Alkylation of Dianions of β-Keto Esters

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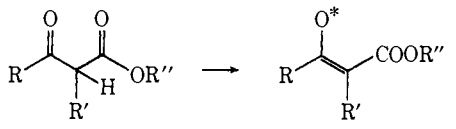
Abstract: The dianions from a variety of β-keto esters have been generated using 1 equiv of sodium hydride and 1 equiv of *n*-butyllithium or methyllithium or 2 equiv of lithium diisopropylamide. The dianions react with a range of alkylating agents to produce γ-alkylated products exclusively in good yield. Reaction of these dianions with α,ω-dihaloalkanes yields cyclic 1:1 adducts, cyclic 1:2 adducts, or acyclic 1:2 adducts, depending on the alkylating agent and the reaction conditions. This method offers ready access to a wide range of compounds which were previously difficult to obtain.

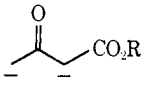
Recently we had envisioned the synthesis of a number of aromatic antibiotics and antitumor agents which can be broadly classified as acetogenins.[1] In this analysis the importance of β-keto esters and their derivatives became increasingly obvious. Many reactions can be effected at the α carbon of a β-keto ester. These reactions proceed *via* the enol or enolate **1** and



1, * = H or −

follow from the well known ability of β-dicarbonyl systems to yield the enol or enolate, resulting from transfer of the hydrogen on the carbon flanked by the carbonyl groups and the reactivity of this system with a variety of electrophiles. The apparent greater versatility of β-keto esters compared to β-diketones encouraged us to further pursue the former type compounds in our synthesis of acetogenins. Whereas it is usually difficult to differentiate the two carbonyl carbons in a β-diketone, it is relatively easy to achieve reaction specifically at either one of the two carbonyl groups in a β-keto ester.

Prior to our work, efforts to find a method to induce reactivity at the γ carbon of a β-keto ester had produced very limited success. The dianion **2** of ethyl aceto-



2, R = Et
3, R = Me

acetate has been generated by treating ethyl acetoacetate with potassium amide. However, alkylation of **2** proceeds in variable yield. For example, Wolfe, *et al.*, found no alkylation of **3** with benzyl chloride or *n*-butyl bromide, and only fair yields (27–37%) of alkylation with methyl iodide and ethyl bromide.[2] Using a similar procedure Sugiyama, *et al.*, were able to alkylate dianion **2** with benzyl bromide and *n*-propyl iodide in yields of 60–65%.[3] Unfortunately, these latter workers did not report the time for the alkylation reaction and this appears to be a critical parameter (*vide infra*). Hagarty has reported that the dianion **2** can be alkylated with a variety of allylic chlorides in yields of 13–66%.[4]

There are several possible reasons for the relatively low yields in the alkylation of dianion **3** compared to the high yield in the alkylation of β-diketo dianions and β-keto aldehyde dianions.[5] It is known that metal amides, the bases used in the generation of **2**, can cause aminolysis of esters.[6] Wolfe, *et al.*, also suggested that formation of dianion **2** may not be complete under these conditions, namely potassium amide in liquid ammonia.[2] A final complication may be the reaction temperature (−33°) and the reaction time (usually 1 hr). For these reasons we sought another base to generate the dianion **2**. This base should be strong enough to lead to complete formation of **2**, it should be able to be used in solvents other than liquid ammonia, and finally it should be nonnucleophilic.

Results and Discussion

Treatment of methyl acetoacetate with 2 equiv of *n*-butyllithium in hexane, benzene, or THF at temperatures from −78 to 25° gave mainly carbonyl addition compounds and only traces of methyl acetoacetate were recovered on work-up. Brieger and Spencer have also noted that *n*-butyllithium adds to the carbonyl groups of β-keto esters.[7] However, Mao, *et al.*, overcame this difficulty in the case of phenylacetone by first generating the monoanion of phenylacetone with a metal amide which protected the carbonyl group from nucleophilic attack and then treatment of the monoanion with *n*-butyllithium gave the dianion in excellent yield.[8]

Our initial investigations of β-keto esters involved a similar approach.[9] One equivalent of sodium hydride converted methyl acetoacetate into its monoanion; treatment of this monoanion with *n*-butyllithium gave the dianion **3** (eq 1). As in the above example of phenylacetone, the carbonyl groups in the monoanion were protected from nucleophilic attack by the organometallic reagent. However, it is important to note that

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(2) J. F. Wolfe, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **29**, 3249 (1964).
(3) N. Sugiyama, M. Yamamoto, T. Takano, and C. Kashima, *Bull. Chem. Soc. Jap.*, **40**, 2909 (1967).
(4) J. D. Hagarty, U. S. Patent 3,565,928 (1971); *Chem. Abstr.*, **74**, 140999 (1971).
(5) T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969).
(6) (a) K.-W. Yang, J. G. Cannon, and J. G. Rose, *Tetrahedron Lett.*, 1791 (1970); (b) B. Singh, *Tetrahedron Lett.*, 321 (1971).
(7) G. Brieger and D. G. Spencer, *Tetrahedron Lett.*, 4585 (1971).
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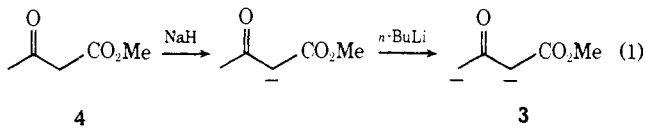


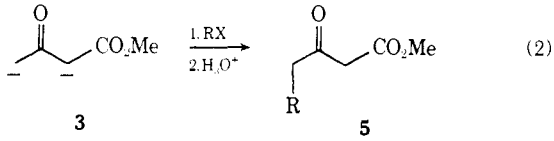
4 3

excess organolithium reagent is not used.[7,10,11] This same procedure has recently been applied to β-keto phosphonium salts[12] and β-keto phosphonates.[13] In the second step of the generation of **3**, the *n*-butyllithium can be replaced by methyllithium.

Using this procedure the dianion **3** could be generated in a variety of dipolar aprotic, ether, or hydrocarbon solvents, although solubility problems were occasionally encountered in the less polar solvents. Generally THF proved very satisfactory and, if solubility problems arose, the addition of small amounts of HMP to the mixture usually alleviated these difficulties.

When the dianion **3** was quenched with D_2O and deuterated trifluoroacetic acid, it was found that the recovered methyl acetoacetate contained two to three deuterium atoms per molecule. The α-deuterium atoms were exchanged with aqueous sodium bicarbonate and, after these exchanges, the mass spectrum of the resulting methyl acetoacetate (**4**) showed that the sample of **4** contained 2 ± 2% d_0, 96 ± 2% d_1, and no detectable d_2 and d_3 compound. The reaction sequence to give **4**-d_1 and the mass spectral fragmentation pattern indicated that the deuterium atom was on the γ carbon. This was shown beyond doubt by the nmr spectrum of the methyl acetoacetate-d_1 which has a three-proton singlet at δ 3.70 (OCH_3), a two-proton singlet at δ 3.46 (CH_2), and a 1:1:1 triplet and a very small singlet at δ 2.2 (DCH_2CO and CH_3CO) which integrated to two protons. The ratio of this triplet and singlet was determined in a variety of ways and found to be 49:1. J_{HD} = 2.15 Hz and $\delta_{CH_3} - \delta_{CH_2D} = -0.016$ ppm, which is in good agreement with the values found for related systems.[14]

Following this evidence that we had generated the dianion **3** (eq 1), we proceeded to investigate its chemistry. The first study involved the alkylation of the intermediate **3**.[9] When a solution of **3** in THF was treated with a range of alkylating agents, a facile reaction often occurred and the monoalkylated products **5**



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(eq 6) were isolated in good yield (Table I).

The alkylation does not proceed in all cases; for example, reaction of dianion **3** with cyclohexyl chloride and *tert*-butyl bromide, not unexpectedly, gave no alkylation products but only returned methyl acetoacetate after 1 hr at 25°. Cyclohexyl bromide reacted very slowly and a low yield of alkylation product could be obtained after 1 hr at 25°. It should be noted that the yields of **5** reported in Table I are after 5–15 min reaction at 0–25°. The reaction time could be shortened but for convenience we chose not to. When the dianion **3** was treated with allyl bromide at −23° for 1 hr, the monoalkylated product **5** (R = allyl) was isolated in 28–32% yield together with 60–65% recovered **4**. The same reaction at −78° for 1 hr failed to yield any product and 92% **4** was recovered. Hence the alkylation (eq 2) is quite temperature dependent, and this could be one source of the low yields reported in previous attempts to alkylate dianion **2**.[2-4] We also investigated the alkylation of **3** with allyl bromide at room temperature and found that after 15 min all the starting material had been consumed but a number of new products were appearing in the vpc of the crude reaction mixture. Hence it appears that maximum yields of alkylation can conveniently be obtained when the reaction is run in the range 0–25° (see Experimental Section).

Table I. Alkylation of Dianion **3** from Methyl Acetoacetate[a]

RX	Yield of **5**,[b] %	Bp of **5**, °C (mm)
MeI	81 (99)	39–40 (1.5)
EtBr	84 (96)	77–79 (14)
i-PrI	73 (90)	52–54 (2)
n-BuBr	72 (95)	66–67 (0.8)
t-BuBr	0	
c-$C_6H_{11}Cl$	0	
c-$C_6H_{11}Br$	(5)[c]	
CH_2=$CHCH_2Br$	83 (98)	99–100 (15)
$C_6H_5CH_2Cl$	81 (94)	102–103 (0.4)

[a] See Experimental Section for details of conditions employed. [b] Yields refer to distilled products. The numbers in parentheses refer to vpc yields. [c] See text.

The alkylation appears to proceed equally well in ether, tetrahydrofuran (THF), dimethoxyethane, and hexamethylphosphoric triamide (HMP), and we chose THF for most of our subsequent studies. In some instances the dianions of complex β-keto esters were not soluble in THF and it was found that addition of small amounts of HMP led to dissolution of these dianions. Alkylation of these dianions in the mixed solvent systems proceeded normally.

A small range of bases was investigated to determine their efficiency in generating dianion **3** in THF. It was found that **3** could be formed directly from methyl acetoacetate using 2 equiv of lithium diisopropylamide, and alkylation with benzyl chloride gave **5** (R = benzyl) in 83% yield (isolated). However, lithium bis(trimethylsilyl)amide apparently is not a strong enough base to generate dianion **3** and, after the attempted alkylation with benzyl chloride, only starting β-keto ester was recovered. This supports the earlier suggestion of Wolfe, *et al.*, that perhaps potassium amide in ammonia is giving only partial formation of the dianion of ethyl acetoacetate.[2] The recently discovered H^+ arpoon bases[15] also appear to be equally proficient in generating dianions of β-dicarbonyl compounds.[16]

It was important to show that the alkylation of **3** had in fact given **5** (eq 2). In all of these reactions only one al-

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(11) (a) R. M. Coates and J. E. Shaw, *J. Amer. Chem. Soc.*, **92**, 5657 (1970); (b) E. Piers and R. D. Smillie, *J. Org. Chem.*, **35**, 3997 (1970).
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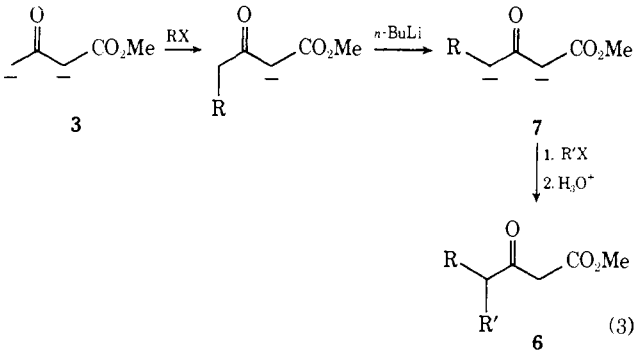
(15) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 582 (1973).
(16) J. F. Kingston and L. Weiler, unpublished results.

kylation product could be isolated. The vpc of the crude reaction mixture occasionally showed the presence of other products; however, these were always present in less than 1–2% of the major product. The spectral evidence clearly showed that the alkylation product was indeed **5**. The ir spectra of these products had bands at ~1740 and ~1710 cm^{-1} due to the β-keto ester system, thus eliminating the possibility of the O-alkylation product. The nmr spectra of these products have a two-proton singlet at δ 3.4–3.5 ($-C(=O)CH_2C(=O)-$) and the absence of a three-proton singlet at *ca.* δ 2.3 was definitive in showing that the alkylation had occurred at the γ-carbon as shown in eq 2. This was further collaborated by the mass spectra of **5**[17] and by vpc differences between authentic α-alkylated methyl acetoacetate and the alkylation products **5**.

It was also found that the dialkylated products **6** could be obtained by alkylation of dianion **3** and generation of dianion **7** with an additional equivalent of *n*-butyllithium, followed by a second alkylation (eq 3).



(3)

However, we generally obtained higher yields of dialkylated product **6** if we isolated and purified the monoalkylated product **5** before proceeding with the second alkylation. The results of several of these reactions are contained in Table II.

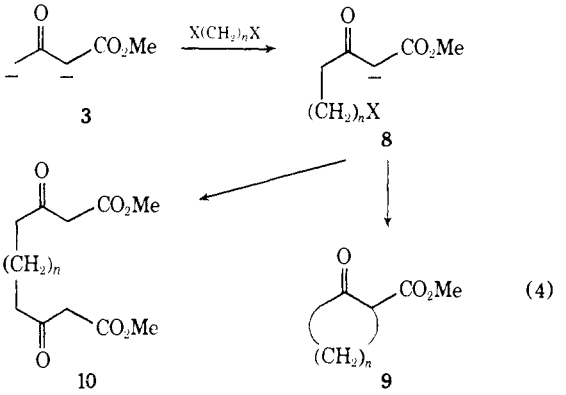
Table II. Alkylation of Dianion from Substituted β-Keto Esters

$RCH_2COCHR'CO_2R''$ R	R′	R″	RX	Yield,[a] %	Bp, °C (mm)
n-Bu	H	Me	MeI	81	54–56 (0.3)
n-Bu	H	Me	CH_2=$CHCH_2Br$	77	82–84 (0.6)
n-Bu	H	Me	$C_6H_5CH_2Cl$	63	122–123 (0.4)
Me	H	Me	$C_6H_5CH_2Cl$	76	104–105 (0.5)
$C_6H_5CH_2$	H	Me	MeI	86	99–100 (0.3)
H	H	Et	CH_2=$CHCH_2Br$	77	106–108 (15)
H	Me	Et	EtBr	78	102–105 (15)
$-(CH_2)_3-$		Me	CH_2=$CHCH_2Br$	67	110–112 (14)

[a] Yields refer to distilled products.

As can be seen from these results, a variety of dianions from β-keto esters undergo γ alkylation and this reaction is not impaired by α-alkyl groups. As before (Table I), these reactions are very facile, being complete in less than 30 min at 0–25°. This should be compared to the α alkylations of β-keto esters which typically require several hours in refluxing solvents, such as ethanol. This would explain why we detect no α alkylation in reaction **2** or **3**, even with an excess of alkylating agent.

The alkylation of dianion **3** with dihaloalkanes was also investigated. In this reaction, there are two possible products, **9** and **10**, depending on the fate of the intermediate **8** (eq 4). This intermediate may undergo

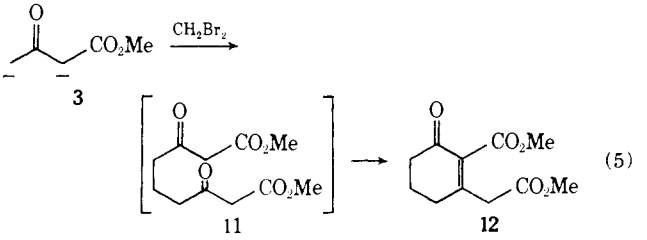


(4)

an intramolecular alkylation to give the cyclic keto ester **9**, or it may react with a second molecule of dianion **3** to give **10**. When 1 equiv of 1,3-dibromopropane was added to a solution of **3**, two products were obtained in approximately equal amounts. These products were separated by chromatography and found to be methyl 2-oxocyclohexanecarboxylate[18] (**9**, $n = 3$) and dimethyl 3,9-dioxoundecanedioate (**10**, $n = 3$).

In view of the difference in reactivity of mono- and dianions of β-keto esters (*vide supra*), formation of the bis adduct **10** should be favored by an excess of dianion **3**. In fact, when only 0.5 equiv of 1,3-dibromopropane was added to a solution of **3**, the only product isolated, in 77% yield, was the bis β-keto ester **10** ($n = 3$). Conversely, to favor the formation of the cyclic product **9**, an excess of dianion should be avoided, and it was found that addition of a dilute solution of **3** to a large excess of 1,3-dibromopropane did give mostly the cyclic product **9**. This procedure, however, produced low yields and would not be convenient if the dihaloalkane was difficult to obtain or costly. A double dilution experiment was performed and was found to give mainly the cyclic product **9** ($n = 3$) in 68% yield. A small amount (11%) of **10** ($n = 3$) was also produced. Reaction of dianion **3** with 0.5 equiv of 1,10-dibromodecane gave dimethyl 3,16-dioxoactadecanedioate (**10**, $n = 10$) in almost quantitative yield. The cyclization of this compound to a muscone intermediate is under investigation.

When dibromomethane was employed in the alkylation (**4**), no evidence for the cyclic product **9** ($n = 1$) or the bis β-keto ester **10** ($n = 1$) was obtained. However, a new compound was produced in reasonable yield, and the spectral and analytical data indicated that the compound had structure **12**, which arises from an



(5)

internal aldol condensation of the expected intermediate **11**. This allows an easy entry into the reduced

(17) L. Weiler, *Can. J. Chem.*, **50**, 2707 (1972).

(18) S. J. Rhoads, J. C. Gilbert, A. W. Desora, T. R. Garland, R. J. Spanger, and M. J. Urbrigkit, *Tetrahedron*, **19**, 1625 (1963).

homophthalic acids of type **12** and should make these compounds more readily available.[19]

Experimental Section

All melting points, which were recorded on a Kofler micro hot stage, and boiling points are uncorrected and are reported in °C. The infrared spectra were recorded on a Perkin-Elmer Model 700 spectrometer and were calibrated with the 1601 cm^{-1} band of polystyrene. The ultraviolet spectra were recorded on a Unicam Model SP 800 or a Cary Model 14 spectrophotometer. The proton nuclear magnetic resonance spectra were recorded on either a Varian T-60 or HA-100 spectrometer and the chemical shifts are reported in δ units from internal tetramethylsilane. Low-resolution mass spectra were recorded on an AEI MS-9 or Atlas CH-4b mass spectrometer, and the high-resolution spectra were recorded on the MS-9 spectrometer. Both instruments were operated at an ionizing potential of 70 eV. Vapor phase chromatograms were obtained on a Varian Aerograph Model 90 P3 chromatograph using one of the following: column A, 5 ft × 1/4 in. column of 3% SE-30 on 60–80 mesh Chromosorb W; column B, 5 ft × 1/4 in. column of 20% DEGS on 60–80 mesh Chromosorb W.

The supports used for all micro-thin-layer and preparative thin-layer chromatography were silica gel PF_{254} (Merck). Merck silica <0.08 mm or finer than 200 mesh was used for column chromatography. Microanalyses were performed by Peter Borda, University of British Columbia, Vancouver, Canada. All new compounds gave analysis to within 0.3% of the calculated value.

All solvents were dried and distilled immediately before use. All reactions were run under an atmosphere of nitrogen or argon. Commercial sodium hydride (50–57% mineral oil) was used without prior washing to remove the mineral oil. Commercial solutions of *n*-butyllithium in hexane were used directly and were standardized by double titration[20] or direct titration.[21]

Generation of Dianion 3. The following procedure was generally used to produce solutions of dianion **3**. Approximately 25 ml of dry THF was distilled from $LiAlH_4$ into a 50-ml flask containing 0.54 g of sodium hydride (50% mineral oil, 11 mmol). The flask was stoppered with a septum cap, flushed with nitrogen, and cooled in ice. Then 1.16 g of methyl acetoacetate (10.0 mmol) was added dropwise and the colorless solution was stirred at 0° for 10 min. To this solution was added dropwise 4.8 ml of 2.2 *M* *n*-butyllithium (10.5 mmol) in hexane and the yellow to orange solution of **3** was stirred at 0° for an additional 10 min before using.

Deuteration of Dianion 3. A solution of **3** was prepared as above from 0.24 g of methyl acetoacetate (2.05 mmol) and this was quenched with a 10% solution of trifluoroacetic acid-d_1 in D_2O (from trifluoroacetic anhydride and D_2O). The aqueous layer was extracted with 3 × 5 ml of ethyl ether. The ether extracts were combined, washed with 4 × 2 ml of D_2O, dried over anhydrous magnesium sulfate, and filtered. The solvents were removed under reduced pressure and the crude product was distilled in a Kugelrohr oven at 60° (15 mm) to yield 0.19 g of deuterated methyl acetoacetate. The nmr of this material indicated that there was less than one proton on the methylene carbon. The deuterium atoms at this position were exchanged by stirring the labeled methyl acetoacetate briefly in 10% aqueous sodium carbonate, acidifying this solution, and reisolating the methyl acetoacetate by ether extraction and distillation as above. A vpc analysis (column A) confirmed the identity and purity of this material: nmr ($CDCl_3$) δ 3.70 (s, 3 H, OCH_3) 3.46 (s, 2 H, $-CH_2-$), 2.23 (t, J = 2.15 Hz, 2 H, $CDCH_2CO$); mass spectrum *m/e* (rel intensity) 116 (1.9), 117 (100), 118 (6.1).

Alkylation of Dianion 3 (Table I). A solution of 10 mmol of dianion **3** in *ca.* 25 ml of THF was prepared as above and 11 mmol of alkylating agent in 2 ml of THF was added. This reaction mixture was allowed to slowly warm to room temperature with stirring. The color of the dianion faded immediately on addition of the alkylating agent. Approximately 15 min after the addition of the alkylating agent, the reaction was quenched with 2 ml of concentrated hydrochloric acid in 5 ml of water and 15 ml of ethyl ether. The aqueous layer was further extracted with 2 × 10 ml of ethyl ether. The extracts were combined, washed with water until neutral,[22] dried over anhydrous magnesium sulfate, and filtered. The solvents were removed under reduced pressure and the crude product was examined by vpc (column A) and distilled.

Methyl 3-oxopentanoate (5, R = methyl) was prepared as above from reaction of **3** and methyl iodide for 15 min to yield 1.06 g (81%) of distilled product: bp 39–40° (1.5 mm); ir ($CHCl_3$) 2990, 2925, 1740, 1715, 1460, 1440, 1410, 1380, 1360, 1320, 1170, 1110, 1070, 1020, 1000 cm^{-1}; nmr ($CDCl_3$) δ 1.08 (t, J = 7.2 Hz, 3 H), 2.59 (q, J = 7.2 Hz, 2 H), 3.48 (s, 2 H), 3.75 (s, 3 H), 4.99 (s);[23] mass spectrum *m/e* (rel intensity) 130 (12), 101 (2), 99 (7), 78 (7), 74 (6), 69 (16), 59 (35), 57 (100), 45 (11), 43 (28), 42 (15).

Methyl 3-oxohexanoate (5, R = ethyl) was prepared as above from reaction of **3** and ethyl bromide for 15 min; yield, 1.21 g (84%) of distilled product; bp 77–79° (15 mm); ir ($CHCl_3$) 2955, 2875, 1740, 1710, 1645, 1620, 1450, 1440, 1405, 1360, 1320, 1160, 1070, 1015, 910 cm^{-1}; nmr ($CDCl_3$) δ 0.92 (t, J = 6.8 Hz, 3 H), 1.60 (sextet, $J \simeq 7$ Hz, 2 H), 2.46 (t, J = 7.2 Hz, 2 H), 3.45 (s, 2 H), 3.74 (s, 3 H), 5.00 (s);[23] mass spectrum *m/e* (rel intensity) 144 (12), 129 (2), 116 (11), 113 (6), 101 (40), 85 (7), 84 (8), 74 (8), 71 (90), 69 (20), 59 (32), 57 (12), 43 (100), 42 (22), 41 (28).

Methyl 5-methyl-3-oxohexanoate (5, R = isopropyl) was prepared as above from reaction of **3** and isopropyl iodide for 10 min: yield, 1.15 g (73%) of distilled product; bp 52–54° (2 mm); ir ($CHCl_3$) 2970, 2890, 1740, 1715, 1655, 1630, 1470, 1455, 1440, 1415, 1375, 1325, 1165, 1120, 1095, 1075, 1050, 1020 cm^{-1}; nmr ($CDCl_3$) δ 0.93 (d, J = 7.0 Hz, 6 H), 2.3 (m, 3 H), 3.44 (s, 2 H), 3.75 (s, 3 H), 4.98 (s);[23] mass spectrum *m/e* (rel intensity) 158 (16), 143 (14), 127 (7), 116 (50), 101 (57), 85 (98), 84 (26), 74 (23), 69 (33), 59 (34), 57 (100), 43 (53), 42 (20), 41 (28).

Methyl 3-oxooctanoate (5, R = *n*-butyl) was prepared as above from reaction of **3** and *n*-butyl bromide for 25 min: yield, 1.22 g (72%) of distilled product; bp 66–67° (0.8 mm); ir ($CHCl_3$) 2950, 2930, 2860, 1740, 1710, 1650, 1625, 1450, 1440, 1410, 1320, 1155, 1105, 1045, 1020 cm^{-1}; nmr ($CDCl_3$) δ 0.89 (br t, J = 7 Hz, 3 H), 1.3 (m, 6 H), 2.53 (t, J = 7 Hz, 2 H), 3.46 (s, 2 H), 3.73 (s, 3 H), 4.99 (s);[23] mass spectrum *m/e* (rel intensity) 172 (5), 154 (3), 143 (2), 141 (4), 130 (6), 129 (19), 117 (14), 116 (82), 101 (39), 99 (55), 85 (15), 84 (27), 74 (37), 71 (35), 69 (25), 59 (36), 57 (13), 56 (16), 55 (23), 43 (100), 42 (23), 41 (32).

Methyl 3-oxo-4-cyclohexylbutanoate (5, R = cyclohexyl) was prepared from reaction of **3** and cyclohexyl bromide for 1 hr at 25°: yield, 5% by vpc (column A, 140°). This material was isolated by preparative vpc (column A, 170°) and distilled (Kugelrohr) at 90–95° (0.4 mm): ir ($CHCl_3$) 2960, 2920, 2870, 1740, 1710, 1660, 1625, 1450, 1435, 1410, 1305, 1160, 1030, 1000 cm^{-1}; nmr ($CDCl_3$) δ 1.1–2.0 (m, 11 H), 2.42 (d, J = 7.0 Hz, 2 H), 3.45 (w, 2 H), 3.75 (s, 3 H), 5.00 (s);[23] mass spectrum *m/e* (rel intensity) 198 (19), 125 (60), 124 (12), 116 (65), 105 (7), 101 (45), 97 (38), 83 (5), 82 (19), 74 (21), 69 (23), 59 (47), 43 (100), 42 (12), 41 (57).

Methyl 3-oxohept-6-enoate (5, R = allyl) was prepared as above from reaction of **3** and allyl bromide for 5 min: yield, 1.30 g (83%) of distilled product; bp 99–100° (15 mm); ir ($CHCl_3$) 3050, 3000, 2990, 2950, 2850, 1735, 1710, 1640, 1610, 1440, 1405, 1360, 1320, 1160, 1095, 1005, 930 cm^{-1}; nmr ($CDCl_3$) δ 2.5 (m, 4 H), 3.47 (s, 2 H), 3.76 (s, 3 H), 4.8–5.2 (m, 2 H), 5.3–6.0 (m, 1 H); mass spectrum *m/e* (rel intensity) 156 (11), 138 (2), 125 (5), 124 (17), 101 (46), 96 (8), 85 (6), 83 (39), 82 (58), 74 (7), 69 (33), 59 (51), 57 (18), 55 (100), 54 (48), 43 (74), 42 (23), 41 (25).

Methyl 3-oxo-5-phenylpentanoate (5, R = benzyl) was prepared as above from reaction of **3** and 15 mmol of benzyl chloride for 30 min: yield, 1.67 g (81%) of distilled product; bp 102–103° (0.4 mm); ir ($CHCl_3$) 3000, 2950, 2850, 1740, 1710, 1645, 1630, 1600, 1495, 1450, 1440, 1405, 1365, 1320, 1180, 1160, 1080, 1035, 700 cm^{-1}; nmr ($CDCl_3$) δ 2.86 (s, 4 H), 3.39 (s, 2 H), 3.67 (s, 3 H), 4.96 (s),[23] 7.22 (s, 5 H); mass spectrum *m/e* (rel intensity) 206 (1), 159 (2), 148 (67), 133 (17), 117 (24), 106 (11), 105 (98), 104 (17), 103 (11), 101 (11), 92 (10), 91 (100), 85 (24), 79 (15), 78 (18), 77 (25), 65 (18), 63 (10), 55 (11), 51 (24), 43 (20), 41 (15).

Generation of Dianion 3 with Lithium Diisopropylamide. A sample of 1.130 g (11.2 mmol) of diisopropylamine (dried over KOH) was weighed into an oven dried 40-ml flask and 25 ml of THF was distilled directly into the flask. This flask was stoppered, cooled in ice, and flushed with N_2. The 5.0 ml of 2.35 *M* (11.7 mmol) *n*-butyllithium was added dropwise to give a yellow solution

(19) For an introduction to the utility of these compounds, see Y. Arai, T. Kamikawa, and T. Kubota, *Tetrahedron Lett.*, 1615 (1972).

(20) R. R. Turner, A. G. Altenceau, and T. C. Cheng, *Anal. Chem.*, **42**, 1835 (1970).

(21) S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).

(22) Note that the extracts must be completely free of all traces of acids and bases to achieve reasonable yields in the isolation. β-Keto esters are sensitive to heat in the presence of small amounts of acids and bases.

(23) Small peak due to vinyl hydrogen of the enolic form.

which was stirred for 20 min. A sample of 0.641 g (5.5 mmol) of methyl acetoacetate was added slowly to the solution of lithium diisopropylamide and the resulting solution was stirred at 0° for 20 min. Finally 0.696 g (5.5 mmol) of benzyl chloride was added, and the reaction mixture was stirred at 0° for 20 min and worked up as above to yield 1.103 g (83%) of **5** (R = benzyl): bp 106–108° (0.3 mm). This was identical by vpc, ir, and nmr to the sample prepared above.

Attempted Generation of Dianion 3 with Lithium Bis(trimethylsilyl)amide. Lithium bis(trimethylsilyl)amide, bp 105–106° (0.5–0.7 mm), prepared from hexamethyldisilazane and *n*-butyllithium by the method of Amonoo-Neizer, *et al.*,[24] was dissolved in freshly distilled THF to give a 1.52 *M* solution. A solution of 0.385 g (3.32 mmol) of methyl acetoacetate in 25 ml of THF in a 50-ml three-necked flask was flushed with N_2. To this was slowly added 5.0 ml of 1.52 *M* lithium bis(trimethylsilyl)amide and the resulting solution was refluxed under N_2 for 0.5 hr, treated with 0.420 g (3.40 mmol) of benzyl chloride, and stirred for 20 min. The reaction mixture was worked up as above to give a pale brown oil which contained only methyl acetoacetate and no detectable alkylation product by tlc.

Generation of the Dianion 3 Using Methyllithium. The dianion **3** was prepared as above from 1.161 g (10.0 mmol) of methyl acetoacetate, 0.465 g (11.0 mmol) of sodium hydride, and 5.0 ml of 2.1 *M* (10.5 mmol) methyllithium in hexane in 25 ml of THF. This was alkylated with allyl bromide (1.332 g, 11.0 mmol) for 10 min and worked up as above to give 1.170 g (75%) of **5** (R = allyl): bp 99–101° (14 mm), which was identical to the compound prepared above by spectroscopic analysis and vpc (column A, 120°, and column B, 140°).

Methyl 3-Oxo-4-methyloctanoate (6, R = *n*-Butyl, R′ = Methyl). The dianion **7** (R = *n*-butyl) was prepared from 1.72 g (10.0 mmol) of methyl 3-oxooctanoate (**5**, R = *n*-butyl), 0.54 g (11.0 mmol) of sodium hydride, and 5.0 ml of 2.2 *M* *n*-butyllithium (11.0 mmol) in 25 ml of THF. This dianion was alkylated with 1.70 g (12.0 mmol) of methyl iodide for 15 min at 0° and worked up as above to give 1.51 g (81%) of distilled product: bp 54–56° (0.3 mm); ir ($CHCl_3$) 3010, 2950, 2940, 2860, 1740, 1705, 1645, 1620, 1450, 1440, 1380, 1320, 1160, 1005 cm^{-1}; nmr ($CDCl_3$) δ 0.88 (br t, $J \simeq 7$ Hz, 3 H), 0.99 (d, $J = 6.8$ Hz, 3 H), 1–1.8 (m, 6 H), 2.8 (m, 1 H), 3.45 (s, 2 H), 3.75 (s, 3 H), 4.98 (s).[23]

Methyl 3-Oxo-4-allyloctanoate (6, R = *n*-Butyl, R′ = Allyl). The dianion **7** (R = *n*-butyl) was prepared from 1.72 g (10.0 mmol) of methyl 3-oxooctanoate (**5**, R = *n*-butyl), 0.58 g (11.5 mmol) of sodium hydride, and 4.8 ml of 2.2 *M* (10.6 mmol) *n*-butyllithium in THF. This dianion was alkylated with 1.22 g (10.0 mmol) of allyl bromide and worked up as above after 10 min at 0° to give 1.60 g (76%) of distilled product: bp 82–84° (0.6 mm); ir ($CHCl_3$) 3050, 3025, 3000, 2950, 2940, 2860, 1740, 1705, 1640, 1620, 1450, 1440, 1405, 1320, 1155, 1040, 1020, 1005, 930 cm^{-1}; nmr ($CDCl_3$) δ 0.87 (br t, 3 H), 1–1.8 (m, 6 H), 2–2.8 (m, 3 H), 3.46 (s, 2 H), 3.74 (s, 3 H), 4.8–5.2 (m, 2 H), 5.3–6.0 (m, 1 H); mass spectrum *m/e* (rel intensity) 212 (7), 172 (9), 169 (11), 156 (34), 155 (14), 141 (8), 139 (11), 138 (13), 130 (15), 129 (26), 124 (14), 117 (12), 116 (100), 101 (94), 99 (52), 98 (20), 97 (22), 84 (39), 82 (48), 81 (20), 74 (41), 71 (30), 69 (80), 59 (55), 57 (23), 55 (66), 43 (86), 41 (87).

Methyl 3-Oxo-4-benzyloctanoate (6, R = *n*-Butyl, R′ = Benzyl). The dianion **7** (R = *n*-butyl) was prepared from 1.72 g (10.0 mmol) of methyl 3-oxooctanoate (**5**, R = *n*-butyl), 0.52 g (10.8 mmol) of sodium hydride, and 4.8 ml of 2.2 *M* (10.6 mmol) *n*-butyllithium in THF. This dianion was alkylated with 1.52 g (12 mmol) of benzyl chloride at room temperature for 0.5 hr and worked up as above to give 1.64 g (63%) of distilled product: bp 122–123° (0.4 mm); ir ($CHCl_3$) 3025, 3000, 2950, 2930, 2855, 1740, 1705, 1645, 1625, 1605, 1495, 1450, 1440, 1405, 1370, 1315, 1155, 1080, 1020, 700 cm^{-1}; nmr ($CDCl_3$) δ 0.87 (br s, 3 H), 1–2 (m, 6 H), 2.8 (m, 3 H), 3.25 (s, 2 H), 3.66 (s, 3 H), 4.85 (s),[23] 7.23 (br s, 5 H); mass spectrum *m/e* (rel intensity) 262 (9), 206 (9), 205 (32), 189 (8), 153 (15), 131 (21), 119 (10), 101 (21), 91 (100), 69 (11), 59 (11), 41 (11).

Methyl 3-Oxo-4-benzylpentanoate (6, R = Methyl, R′ = Benzyl). The dianion **7** (R = methyl) was prepared from 1.30 g (10.0 mmol) of methyl 3-oxopentanoate (**5**, R = methyl), 0.52 g (10.8 mmol) of sodium hydride, and 4.8 ml of 2.2 *M* *n*-butyllithium (10.5 mmol) in THF. This dianion was alkylated with 1.40 g (11.0 mmol) of benzyl chloride for 20 min at 0° and worked up as above to give 1.68 g (76%) of distilled product: bp 104–105° (0.5 mm); ir ($CHCl_3$) 3050, 3000, 2950, 2930, 2875, 2850, 1735, 1705, 1645, 1620, 1600, 1495, 1450, 1440, 1410, 1375, 1360, 1315, 1160, 1080, 1035, 1005, 700 cm^{-1}; nmr ($CDCl_3$) δ 1.10 (d, $J = 6.6$ Hz, 3 H), 2.4–3.2 (m, 3 H), 3.37 (s, 2 H), 3.65 (s, 3 H), 4.92 (s),[23] 7.23 (br s, 5 H); mass spectrum *m/e* (rel intensity) 220 (12), 147 (14), 146 (11), 119 (11), 118 (19), 101 (18), 91 (100), 69 (9), 65 (11), 59 (11), 42 (12).

This same compound was also prepared from the dianion **7** (R = benzyl) which was generated from 1.03 g (5.0 mmol) of methyl 3-oxo-5-phenylpentanoate (**5**, R = benzyl), 0.25 g (15.4 mmol) of sodium hydride, and 2.5 ml of 2.2 *M* *n*-butyllithium (5.4 mmol) and 0.80 g (5.6 mmol) of methyl iodide to give 0.95 g of product, bp 99–100° (0.3 mm), identical to the compound obtained above.

Ethyl 3-Oxohept-6-enoate. The dianion **2** was prepared as above from 1.30 g (10.0 mmol) of ethyl acetoacetate, 0.54 g (10.8 mmol) of sodium hydride, and 4.8 ml of 2.2 *M* *n*-butyllithium (10.5 mmol). This dianion was alkylated with 1.33 g (11.0 mmol) of allyl bromide at 0° for 5 min to give 1.30 g (77%) of distilled product: bp 106–108° (15 mm); ir ($CHCl_3$) 3075, 3025, 2980, 2930, 1735, 1710, 1640, 1465, 1445, 1415, 1375, 1320, 1160, 1100, 1040, 1005, 930 cm^{-1}; nmr ($CDCl_3$) δ 1.27 (t, $J = 7.0$ Hz, 3 H), 2–2.8 (m, 4 H), 3.44 (s, 2 H), 4.19 (q, $J = 7.0$ Hz, 2 H), 4.8–5.3 (m, 2 H), 4.98 (s),[23] 5.5–6.2 (m, 1 H); mass spectrum *m/e* (rel intensity) 170 (11), 125 (7), 124 (14), 115 (19), 96 (16), 87 (39), 83 (43), 82 (56), 81 (11), 69 (59), 55 (100), 54 (62), 53 (21), 43 (83), 42 (39), 41 (46).

Ethyl 3-Oxo-2-methylhexanoate. The dianion from an α-substituted β-keto ester was prepared as above from 1.44 g (10.0 mmol) of ethyl 2-methylacetoacetate, 0.54 g (10.5 mmol) of sodium hydride, and 4.8 ml of 2.2 *M* *n*-butyllithium (10.5 mmol). This dianion was then alkylated with 1.20 g (11.0 mmol) of ethyl bromide for 15 min to give 1.34 g (78%) of distilled product: bp 102–105° (15 mm); ir ($CHCl_3$) 2960, 2930, 2875, 1735, 1705, 1600, 1455, 1380, 1365, 1320, 1300, 1190, 1020, 860 cm^{-1}; nmr ($CDCl_3$) δ 0.90 (t, $J = 6.8$ Hz, 3 H), 1.25 (t, $J = 7$ Hz, 3 H), 1.32 (d, $J = 7$ Hz, 3 H), 1.3–1.9 (m, 2 H), 2.51 (t, $J \simeq 7$ Hz, 2 H), 3.51 (q, $J = 7$ Hz, 1 H), 4.18 (q, $J = 7$ Hz, 2 H); mass spectrum *m/e* (rel intensity), 172 (1), 120 (3), 118 (3), 102 (3), 87 (11), 85 (66), 83 (100), 48 (11), 47 (24), 43 (12).

Methyl 2-Oxo-3-allylcyclohexanecarboxylate. The dianion of methyl 2-oxocyclohexanecarboxylate was generated by treating 0.233 g (1.50 mmol) of the above ester [bp 97–100° (14 mm), prepared by the method of Rhoads, *et al.*[18]] with 0.075 g (1.65 mmol) of sodium hydride and 0.70 ml of 2.3 *M* *n*-butyllithium (1.61 mmol) in *ca.* 25 ml of THF. This dianion was alkylated with 0.198 g (1.65 mmol) of allyl bromide to give 0.197 g (67%) of distilled product: bp 110–112° (14 mm); ir ($CHCl_3$) 3550, 3025, 2960, 2890, 1740, 1710, 1650, 1610, 1440, 1360, 1300, 1170, 1005, 920 cm^{-1}; nmr ($CDCl_3$) δ 1.1–2.7 (m, 9 H), 3.70 (s, 3 H), 4.8–5.2 (m, 2 H), 5.3–6.0 (m, 1 H), 14.23 (br s, exchangeable D_2O, 1 H); mass spectrum *m/e* (rel intensity) 196 (55), 165 (37), 164 (60), 155 (24), 154 (51), 137 (36), 136 (49), 125 (32), 123 (100), 122 (30), 119 (49), 109 (24), 108 (77), 95 (70), 94 (48), 93 (47), 87 (54), 79 (77), 68 (65), 55 (90), 41 (100).

Alkylation of Dianion 3 with 1,3-Dibromopropane. (a) With 1 Equiv of Alkylating Agent. The dianion **3** was prepared as above from 1.16 g (10.0 mmol) of methyl acetoacetate and subsequently treated with 2.02 g (10.0 mmol) of 1,3-dibromopropane for 10 min. After the usual work-up a yellow oil was obtained which was chromatographed on silica gel using chloroform eluent to yield 0.52 g (33%) of methyl 2-oxocyclohexanecarboxylate (**9**, $n = 3$), which was identified by comparison of its ir and nmr spectra and tlc with an authentic sample,[18] and 0.50 g (37%) of dimethyl 3,9-dioxoundecanedioate (**10**, $n = 3$): bp 117–119° (0.2 mm); ir ($CHCl_3$) 3060, 2990, 2910, 1745, 1720, 1660, 1640, 1440, 1415, 1370, 1325, 1170, 1020, 940 cm^{-1}; nmr ($CDCl_3$) δ 1.1–1.9 (m, 6 H), 2.37 (t, $J = 6$ Hz, 4 H), 3.43 (s, 4 H), 3.76 (s, 6 H), 5.01 (s);[23] mass spectrum *m/e* (rel intensity) 254 (65), 167 (85), 157 (55), 139 (17), 129 (16), 121 (50), 116 (39), 101 (25), 82 (68), 59 (40), 55 (58), 43 (100).

(b) With 0.5 Equiv of Alkylating Agent. This reaction was performed in the same manner as the previous experiment using 1.16 g (10.0 mmol) of methyl acetoacetate and 1.01 g (5.0 mmol) of 1,3-dibromopropane to yield 1.05 g (77%) of distilled dimethyl 3,9-dioxoundecanedioate (**10**, $n = 3$) identical to the sample prepared in previous experiment.

(c) Dilution Study. A solution of dianion **3** was prepared from 1.16 g (10.0 mmol) of methyl acetoacetate in *ca.* 25 ml of THF. A solution of 2.02 g (10.0 mmol) of 1,3-dibromopropane in *ca.* 25 ml of THF was also prepared. A 250-ml flask was equipped with a Soxhlet extractor which carried a three-necked adapter and reflux

(24) E. H. Amonoo-Neizer, R. A. Shaw, D. O. Shovlin, and B. C. Smith, *J. Chem. Soc.*, 2997 (1965).

condenser. Approximately 50 ml of THF was added to the apparatus and it was heated to a moderate reflux. The solutions of dianion **3** and 1,3-dibromopropane were then added to the Soxhlet extractor *via* stainless steel cannulae at such a rate that one drop of each solution was added to each cycle of the extractor. After the addition was complete, reflux was maintained for several more cycles and the apparatus was allowed to cool before the reaction was worked up as above to give 1.06 g (68%) of distilled methyl 2-oxocyclohexanecarboxylate (**9**, $n = 3$) which was identical to the sample of **9** ($n = 3$) prepared previously. The residue from the distillation was chromatographed on silica gel using chloroform eluent to give 0.15 g (11%) of dimethyl 3,9-dioxoundecanedioate (**10**, $n = 15$).

Methyl 2-(2'-Carbomethoxy-3'-oxocyclohex-1'-enyl)acetate (12). The dianion **3** from 1.16 g (10.0 mmol) of methyl acetoacetate was alkylated with 0.87 g (5.0 mmol) of dibromomethane as in section b of the previous experiment to yield 0.70 (62%) of distilled **12**: bp 75–78° (0.2 mm); ir ($CHCl_3$) 3575, 3075, 3010, 2940, 1740, 1735, 1685, 1640, 1445, 1380, 1360, 1340, 1320, 1180, 1080, 1060, 1020, 965, 940, 860, 810 cm^{-1}; nmr ($CDCl_3$) δ 1.8–2.2 (m, 2 H), 2.3–2.7 (m, 4 H), 3.35 (s, 2 H), 3.75 (s, 3 H), 3.83 (s, 3 H); uv (CH_3OH) 288 nm (ϵ 1.2 × 10^4); mass spectrum *m/e* (rel intensity) 226 (19), 195 (43), 194 (100), 166 (45), 162 (100), 138 (40), 129 (23), 112 (24), 107 (28), 101 (21), 82 (38), 79 (48), 70 (46), 59 (51), 43 (57).

Dimethyl 3,16-Dioxooctadecanedioate (10, $n = 10$). The dianion **3** from 1.16 g (10.0 mmol) of methyl acetoacetate was reacted with 1.50 g (5.0 mmol) of 1,10-dibromodecane to give a crude product which solidified on standing overnight and was subsequently recrystallized from ether to give 1.52 g (98%) of **10** ($n = 10$): mp 80–82°; ir ($CHCl_3$) 3090, 3050, 2970, 2900, 1745, 1720, 1640, 1620, 1450, 1420, 1335, 1170, 1030, 940 cm^{-1}; nmr ($CDCl_3$) δ 1.2 (m, 20 H), 2.43 (t, $J = 6$ Hz, 4 H), 3.27 (s, 4 H), 3.70 (s, 6 H), 4.90 (s);[23] mass spectrum *m/e* (rel intensity) 370 (10), 339 (13), 338 (12), 320 (16), 296 (24), 265 (18), 256 (17), 255 (100), 237 (21), 223 (14). 205 (22), 195 (11), 181 (23), 178 (14), 163 (27), 158 (12), 143 (9), 129 (71), 116 (90), 101 (51), 69 (58), 59 (95), 43 (65).

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Electrochemical Generation of Carbazoles from Aromatic Amines

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Abstract: It has been found that substituted di- and triphenylamines cyclize to form the corresponding carbazoles in acetonitrile upon anodic oxidation at platinum. The reaction occurs through the dication and will take place only if the cation radical is stable. This same overall process occurs photochemically, and comparisons are made between the two pathways; it was not established that there is common mechanistic ground but some possible parallels are explored. A recent report of the same type of reaction for tetraarylethylenes suggests that this may be a general anodic oxidation pathway for electrolytically generated aromatic dications.

The conversion of aromatic amines to carbazoles *via* an intramolecular cyclization pathway has been effected by a number of chemical methods. Carbazole has been generated from 2-aminobiphenyl by both thermal cyclization[2,3] and glow discharge[4] techniques. Photochemical processes involving this same pathway have been shown to lead from *N*-arylenamines to 2,3-dihydroindoles[5a] and indolines.[5b] However, most of the photochemical studies have been concerned with the conversion of di- and triphenylamines to the corresponding carbazoles.[6-13] These latter investigations, and some additional reports, have been involved with the photochemical mechanism by which this transformation occurs. A good deal of controversy still exists over the kinetics of the process and the nature of the intermediates involved,[11-16] but it is more or less firmly established that reaction occurs through the amine triplet, which can decay back to the ground state by energy transfer to the solvent or oxygen or it can cyclize to an 11,12-dihydrocarbazole which eliminates hydrogen to form a carbazole (*e.g.*, *N*-phenylcarbazole from triphenylamine). Mass spectrometric data indicate that the 11,12 hydrogens are trans to one another in the dihydrocarbazole since they are lost stepwise rather than as molecular hydrogen.[17,18]

Since some of these reactions have been characterized as being photooxidations, we have been concerned with analogous cyclizations in the electrochemical oxidations of aromatic amines in nonaqueous media. Our primary concern has been with the decomposition pathways of amine cation radicals, and in studying these

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