Acknowledgment. This research was supported in part by the Consejo Nacional de Investigaciones Cientificas y Tecnicas and Secretaria de Estado de Ciencia y Tecnologia, Argentina.

Registry No. 4, 1582-09-8; 5·K (R = $CH_3CHCH_2CH_3$; R^1 = H), 79816-18-5; 5·K (R = $CH_3(CH_2)_3$; R^1 = H), 79871-51-5; 5·K (R = R^1 = $-(CH_2)_5-$), 79816-19-6; 5·2K (R = cH_3CHCO_2H; R^1 = H), 79816-20-9; 5·2K (R = $CH_3CHOHCHCO_2H$; R^1 = H), 79827-20-6; 9, 10223-72-0; *sec*-butylamine, 13952-84-6; piperidine, 110-89-4; alanine, 56-41-7; threonine, 72-19-5; *n*-butylamine, 109-73-9.

Supplementary Material Available: Table of UV-vis spectral data on solutions of 4 + piperidine in Me_2SO-H_2O (3 pages). Ordering information is given on any current masthead page.

Electroreductive Cyclopropylcarbonylation of Aromatic Ketones and Their Schiff Bases

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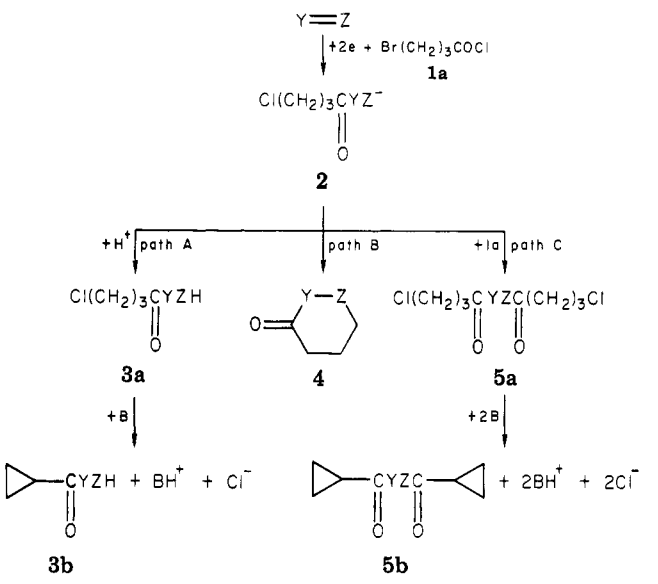
Mono- and dicyclopropylcarbonyl derivatives have been obtained by electroreduction of fluorenone, benzophenone, fluorenone anil, and benzophenone anil in the presence of 1 equiv of 4-bromo(or chloro)butyryl chloride (**1a** or **1b**). The electrolyses are carried out in DMF or MeCN according to two methods. In method A, **1a** (or **1b**) is added dropwise during the electrolysis. In method B, the total amount of **1a** (or **1b**) is added at the beginning of the experiment. The electrogenerated bases which are necessary to perform the cyclopropylcarbonylation reactions are either the radical anions of the depolarizers or their acylated anions. The distribution of the compounds and their yields, which are moderate, depend on two main factors which are the method applied and the solvent. It is shown that the properties of acid chlorides **1a** and **1b** differ in DMF and MeCN. The highest yields of cyclopropyl derivatives are reached in MeCN when method B is applied. However, in this solvent the acylation reaction is less specifically orientated than in DMF, and unexpected propionitrile derivatives are isolated. In the case of the anils, results of chemical reduction by alkali metals and electrochemical reduction are compared.

In a previous publication,[1] we have reported the electrosynthesis in *N,N*-dimethylformamide (DMF) of numerous acylated compounds. During the electrochemical reduction of unsaturated compounds Y=Z in the presence of 1 equiv of 4-bromobutyryl chloride (**1a**), we have obtained,[1] via the intermediate anion **2**, the monoacylated compounds **3a**, the cyclic compounds **4**, and the diacylated compounds **5a** (Scheme I).

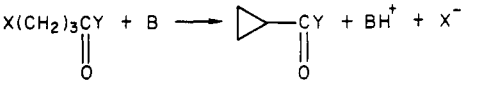
The formation of **3a** is favored if the intermediate acylated anion **2** presents a basic character and the competitive formation of **4** and **5a** occurs when **2** has nucleophilic properties.

In this report, we describe the electrosynthesis of cyclopropyl derivatives **3b** and **5b** (ketones, esters, and amides) during the electrolyses in DMF or acetonitrile (MeCN) of aromatic ketones (fluorenone (**6**), benzophenone) and Schiff bases (fluorenone anil (**7**), benzophenone anil (**8**)) in the presence of 1 equiv of **1a** or 4-chlorobutyryl chloride (**1b**). For the cyclopropylcarbonylation according to Scheme II, strong bases (B) and, in many cases, high temperatures are required.[2-4] We will show that, under in our experimental conditions, strong bases (B) are electrochemically generated which favor the transformation of **3a** to **3b** and that of **5a** to **5b** (Scheme I).

Scheme I



Scheme II[a]



[a] X = halogen; Y = R, OR, X, NR_2.

On the account of the known acidic properties of MeCN, we may anticipate that the nature and the distribution of the electrolysis compounds will depend on the solvent. If

(1) C. Degrand, P.-L. Compagnon, G. Belot, and D. Jacquin, *J. Org. Chem.*, **45**, 1189 (1980).
(2) G. W. Cannon, R. C. Ellis and J. R. Leal in "Organic Syntheses", Collect. Vol. IV, Wiley, New York; 1963, p 597.
(3) B. W. Horrom and L. R. Swett (Abbott Laboratories), U.S. Patent 2 992 269 (1961).
(4) R. E. A. Dear and E. E. Gilbert, *J. Org. Chem.*, **33**, 1690 (1968).

0022-3263/82/1947-0325$01.25/0

strong bases are electrochemically generated in MeCN during electrolyses, they may abstract protons from the solvent and lead to the formation of anions $^-CH_2CN$ which can react with electrophilic moieties present in the catholyte.[5-7] On the other hand, as shown in the following part, the electrochemical behavior of aliphatic acid chlorides differs in DMF and in MeCN.

Two types of electrolyses are performed. In method A, colored radical anions of depolarizer are first electrogenerated; then **1a** (or **1b**) is added dropwise in order that the color of the catholyte never vanishes. In method B, the starting material is reduced in the presence of an equivalent of **1a** (or **1b**). Due to the instability in DMF of Schiff bases when an aliphatic acid chloride is added,[1] the decomposition of anils **7** and **8** is avoided in a large extent by carrying out the experiments in DMF according to method A. In MeCN, **7** and **8** are stable in the presence of **1a** (or **1b**) so that the electrolyses can be performed either with method A or with method B. As shown in the following part, striking differences in the results are obtained in MeCN, depending on the method applied.

In the case of Schiff bases **7** and **8**, electrochemical results are compared with the results obtained by chemical reduction with alkali metals (Li, Na, K) in diethyl ether of hexamethylphosphoric triamide (HMPT).

Results and Discussion

(A) Polarographic and Voltammetric Behavior of Aliphatic Acid Chlorides in DMF and MeCN. DMF as Solvent. We have already mentioned that, in DMF and on a dropping mercury electrode, the reduction of aliphatic acid chlorides RCOCl takes place at -1.40 ± 0.05 V vs. SCE.[1] We have recently observed that, besides the cathodic wave, two oxidation waves appear ($E_{1/2} = -0.19 \pm 0.04$ and $+0.13 \pm 0.04$ V) on the polarograms of **1b** and acetyl chloride. Under the same experimental conditions, the two oxidation waves of lithium chloride[8] have similar half-wave potentials and heights. It may be concluded that **1b**, acetyl chloride, and more generally aliphatic acid chlorides are completely dissociated into chloride anions and acylium cations which have been shown[9,10] to react with the solvent to form an immonium salt, **9**. Therefore, the reduction wave observed at about −1.4 V corresponds to the reduction of **9**.

$$(CH_3)_2\overset{+}{N}=CHOCR,\ Cl^-$$
$$\qquad\qquad\quad \|$$
$$\qquad\qquad\quad O$$

9

Bromo acid chloride **1a** gives the same immonium salt **9** (R = $(CH_2)_3Cl$) as **1b** since it is known[11] that in DMF the order of nucleophilicity is $Cl^- > Br^- > I^-$. This is the reason that in Scheme I the reduction of unsaturated compounds in the presence of **1a** leads to the formation of chloroderivatives **2**, **3a**, **4**, and **5a**.

$$Br(CH_2)_3C(O)Cl + (CH_3)_2NC(O)H \rightarrow$$
$$(CH_3)_2N^+=CHOC(O)(CH_2)_3Br + Cl^- \rightarrow$$
$$(CH_3)_2N^+=CHOC(O)(CH_2)_3Cl + Br^-$$

(5) E. M. Abbot, A. J. Bellamy and J. Kerr, *Chem. Ind. (London)*, 828 (1974).
(6) A. J. Bellamy, *J. Chem. Soc., Chem. Commun.*, 944 (1975).
(7) A. J. Bellamy, A. Howat, and J. S. MacKirdy, *J. Chem. Soc., Perkin Trans. 2*, 786 (1978), and references therein.
(8) P. H. Given and M. E. Peover, *J. Electrochem.*, 1602 (1959).
(9) S. Nadzhimutdinov, T. Khalikov, and K. U. Usmanov, *Dokl. Akad. Nauk SSSR*, **211**, 642 (1973).
(10) G. J. Martin, and N. Naulet, *Tetrahedron Lett.*, 357 (1976).
(11) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

Table I. Polarographic Reduction in DMF and MeCN of Fluorenone 6 and Anils 7 and 8 in the Presence of 1 Equiv of Acid Chloride 1a or 1b

		$-E_{1/2}$ [a]			
compd	solvent	A	C	C′	D
6	DMF	1.35	0.66		1.07
	MeCN	1.35			1.25
7	DMF	1.40	0.43	0.78	1.25
	MeCN	1.55	0.65	0.95	1.45
8	DMF	1.85	0.70	1.13	1.76
	MeCN	1.85			1.85

[a] Potentials, in volts, with respect to the SCE. See Figure 1 for A, C, C′, and D.

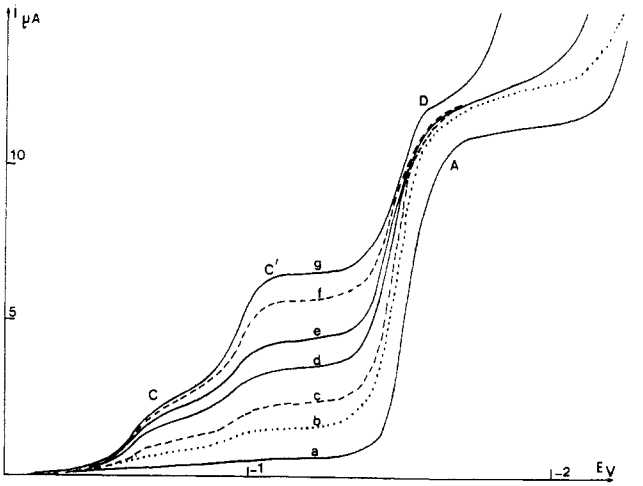


Figure 1. Polarograms of **7** in the presence of increasing amounts of **1b** in MeCN (Bu_4NPF_6 at 0.1 M). Curve a is **7** alone (1 mmol/L). The remaining curves for different molar ratios of **1b**/**7** are as follows: b, 1; c, 2; d, 3; e, 5; f, 10; g, 20.

MeCN as Solvent. The electrochemical behavior of aliphatic acid chlorides in MeCN differs from that in DMF. The anodic waves are no longer observed, and the cathodic wave appears at more negative ptentials ($E_{1/2} = -2.14$ V for **1a** and **1b**, −2.46 V for acetylchloride, and −2.0 V for succinyl chloride). The conclusion which can be drawn from these results is that aliphatic acid chlorides are not dissociated in MeCN. A consequence is that a different reactivity of acid chlorides toward a nucleophilic attack can be expected, depending on the solvent.

(B) Polarographic Reduction of Ketone 6 and of Anils 7 and 8 in the Presence of Acid Chlorides 1a or 1b. In the absence of acid chloride, the polarographic behavior of **6** is described in ref 12 and that of **7** and **8** in ref 13 in which the basic properties of the radical anions of anils **7** and **8** are shown.

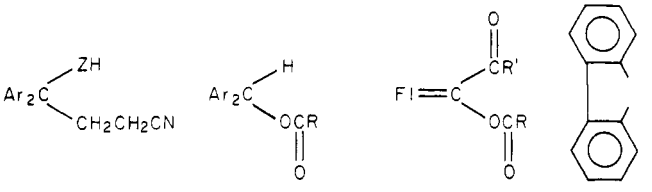
Fluorenone (6). We have described elsewhere[1] the polarographic behavior in DMF of **6** in the presence of 1 equiv of acid chloride. Besides wave A corresponding to the formation of a stable radical anion, two more positive waves C and D appear when **1a** is added. It has been shown[1] that, at potentials corresponding to the plateau of either wave C or D, an acylated radical is formed which is further reduced to an anion. In MeCN, the more positive wave observed in DMF (kinetic wave C) is absent; it shows that no acylated cation whose reduction corresponds to wave C in DMF is present in solution. In Table I are listed the half-wave potentials ($E_{1/2}$) of waves A, C and D of **6** in DMF and MeCN.

(12) M. K. Kalinowski, *Chem. Phys. Lett.*, **7**, 55 (1970).
(13) C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.*, **33**, 455 (1971).

Anils 7 and 8. In DMF, the polarograms of **7** and **8** present one more kinetic wave (wave C′) situated between waves C and D (Table I). In MeCN, waves A and D have same $E_{1/2}$ values in the case of **8**; in other words, only an increase of the limit current of wave A is observed when **1a** or **1b** is added. In the case of **7**, the polarographic behavior in MeCN is rather similar to that in DMF (Figure 1). These results are summarized in Table I. The origin of a double kinetic wave is not yet elucidated and may be due to adsorption phenomena since their relative height changes with the depolarizer concentration (Figure 1).

All electrolyses hereunder described are performed at potentials corresponding to wave D.

(C) Preparative Scale Electroreduction of Ketone 6 and Schiff Bases 7 and 8 in the Presence of Acid Chlorides 1a or 1b. Fluorenone (6) in MeCN as Solvent. An electrolysis of **6** (11×10^{-3} M) is carried out on a mercury electrode in the presence of 1 equiv of **1b** (method B, applied potential = -1.35 ± 0.05 V). It is stopped after total consumption of **1b**, that is to say when a red coloration characteristic of the presence of stable radical anions starts to appear in the bulk of the catholyte. Under these experimental conditions, 1.7 F are consumed, and we isolate a mixture of starting material left (15%), fluorenol (11%), unexpected nitrile derivatives **10a** (5%), monoacylated compound **11a** (3.5%), and diacylated compounds **12b** (17%) and **12c** (8%). The yields are given after purification by column chromatography.



10a, Ar_2 = Fl; ZH = OH
b, Ar_2 = Fl; ZH = NHPh
c, Ar = Ph; ZH = NHph

11a, Ar_2 = Fl; R = $(CH_2)_3Cl$
b, Ar_2 = Fl; R = c-Pr
c, Ar = Ph; R = c-Pr

12a, R = R′ = $(CH_2)_3Cl$
b, R = $(CH_2)_3Cl$; R′ = c-Pr
c, R = R′ = c-Pr

Fl

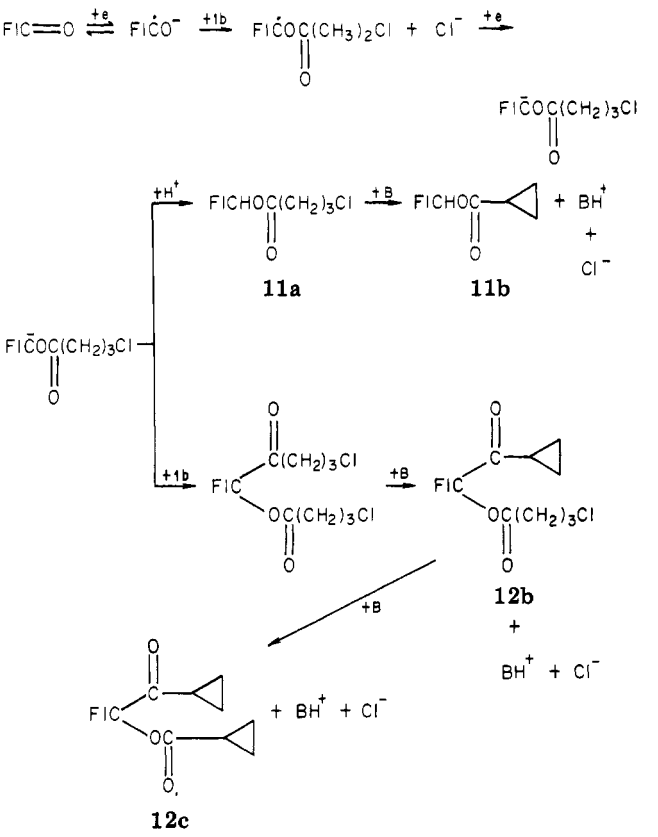
During the electrolysis, **12c** is generated at the expense of **12b**, and compound **11a** appears at the end of the electrolysis, after consumption of a large amount of acid chloride. A further transformation of **11a** to **11b** and of **12b** to **12c** is observed if the experiment is carried out longer. On the other hand, the transformation of **12b** to **12c** also occurs when **6** is reduced in the presence of **12b**; meanwhile some bifluorenol is formed.

Scheme III accounts for this whole set of results, except the origin of **10a** which will be discussed later. The strong bases B which are able to abstract protons from **11a** and **12a** are either the fluorenone radical anions or the intermediate acylated anions.

Carboxylic acid cyclopropyl esters **11b** and **12c** are unstable in the bulk of the catholyte. A study on their instability and their electrochemical properties will be reported later.[14]

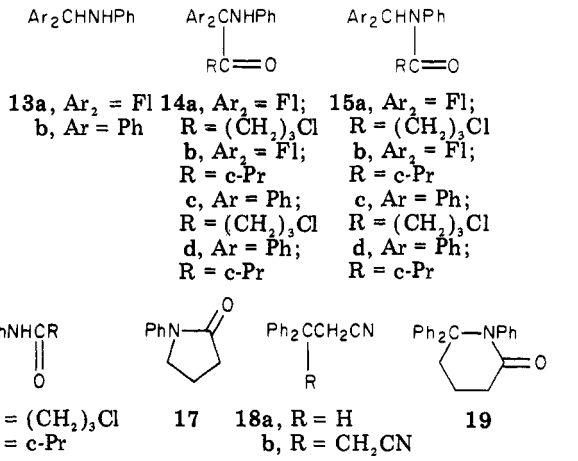
Anils 7 and 8 in MeCN or DMF as Solvent. In the case of **7** and **8**, a series of preparative electrolyses are carried out by changing the solvent (DMF or MeCN), the method (A or B), the nature of the cathode (mercury pool or glassy carbon cloth), and the temperature. Table II gives the structures of the isolated compounds and their yield after purification by column chromatography for a series of six electrolyses performed on a mercury pool

Scheme III



11a **11b** **12b** **12c**

Chart I



13a, Ar_2 = Fl; **b**, Ar = Ph

14a, Ar_2 = Fl; R = $(CH_2)_3Cl$
b, Ar_2 = Fl; R = c-Pr
c, Ar = Ph; R = $(CH_2)_3Cl$
d, Ar = Ph; R = c-Pr

15a, Ar_2 = Fl; R = $(CH_2)_3Cl$
b, Ar_2 = Fl; R = c-Pr
c, Ar = Ph; R = $(CH_2)_3Cl$
d, Ar = Ph; R = c-Pr

16a, R = $(CH_2)_3Cl$
b, R = c-Pr

17

18a, R = H
b, R = CH_2CN

19

electrode at 18 °C in DMF (method A) or MeCN (methods A and B).

An electrolysis similar to expt 1 of Table II, but performed on a glassy carbon cloth as cathode, does not modify the product distribution; the same conclusion holds if acid chloride **1b** is added instead of **1a** in expt 1. Changing the temperature from +18 to −15 °C does not affect the distribution and the yields of the compounds.

Taking into account the method applied, it is worthwile to draw the following comments from results of Table II.

Method A. In DMF where only method A can be applied (expts 1 and 4), the radical anion of **7** and **8** is basic enough to abstract protons from the catholyte (protonation by residual water)[15] as soon as it is generated, so that high yields of saturated amines **13a** (expt 1) and **13b** (expt 4) are obtained (see Chart I). In expt 4, the formation of **11c** which derivates from benzophenone shows that a

(14) C. Degrand and G. Belot, unpublished results.

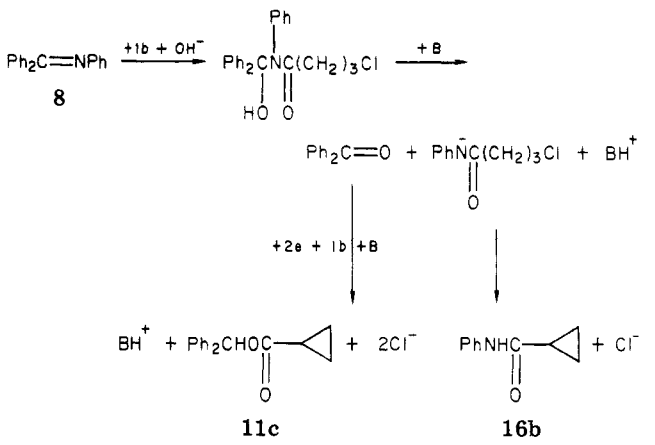
(15) T. Troll and M. M. Baizer, *Electrochim. Acta*, **20**, 33 (1975).

Table II. Electrochemical or Chemical Reduction in DMF and MeCN of Anils 7 and 8 in the Presence of Acid Chloride 1a or 1b

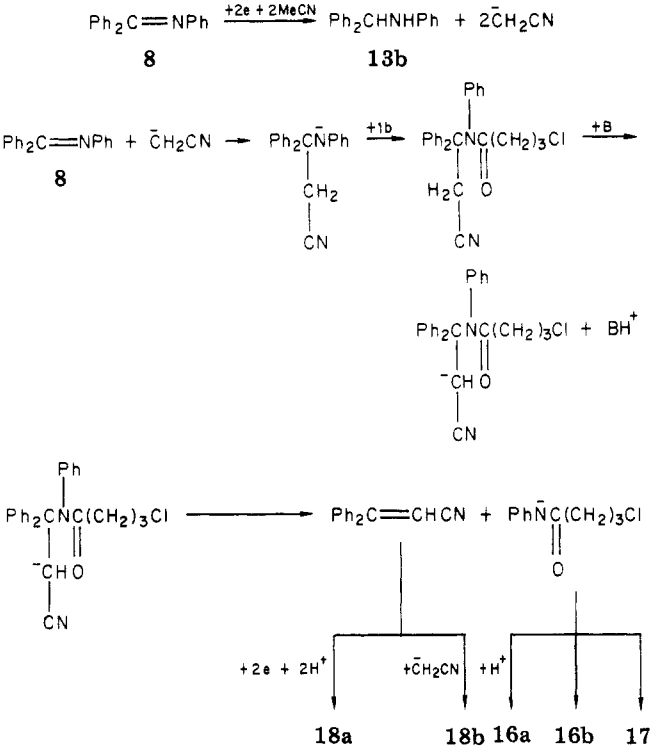
expt	Schiff bases	solvent	acid chloride	method	isolated compds (% yield)						
					$Ar_2CHNHPh$	$Ar_2C(C(O)R)NHPh$ R = $(CH_2)_3Cl$	$Ar_2C(C(O)R)NHPh$ R = c-Pr	$Ar_2CHN(C(O)R)Ph$ R = $(CH_2)_3Cl$	$Ar_2CHN(C(O)R)Ph$ R = c-Pr	cleaved *N*-phenylamide	nitrile derivatives	miscellaneous
1	7	DMF	1a	A	**13a** (48)		**14b** (20)					
2	7	MeCN	1b	A	**13a** (15)	**14a** (21)	**14b** (15)	**15a** (12)		**16a** (3.5), **17** (5.5)		
3	7	MeCN	1b	B	**13a** (16)		**14b** (31)		**15b** (3)	**16b** (8)	**10b** (11)	
4	8	DMF	1b	A	**13b** (56)					**16b** (18)		**11c** (20)
5	8	MeCN	1b	A	**13b** (33)					**16a** (3.5), **16b** (2), **17** (12)	**18a** (14), **18b** (8)	
6	8	MeCN	1b	B	**13b** (23)		**14d** (9)	**15c** (8)	**15d** (20)		**10c** (6)	**19** (6)
7	7	Et_2O or HMPT	1a	chem[a] (Li, Na, K)			**14b** (0–20)					**6** (15–20), **7** (20–30), fluorenol (40–50)
8	8	HMPT	1a	chem[a] (Na)	**13b** (69)					**16b** (5)		diphenylmethane (5)

[a] Chemical reduction.

Scheme IV



Scheme V

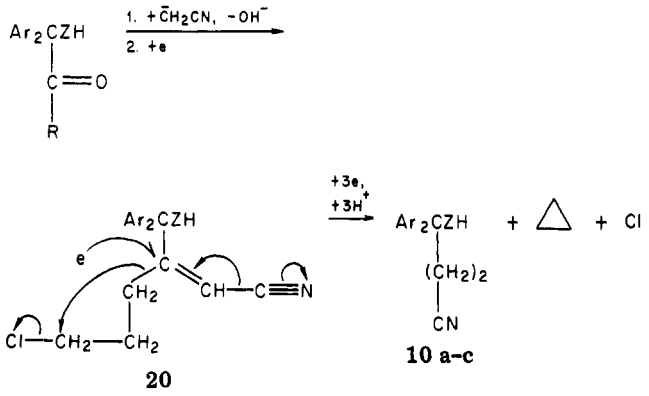


partial decomposition of **8** by **1b** and residual water occurs during the electrolysis (Scheme IV).

In Scheme IV, B is a strong base which may be, for instance, the radical anion of **8** or OH^-.

When method A is applied to the electroreduction of **8** in MeCN (expt 5), benzophenone anil radicals generated are sufficiently basic to abstract protons from the solvent, so that $^-CH_2CN$ anions appear which react with the depolarizer, leading to nitrile derivatives **18a** and **18b**. The total yield (17.5%) of *N*-phenyl amide derivatives **16a**, **16b** and **17** is close to that of **18a** + **18b** (22%), and therefore it is in agreement with the one expected from Scheme V. Nitrile derivatives **18a** and **18b** are also obtained by electroreduction of benzophenone in MeCN.[5-7] In expt 2 where method A is applied to **7**, the formation of **16a** + **17** (total yield 8%) may probably be described by a scheme of the same type. However, no nitrile derivative was isolated by column chromatography. Further, we notice the presence of some unidentified polymeric material left on the head of the column. This suggests the formation of unstable intermediate acrylonitrile derivatives which polymerize.

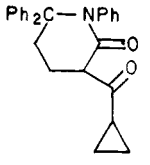
Scheme VI[a]



[a] ZH = OH or NHPh, R = $(CH_2)_3Cl$.

Method B. When **7** and **8** are reduced in MeCN according to method B, the unexpected formation of propionitrile derivatives **10b** and **10c** is observed. In the same manner, as already stressed in the foregoing results, nitrile derivative **10a** is also isolated when fluorenone (**6**) is reduced in MeCN according to method B. Since the formation of such compounds never occurs when method A is applied or when aromatic ketones are reduced in MeCN,[5-7] it seems that the propionitrile derivatives isolated do not arise from an attack of the depolarizer by $^-CH_2CN$ but from an attack of some acylated intermediates by this anion. According to this hypothesis, a reductive cleavage of an intermediate acrylonitrile (compound **20** in Scheme VI) should occur. In order to verify if Scheme VI may account for the formation of compounds **10a–c**, further studies are on progress.

(D) Chemical Reduction of Anils 7 and 8 in the Presence of 1b. Chemical reduction of **7** by various alkali metals (Li, Na, K) in diethyl ether or HMPT leads to a mixture of starting material, fluorenone, fluorenol, and **14b** except when lithium in ether is used. In that case, no **14b** is obtained. The yields of **14b** range from 10% to 20%. These results are summarized in expt 7 of Table II. Chemical reduction of **8** by sodium in HMPT leads to the saturated amine **13b** as the major compound and to diphenylmethane and **16b** as minor compounds (expt 8). It is interesting to note that chemical reduction of **8** in THF leads to a mixture of **13b**, **15d**, and **21** when ethyl 4-chlorobutyrate is added.[16]



21

Conclusion

Dicyclopropyl derivatives **12c** and monocyclopropyl derivatives **11c**, **12b**, **14b,d**, **15b,d**, and **16b** have been obtained in moderated yields by electroreduction of fluorenone, benzophenone, fluorenone anil, and benzophenone anil in the presence of **1a** or **1b**. Compounds **14b**, **15d**, and **16b** can also be prepared by chemical reduction of **7** and **8**.

Three main factors control the distribution of the products and their yields: the method applied, the nature of the solvent, and the properties of acid chlorides **1a** and **1b** which differ in DMF and in MeCN.

In case of the anils, the highest total yields of cyclopropyl derivatives are reached when method B is applied (up to 34% after purification). In the case of method A, two factors account for the lower yields of cyclopropyl derivatives; they are the instability of the anils during the electrolyses (only in DMF) and the basic properties of their radical anions which abstract protons from the catholyte to give high yields of hydrosaturated derivatives.[13] In MeCN, nucleophilic $^-CH_2CN$ anions are thus generated which may react with the depolarizer, so that nitrile derivatives are formed. In this solvent, the acylation reaction is less specifically orientated than in DMF: a comparison of the results obtained for anil **7** in DMF with those obtained in MeCN shows that only a C-acylation is observed in DMF whereas C- and N-acylations occur in MeCN. In the latter solvent, no diacylated derivatives are obtained for **7**, as in the case of fluorenone (**6**; cf. Scheme III). This is in agreement with the fact that the intermediately generated acylated anion is more basic in the case of **7** that in the case of **6**, so that its protonation is faster in the former case.

The formation of **19** is an illustration of path B of Scheme I. Propionitrile derivatives of the same type as **10a–c** can be obtained by electroreduction of ketones in the presence of acrylonitrile.[17] However, the formation of compounds **10a–c** when method B is applied is quite unexpected since it corresponds to the introduction of one more methylene group in the nitrile derivatives obtained when $^-CH_2CN$ anions are added to the starting materials. Further studies on the origin of compounds **10a–c** are on progress.

Experimental Section

Compounds **1a,b** and **6** are commercially available. Fluorenone anil (**7**) and benzophenone anil (**8**) are prepared according to ref 18. Solvents (MeCN and DMF) of analytical grade are carefully dried on 4-Å molecular sieves and then on neutral alumina.

An Amel-552 potentiostat, a Tacussel-IG5-N integrator, and a three-electrode Tacussel-Tipol polarograph are used. The general electrolysis procedure is described in ref 1.

^1H NMR spectra are recorded on a Perkin-Elmer R-24 spectrometer and ^{13}C NMR spectra on a JEOL FX-100 spectrometer ($CDCl_3$ solvent, Me_4Si internal standard). IR spectra are recorded on a Beckman IR-8 or a Perkin-Elmer 577 spectrophotometer. Mass spectra are recorded on a Finnigan 3003 spectrometer (direct introduction, EI, 70 eV). Microanalysis are worked out by Service Central d'Analyse CNRS, Lyon.

Electroreduction of Fluorenone (6) in the Presence of 4-Chlorobutyryl Chloride (1b) in MeCN (Method B). Substrate (2 g, 11.1 mmol) is reduced in the presence of **1b** (1.25 mL, 11.1 mmol) at −1.35 ● 0.05 V in MeCN ($E_{1/2}$ = −1.35 V): n = 1.7; crude product, 2.29 g; column chromatography, eluant 25:75 diethyl ether–hexane. The compounds are isolated in the following order: **11a** (3.5%), **6** (15%), **12b** (17%), **12c** (8%), fluorenol (11%), **10a** (5%).

9-[(4-Chlorobutyroyl)oxy]fluorene (11a): viscous liquid IR (film) 1748 (OC=O), 1630, 1465, 1200, 1150, 767, 747 cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.8 (m, 4 H, $COCH_2CH_2$), 3.5 (t, J = 6 Hz, 2 H, CH_2Cl), 6.68 (s, 1 H), 7.0–7.8 (m, 8 H, aromatic H); mass spectrum, m/e (relative intensity) 288 (10, M^+, ^{37}Cl), 286 (26, M^+, ^{35}Cl), 183 (12), 182 (100, $FlCHOH^+$), 181 (87), 166 (13), 165 (94, $FlCH^+$), 164 (30), 163 (30), 153 (17), 152 (46), 151 (19), 105 (59). Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.2; H, 5.27; Cl, 12.36; O, 11.16. Found: C, 71.94; H, 5.25; Cl, 11.39; O, 11.12.

9-[(4-Chlorobutyroyl)oxy]-9-(cyclopropylcarbonyl)-fluorene (12b): colorless crystals; mp 88 °C ($CHCl_3$–hexane); IR (KBr) 1740 (OC=O), 1705 (C=O), 1445, 1375, 1193, 1135, 765,

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733 cm^{-1}; NMR ($CDCl_3$) δ 0.4–1.6 (m, 5 H, cyclopropyl H), 1.7–2.8 (m, 4 H, $COCH_2CH_2$), 3.6 (t, J = 6 Hz, 2 H, CH_2Cl), 7.1–7.9 (m, 8 H, aromatic H); mass spectrum, (relative (rel. intensity) 356 (2, M^+, ^{37}Cl), 354 (6, M^+, ^{35}Cl) 287 (6), 285 (17), 249 (15), 181 (100, $FlCOH^+$), 164 (24), 152 (59), 105 (98). Anal. Calcd for $C_{21}H_{19}ClO_3$: C, 71.08; H, 5.39; Cl, 9.99; O, 13.52. Found: C, 70.74; H, 5.50; Cl, 10.21; O, 13.64.

9-(Cyclopropylcarbonyl)-9-[(cyclopropylcarbonyl)oxy]fluorene (12c). colorless crystal; mp 140 °C (hexane); IR (KBr) 1715 (OC=O), 1695 (C=O), 1440, 1380, 1165, 1155, 920, 760, 750, 730 cm^{-1}; NMR ($CDCl_3$) δ 0.4–1.9 (m, 10 H, cyclopropyl H), 6.9–7.9 (m, 8 H, aromatic H); mass spectrum, m/e (relative intensity) 318 (33, M^+), 317 (17), 250 (19), 249 (100, $FlCO^+$–CO–cPr), 248 (27), 181 (25), 180 (45), 165 (17), 164 (20), 163 (25), 152 (35), 151 (18). Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.25; H, 5.70; O, 15.08. Found: C, 79.47; H, 5.81; O, 14.32.

9-(Cyanoethyl)-9-hydroxyfluorene (10a): colorless crystals; mp 89 °C (diethyl ether–hexane) [lit.[19] mp 100 °C (benzene–petroleum ether)]; IR (KBr) 3400 (OH), 3300 (bounded OH), 2260 (C≡N), 1600, 1450, 1078, 1062, 1018, 776, 738 cm^{-1}; NMR ($CDCl_3$) δ 1.70–2.50 (m, symetrical, 4 H, CH_2CH_2), 2.65 (br, 1 H, exchangeable with D_2O, OH), 7.10–7.75 (m, 8 H, aromatic H) mass spectrum, m/e (relative intensity) 235 (19, M^+), 181 (100, $FlCOH^+$), 165 (5), 152 (15).

Expt 1: Electroreduction of Fluorenone Anil (7) in DMF. 4-Bromobutyryl chloride (**1a**) is added progressively as the reduction proceeds (method A). The substrate (0.7 g, 2.7 mmol) is reduced at −1.46 V: **1a** (0.4 mL, 2.9 mmol); n = 2.36; crude product, 0.815 g; column chromatography, eluant benzene. The compounds are isolated in the order **13a** (48%) and **14b** (20%).

9-Anilinofluorene (13a), mp 124 °C (diethyl ether–hexane [lit.[20] mp 121 °C (acetone)].

9-(Cyclopropylcarbonyl)-9-anilinofluorene (14b): colorless crystals; mp 132 °C (diethyl ether–hexane); IR (KBr) 3360 (NH), 1687 (C=O), 1595, 1495, 1378, 1350, 1055, 1020, 745, 725, 685, 615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2–1.3 (m, 5 H, cyclopropyl H), 5.8–8.0 (m, 13 H, aromatic H), 6.25 (br, 1 H, exchangeable with D_2O, NH); ^{13}C NMR ($CDCl_3$) δ 12.2–15.2 (cyclopropyl), 204.7 (C=O); mass spectrum, m/e (relative intensity) 326 (5, M + 1), 325 (15, M^+), 257 (96), 254 (75), 179 (50), 178 (95, $FlC{=}N^+$), 177 (39), 165 (42), 164 (41), 163 (68), 153 (31), 152 (100, Fl^+), 151 (96), 150 (23). Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30; O, 4.92. Found: C, 84.22; H, 5.76; N, 4.29; O, 4.93.

Expt 2: Electroreduction of Fluorenone Anil (7) in MeCN. 4-Chlorobutyryl chloride (**1b**) is added progressively as the reduction proceeds (method A). The substrate (2 g, 7.84 mmol) is reduced at −1.40 V: **1b** (1 mL, 8.51 mmol); n = 1.78; crude product, 2.503 g; column chromatography, eluant 75:25 chloroform–hexane. The compounds are isolated in the order **13a** (15%), **14b** (15%), **14a** (21%), **15a** (12%), **16a** (3.5%), and **17** (5.5%).

9-(4-Chloropropionyl)-9-anilinofluorene (14a): colorless crystals; mp 129 °C (diethyl ether–heptane); IR (KBr) 3390 (NH), 1709 (C=O), 1600, 1531, 1445, 1428, 1324, 1042, 747, 741, 733, 689 cm^{-1}; NMR ($CDCl_3$) δ 1.4–2.0 (m, 4 H, $COCH_2CH_2$), 3.0–3.3 (t, J = 7 Hz, 2 H, CH_2Cl), 5.85–8.05 (m, 13 H, aromatic H), 6.15 (br, 1 H, exchangeable with D_2O, NH); mass spectrum, m/e (relative intensity) 363 (0.3, M^+, ^{37}Cl), 361 (1, M^+, ^{35}Cl), 257 (14), 256 (100, $FlCNHPh^+$), 183 (24), 164 (9), 152 (13). Anal. Calcd for $C_{23}H_{20}ClNO$: C, 76.33; H, 5.57; Cl, 9.80; N, 3.87; O, 4.42. Found: C, 76.54; H, 5.49; Cl, 9.15; N, 3.82; O, 4.68.

9-[*N*-(Chloropropionyl)-*N*-phenylamino]fluorene (15a): colorless crystals; mp 132 °C (diethyl ether–hexane); IR (KBr) 1652 (NC=O), 1592, 1497, 1445, 1389, 1323, 1250, 857, 847, 801, 790, 760, 740, 695, 645 cm^{-1}; NMR ($CDCl_3$) δ 1.90–2.55 (m, 4 H, CH_2CH_2CO), 3.45–3.85 (t, J = 7 Hz, 2 H, CH_2Cl), 6.5–7.8 (m, 14 H, aromatic H); mass spectrum, m/e (relative intensity) 363 (13, M^+, ^{37}Cl) 361 (37, M^+, ^{35}Cl), 326 (3), 257 (7), 256 (8), 166 (15), 165 (100, $FlCH^+$), 164 (8), 163 (5). Anal. Calcd for $C_{23}H_{20}ClNO$: C, 76.33; H, 5.57; Cl, 9.80; N, 3.87; O, 4.42. Found: C, 77.35; H, 5.46; Cl, 8.86; N, 3.59; O, 4.51.

4-Chlorobutananilide (16a): colorless crystals; mp 69 °C (benzene–hexane) [lit.[21] mp 69–70 °C (benzene–petroleum ether)].

***N*-Phenyl-2-pyrrolidone (17)**: colorless crystals; mp 67 °C (diethyl ether–hexane) [lit.[22] mp 68–69 °C (alcohol)].

Expt 3: Electroreduction of Fluorenone Anil (7) in MeCN in the Presence of 4-Chlorobutyryl Chloride (1b, Method B). The substrate (0.528 g, 2.07 mmol) is reduced at −1.42 ± 0.08 V in the presence of **1b** (0.24 mM, 2.13 mmol): n = 2.06; crude product, 0.519 g; column chromatography, eluant 70:30 diethyl ether–hexane. The compounds are separated in the order **13a** (16%), **14b** (31%), **15b** (3%), **10b** (11%), and **16b** (8%).

9-[*N*-(Cyclopropylcarbonyl)-*N*-phenylamino]fluorene (15b): colorless crystals; mp 158–160 °C (diethyl ether–hexane); IR (KBr) 1642 (NC=O), 1592, 1492, 1449, 1406, 1264, 1251, 979, 764, 746, 739, 701 cm^{-1}; NMR ($CDCl_3$) δ 0.6–1.9 (m, 5 H, cyclopropyl H), 6.5–7.9 (m, 14 H, aromatic H); mass spectrum, m/e (relative intensity) 326 (3, M + 1), 325 (11, M^+), 256 (7), 178 (24), 166 (16), 165 (100, $FlCH^+$), 149 (13).

9-(Cyanoethyl)-9-anilinofluorene (10b): colorless crystals; mp 157 °C (benzene–hexane); IR (KBr) 3400 (NH), 2257 (C≡N), 1597, 1524, 1495, 1433, 1317, 1264, 749, 737, 692 cm^{-1}; NMR ($CDCl_3$) δ 1.50–1.90 (m, 2 H, CCH_2), 2.20–2.60 (m, 2 H, CH_2CN), 4.4 (br, 1 H, exchangeable with D_2O, NH), 5.85–7.90 (m, 13 H, aromatic H); mass spectrum, m/e (relative intensity) 311 (27, M + 1), 310 (100, M^+), 309 (13), 256 (46), 218 (74), 191 (28), 178 (76, $FlC{=}N^+$), 165 (8), 152 (19), 127 (10), 93 (70). Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.12; H, 5.85; N, 9.03. Found: C, 85.22; H, 5.93; N, 8.95.

***N*-Phenylcyclopropanecarboxamide (16b)**: colorless crystals; mp 109 °C (benzene–hexane) [lit.[23] 110 °C (alcohol)].

Expt 4: Electroreduction of Benzophenone Anil (8) in DMF. 4-Chlorobutyryl chloride (**1b**) is added progressively as the reduction proceeds (method A). The substrate (1.5 g, 5.83 mmol) is reduced at −1.9 V: **1b** (0.66 mL, 5.84 mmol); n = 2.0; crude product, 1.560 g; column chromatography, eluant benzene. The compounds are isolated in the order **13b** (56%), **11c** (20%), and **16b** (18%).

***N*-Phenylbenzhydrylamine (13b)**: white solid; mp 55 °C (alcohol) [lit.[24] mp 58 °C (alcohol)].

Diphenylmethanol cyclopropylcarboxylate (11c): colorless crystals; mp 65 °C (benzene); IR (KBr) 1706 (OC=O), 1488, 1436, 1387, 1160, 983, 878, 760, 742, 700 cm^{-1}; NMR ($CDCl_3$) δ 0.65–1.35 (m, 4 H, cyclopropyl H), 1.45–1.95 (m, 1 H, cyclopropyl H), 6.85 (s, 1 H, Ar_2CHO), 7.00–7.75 (m, 10 H, aromatic H); mass spectrum, m/e (relative intensity) 253 (6, M + 1), 252 (32, M^+), 183 (10), 167 (36, Ph_2CH^+), 166 (100), 165 (79, $FlCH^+$), 152 (19), 105 (16), 77 (25). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; O, 12.68. Found: C, 81.18; H, 6.54; O, 12.27.

Expt 5: Electroreduction of Benzophenone Anil (8) in MeCN. 4-Chlorobutyryl chloride (**1b**) is added progressively as the reduction proceeds (method A). The substrate (2 g, 7.78 mmol) is reduced at −1.9 V: **1b** (1 mL, 8.51 mmol); n = 1.59; crude product, 2.138 g; column chromatography, eluant 10:90 acetone–hexane. The compounds are isolated in the order **13b** (33%), **18a** (14%), **16a** (3.5%), **18b** (8%), **17** (12%), and **16b** (2%).

2,2-Diphenylpropionitrile (18a): colorless crystals, mp 90 °C (diethyl ether–hexane) [lit.[25] mp 100 °C (ligroine)]; IR (KBr) 2257 (C≡N), 1597, 1492, 1453, 1445, 1426, 1083, 782, 754, 737, 703, 695, 634 cm^{-1}; NMR ($CDCl_3$) δ 2.95 (d, J = 7 Hz, 2 H, CH_2CN), 4.35 (t, J = 7 Hz, 1 H, Ph_2CH), 6.95–7.50 (m, 10 H, aromatic H); mass spectrum, m/e (relative intensity) 208 (2, M + 1), 207 (16, M^+), 168 (12), 167 (100, Ph_2CH^+), 166 (36), 165 (48), 164 (12), 152 (23), 77 (22).

3,3-Diphenylglutaronitrile (18b): colorless crystals: mp 120 °C (chloroforme–hexane) [lit.[26] mp 124–125 °C (methanol)]; IR (KBr) 2257 (C≡N), 1597, 1579, 1492, 1445, 1428, 818, 758, 722, 702, 634 cm^{-1}; NMR ($CDCl_3$) δ 3.25 (s, 4 H, CH_2CN), 6.8–7.6 (m, 10 H, aromatic H); mass spectrum, m/e (relative intensity) 247 (4, M + 1), 246 (20, M^+), 208 (15), 207 (93), 179 (40), 178 (40),

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166 (30), 165 (100, Ph_2C^+-H), 77 (48). Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.89; H, 5.73; N, 11.37. Found: C, 82.55; H, 5.67; N, 10.84.

Expt 6: Electroreduction of Benzophenone Anil (8) in MeCN in the Presence of 4-Chlorobutyryl Chloride (1b, Method B). The substrate (0.6 g, 2.33 mmol) is reduced at -1.78 ± 0.08 V in the presence of **1b** (0.27 mL, 2.4 mmol): n = 2.21; crude product, 0.685 g. The first time, the chromatographic column is eluted with benzene; **13b** (23%) and **14d** (9%) are thus isolated. Then the column is eluted with diethyl ether, and 0.415 g of a mixture of four compounds is collected. In a second experiment, the column is eluted with 70:30 diethyl ether–hexane, and **15d** (20%), **10c** (6%), and **15c** (8%) are isolated. At least, **19** (5%) is collected from the column with diethyl ether as the eluant.

α,α-Diphenyl-α-anilinoacetylcyclopropane (14d): mp 157 °C (hexane); IR (KBr) 3400 (NH), 1692 (C=O), 1592, 1497, 1445, 1424, 1368, 1315, 1156, 1055, 746, 727, 706, 689 cm^{-1}; NMR ($CDCl_3$) δ 0.6–1.6 (m, 4 H, cyclopropyl H), 1.8–2.4 (m, 1 H, cyclopropyl H), 5.7 (br, 1 H, exchangeable with D_2O, NH), 6.2–7.8 (m, 15 H, aromatic H); mass spectrum, m/e (relative intensity) 327 (1, M^+), 259 (16), 258 (100, Ph_2CNHPh^+), 257 (6), 180 (11), 155 (6), 77 (16). Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28; O, 4.89. Found: C, 84.25; H, 6.45; N, 4.25; O, 4.93.

***N*-Benzhydryl-*N*-phenylcyclopropanecarboxamide (15d)**, mp 75 °C (benzene) [lit.[16] mp 74–77 °C (petroleum ether)].

4,4-Diphenyl-4-anilinobutyronitrile (10c): colorless crystals; mp 188 °C ($CHCl_3$); IR (KBr) 3425 (NH), 2245 (C≡N), 1592, 1488, 1439, 765, 750, 742, 704, 695, 689, 635 cm^{-1}; NMR ($CDCl_3$) δ 1.95–2.45 (m, 2 H, CCH_2), 2.75–3.25 (m, 2 H, CH_2CN), 4.45 (br, 1 H, NH), 6.25–7.15 (m, 15 H, aromatic H); mass spectrum, m/e (relative intensity) 313 (13, M + 1), 312 (59, M^+), 311 (32), 259 (16), 258 (91), 221 (21), 220 (100, $Ph_2C(CH_2)_2CN^+$), 219 (9), 181 (9), 180 (66), 179 (67), 178 (35), 165 (38), 115 (39), 93 (71), 77 (58).

***N*-Benzyhydryl-4-chlorobutananilide (15c)**: viscous liquid; IR (film) 1655 (NC=O), 1592, 1492, 1389, 1254, 698 cm^{-1}; NMR ($CDCl_3$) 1.8–2.6 (m, 4 H, $COCH_2CH_2$), 3.52 (t, J = 6 Hz, 2 H, CH_2Cl), 6.65–7.50 (m, 16 H, aromatic H); mass spectrum, m/e (relative intensity) 365 (11, M^+, ^{37}Cl), 363 (32, M^+, ^{35}Cl), 327 (2), 258 (4), 168 (15), 167 (100, Ph_2CH^+), 166 (9), 165 (23), 152 (17), 77 (15). An authentic sample of **15c** was prepared from *N*-benzhydrylaniline and 4-chlorobutyryl chloride (**1b**). Spectral data were identical with those observed for **15c**.

1,6,6-Triphenyl-2-piperidinone (19): colorless crystals; mp 172 °C (diethyl ether–hexane) [lit.[16] mp 172.5–173.5 °C (methanol)]; IR (KBr) 1639 (NC=O), 1587, 1488, 1432, 1353, 1329, 762, 746, 712, 702, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.4–1.8 (m, 2 H, CH_2), 2.5–2.9 (m, 4 H, $COCH_2CH_2CH_2$), 6.9 and 7.25 (double s, 15 H, aromatic H); mass spectrum, m/e (relative intensity) 328 (10, M + 1), 327 (37, M^+), 250 (2), 207 (6), 206 (24), 193 (40), 192 (52), 180 (30), 179 (21), 178 (37), 165 (33), 129 (15), 128 (15), 115 (50), 103 (8), 93 (100, $PhNH_2^+$), 91 (38), 77 (10). Anal. Calcd for $C_{23}H_{21}NO$: C, 84.36; H, 6.46; N, 4.27; O, 4.88. Found: C, 83.67; H, 6.48; N, 4.33.

Expts 7 and 8. The chemical reductions by alkali metals of **7** in diethyl ether or HMPT and that of **8** in HMPT are performed according to an experimental procedure described in ref 1.

Registry No. 1a, 927-58-2; **1b**, 4635-59-0; **6**, 486-25-9; **7**, 10183-82-1; **8**, 574-45-8; **10a**, 79817-28-0; **10b**, 79817-29-1; **10c**, 79817-30-4; **11a**, 79817-31-5; **11c**, 79817-32-6; **12b**, 79817-33-7; **12c**, 79817-34-8; **13a**, 31859-87-7; **13b**, 1865-12-9; **14a**, 79817-35-9; **14b**, 79817-36-0; **14d**, 79817-37-1; **15a**, 79817-38-2; **15b**, 79817-39-3; **15c**, 79817-40-6; **15d**, 59434-94-5; **16a**, 7578-45-2; **16b**, 2759-52-6; **17**, 4641-57-0; **18a**, 2286-54-6; **18b**, 3531-25-7; **19**, 59434-96-7; fluorenol, 1689-64-1.

Intramolecular Photochemical Cycloaddition Reactions of 3-(1,5-Dimethylhex-4-enyl)cyclohex-2-enone: Regio- and Stereochemical Aspects

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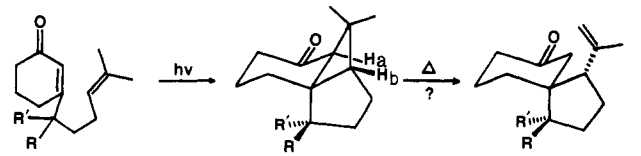
The intramolecular photocycloaddition reaction of the title enone (1) and its 1-demethyl analogue (2) gives head-to-head, [2 + 2] adducts containing cyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one skeletons and none of the head-to-tail isomers of the tricyclo[5.3.1.$0^{2,7}$]undecan-3-one variety. In addition, formal photoene adducts of a spiro[5,4]decan-3-one nature which are related to the acorane sesquiterpene carbon skeleton are also observed. The stereochemical consequences of the acyclic methyl-bearing chiral center in 1 are probed, and the ratio of epimeric products is found to be temperature dependent. Attempts to thermally convert the *gem*-dimethylcyclobutane moiety in the [2 + 2] adducts to spirocyclic precursors of the acoranes results instead in reversion to starting enone.

Intramolecular [2 + 2] photocycloaddition reactions of olefinic enones[2] and the retro-ene reaction of *cis*-1-acyl-2-alkylcyclopropanes and -butanes[3] are well-established synthetic transformations. We have attempted to apply these reactions sequentially to natural product synthesis. Specifically, we have studied the irradiation of enones 1 and 2 with the intention of first forming and then pyrolyzing the cyclobutanes 3 and 4 to provide the spirocyclic isopropenyl compounds 5 and 6.[4] Methyl epimers **5a** and



1 R,R′ = CH_3, H
2 R,R′ = H, H

3a R = CH_3, R′ = H
3b R = H, R′ = CH_3
4 R,R′ = H, H

5a R = CH_3, R′ = H
5b R = H, R′ = CH_3
6 R,R′ = H, H

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