. Found: C, 84.18; H, 6.48; N, 4.17.

An authentic sample of 18 was prepared from *N*-benzhydrylaniline and cyclopropanecarboxylic acid chloride, mp 94–96 °C, mmp 95–97 °C with both the lower and the higher melting polymorphs. Spectral data were identical with those observed for 18.

The crude 19 was crystallized by warming in methanol giving 0.32 g (8%), mp 196–199 °C. An analytical sample obtained by recrystallization from ethanol–25% benzene had mp 199–202 °C; ir (Nujol) 1630 (broad, C=O), 1600, 1580, 1500, 1430, 1340, 760, 730, 700 cm^{-1}; NMR δ 0.5–2.0 (m, 9, aliphatic H), 4.0 (double d, J_1 = 5, J_2 = 7 Hz, 0.3 H, exchanges with basic D_2O, COCHCO), 6.8–7.5 (m, 15, aromatic H), 15.7 (s, 0.7 H, exchanges with D_2O, enol OH); mass spectrum *m/e* (rel intensity) 395 (41, M^+), 327 (32), 326 (100), 324 (41), 180 (50), 166 (39), 93 (42).

Anal. Calcd for $C_{27}H_{25}NO_2$: C, 81.98; H, 6.38; N, 3.54. Found: C, 82.08; H, 6.57; N, 3.56.

The preceding reaction was repeated except that after 20 min reaction at −78 °C, 4 ml of ethanol was added to terminate the reaction. After diluting with water and extracting with ether, VPC analysis of the ether extract showed that no chloro ester remained; instead, a compound with a much shorter retention time was present.

The ether extract was concentrated to 25 ml by fractional distillation and the residue placed under vacuum. The volatile material, collected in a dry ice trap, was redistilled at atmospheric pressure to give 1.3 g (90%) of ethyl cyclopropanecarboxylate, bp 125–130 °C, identified by comparison of its infrared and NMR spectra with those of an authentic sample.

The nonvolatile material (2.63 g) was dissolved in ether and treated with gaseous hydrogen chloride to precipitate *N*-benzhydrylaniline hydrochloride (2.40 g, 81%) which was identified by the spectral properties of the regenerated amine.

The ether filtrate from the amine hydrochloride was washed with sodium carbonate and water, dried, and evaporated. The residue (0.42 g) was purified by preparative TLC on silica gel to give principally one product, the amide 18. After crystallization by treatment with 30–60 °C petroleum ether, 0.27 g (9%) was obtained, mp 87–91 °C, mmp 90–93 °C, identity confirmed via ir spectrum.

The preceding reaction was repeated with 1 (0.01 mol, M = Li). Chromatography of the crude product (3.41 g) using benzene graded to 1:1 benzene–ether gave in order of elution 0.73 g (28%) of *N*-benzhydrylaniline, 0.17 g of a fraction containing benzhydrylaniline and two unidentified compounds, 0.90 g of 18 (27%) which after crystallization with petroleum ether had mp 94–97 °C, 0.36 g (9%) of 19 having mp 190–193 °C after crystallization from methanol, 0.10 g of crude 22, 0.29 g of 21, followed by 0.22 g of a mixture containing 40 mol % of 21 together with 20, and finally 0.45 g of 1,6,6-triphenyl-2-piperidone (20).

The crude 22 (2% yield) was twice recrystallized from methanol to give 32 mg: mp 183–184.5 °C; ir (CCl_4) 3500 (broad, OH), 1700 (C=O), 1650 (amide C=O), 1500, 1450, 1370, 1350, 1320, 700, 690 cm^{-1}; NMR δ 0.9–3.3 (m, 9, aliphatic H), 4.58 (s, 1, OH), 7.10 (s, 5, NPh), 7.2–7.8 (m, 10, Ph_2C); mass spectrum *m/e* (rel intensity) 411 (5, M^+), 342 (57), 221 (32), 205 (47), 193 (53), 180 (100), 179 (32), 165 (37), 115 (42).

Anal. Calcd for $C_{27}H_{25}NO_3$: C, 78.80; H, 6.14; N, 3.40. Found: C, 78.52; H, 6.12; N, 3.33.

The relatively pure fraction of 21 (total yield 10%) was crystallized with 30–60 °C petroleum ether (mp 190–192 °C), then recrystallized from methanol: mp 195.5–197.5 °C; ir (CCl_4) 1670 (C=O), 1600, 1500, 1450, 1360, 1325, 1170, 1140, 690 cm^{-1}; NMR δ 1.9–2.5 (m, 4), 2.77 (distorted t, 2, $C{=}CCH_2$), 3.23 (broad t, 2, J = 8 Hz, $C{=}CCH_2$), 4.17 (t, J = 8 Hz, 2, CH_2O), 6.80 (s, 5, PhN), 7.1–7.5 (m, 10, Ph_2C); mass spectrum *m/e* (rel intensity) 396 (34), 395 (100, M^+), 324 (29), 303 (74), 275 (29), 228 (37), 215 (58), 193 (90), 180 (47), 178 (31), 165 (37), 138 (42), 115 (47), 111 (53), 110 (63).

Anal. Calcd for $C_{27}H_{25}NO_2$: C, 81.98; H, 6.38; N, 3.54. Found: C, 82.20; H, 6.47; N, 3.35.

The fraction consisting essentially of 20 (total yield 17%), mp 165–168 °C, was recrystallized from methanol: mp 172.5–173.5 °C; ir (CCl_4) 1655 (C=O), 1500, 1450, 1360, 1330, 690 cm^{-1}; NMR δ 1.3–1.9 (m, 2, $CH_2CH_2CH_2$), 2.5–2.9 (m, 4, $CH_2CH_2CH_2$), 6.87 (s, 5, NPh), 7.0–7.4 (m, 10, CPh_2); mass spectrum *m/e* (rel intensity) 328 (24), 327 (81, M^+), 206 (31), 193 (50), 192 (44), 180 (30), 178 (33), 165 (32) 115 (44), 93 (100).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.36; H, 6.48; N, 4.28. Found: C, 84.36; H, 6.44; N, 4.09.

Ring Opening of 1,4,4-Triphenyl-2-azetidinone[11] (14). The β-lactam 14 (0.5 g, 0.0016 mol) in 10 ml of tetrahydrofuran was treated at −78 °C with 1 ml of a 2 M solution of *n*-butyllithium in hexane (Ventron). After 12 h the reaction mixture was warmed and diluted with water and the products isolated by ether extraction. The crude product was recrystallized from ethanol to give 0.4 g (80%) yield of 17, mp 131–133 °C, undepressed on mixing with authentic material. Spectral properties were identical with those of authentic 17.

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Registry No.—1 (M = K), 25033-92-5; 1 (M = Li), 25033-90-3; 1 (M = Na), 7765-70-0; 4 (M = Na), 42391-81-1; 5, 7714-87-6; 6, 33672-87-6; 7, 59434-86-5; 8, 59434-87-6; 9, 59434-88-7; 10, 59434-89-8; 11, 59434-90-1; 12, 59434-91-2; 13, 59434-92-3; 14, 19340-70-6; 15, 59434-93-4; 17, 4226-74-8; 18, 59434-94-5; 19, 59434-95-6; 20, 59434-96-7; 21, 59434-97-8; 22, 59434-98-9; chloroethyl chloroformate, 627-11-2; propionyl chloride, 79-03-8; ethyl 3-chloropropionate, 623-71-2; ethyl acrylate, 140-88-5; ethyl chloroacetate, 105-39-5; ethyl 4-chlorobutyrate, 3153-36-4.

References and Notes

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(10) The lower melting form of the amide 18 was obtained in the first experiment in which it was isolated. All subsequent preparations gave the higher melting form.
(11) Reduction of the β-lactam 14 with sodium metal or sodium naphthalenide generated *N*,3,3-triphenylpropionamide.