Zinc-Promoted Reactions. 1. Mechanism of the Clemmensen Reaction. Reduction of Benzophenone in Glacial Acetic Acid

Maria Luisa Di Vona and Vittorio Rosnati*

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via Orazio Raimondo, 00173 Roma, Italy

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The mechanism of the Clemmensen reduction of diaryl ketones was investigated by reducing benzophenone, benzhydryl chloride, and dichlorodiphenylmethane in AcOH under a variety of conditions. Besides diphenylmethane, dimeric products were isolated that were indicative of the formation of radical species. Different product distributions were obtained from reactions run under different conditions. The reduction of deuteriated benzhydryl chloride was also performed. A quite complicated mechanistic pattern, involving ionic and nonionic reactions, emerged from the experimental picture. Two pathways, connected through the protonated substrate, were recognized. According to the first pathway the reduction is promoted by a SET from Zn to the substrate, leading to the formation of a carbon radical having one zinc atom bound to the oxygen of the carbonyl group. Benzhydryl chloride, benzhydryl acetate, and dichlorodiphenylmethane are involved in the process. The product distributions suggest the occurrence of several SETs, which involve the formation of different radical species. Ionic reactions are responsible for the second route to the reduced products. Nucleophilic displacements also participate to the complex mechanism.

Since its discovery,[1] the Clemmensen reaction has been used to reduce a great variety of ketones and aldehydes to the corresponding methylene derivatives.[2,3] The mechanisms at work in this dihydro-de-oxo-bisubstitution remain, however, rather obscure, with the contradictory data reported in the literature only pointing to the conclusion that alcohols are not intermediates in the reaction.[4] Such a conclusion does not take into account that benzylic and allylic alcohols[5,6] do undergo the Clemmensen reduction, since, under the usual experimental conditions, such alcohols form the chlorides.

The present study originated from the hypothesis that chlorides might be intermediates in the Clemmensen reduction of diaryl ketones and that the complex mechanism of the reaction might involve a series of ionic and nonionic pathways. An additional hypothesis was that the electron transfers might result in the formation of organozinc intermediates with the metal bound to the carbonyl oxygen, rather than to the carbonyl carbon, as previously postulated by some of the authors engaged in the problem.[7–15] In the present paper we report the results obtained in the Clemmensen reduction of benzophenone (1), benzhydryl chloride (2), and dichlorodiphenylmethane (3).

Results

The reductions were performed in anhydrous AcOH, both in the presence and in the absence of dry HCl, using pure or amalgamated zinc powder, in refluxing AcOH and occasionally at lower temperatures (10 °C or 25 °C). In a few experiments TFA was employed instead of HCl. The main results are reported in Tables I and II. The data represent the average of two or more experiments and were reproducible within experimental error (2–3%). The experiments run in refluxing AcOH were prolonged up to at least 50% conversion. The product distributions, determined over time, were consistent with the final one. In particular no other intermediate was detected. As shown in the tables, the use of amalgamated zinc may offer advantages or disadvantages with respect to the use of the pure metal, depending on the substrate and the experimental conditions. Thus, in the reduction of 1 in neat AcOH, the use of amalgamated zinc resulted in better conversion and higher yield of diphenylmethane (5). Instead, with 2 the solvolysis was greatly enhanced with the amalgamated metal in AcOH but suppressed in the AcOH/HCl and AcOH/LiCl systems. In the reduction of 3 the amalgamated zinc produced lower yields of the hydrocarbon and larger amounts of dimeric compounds.

Tetraphenylmethane (6) was formed in considerable amounts only when starting from chloride 2. The formation of benzopinacolone (7) and tetraphenylethene (8) was negligible with 2 but important in all the reductions of dichloride 3. In AcOH compounds 7 and 8 were obtained in considerable amounts only in the presence of a stronger acid.

The reductions of 1, 2, and 3, as well as deuteriochlorodiphenylmethane (2′), were also studied in the presence of styrene, as carbene scavenger, in the Zn(Hg)/AcOH/HCl system.

Discussion

At first sight, the results reported in the tables appear quite complicated and their rationalization difficult. Nevertheless, especially when dimeric compounds are taken into consideration, the product distributions obtained under different experimental conditions provide hints for the understanding of the mechanisms involved in the Clemmensen reduction of diaryl ketones. In particular, the results are basically in agreement with the hypothesis that chlorinated intermediates participate in the reduction and that the electron transfers from the zinc

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[2] Martin, E. L. In *Organic Reactions*; John Wiley: New York, 1942; Vol. 1, Chapter 7, pp 155–209.
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[12] Yamamura, S.; Hirata, Y. *J. Chem. Soc.* **1968**, 2287.
[13] Crump, D. R.; Davis, B. R. *J. Chem. Soc., Chem. Commun.* **1970**, 768.
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Table I. Product Distribution in the Reduction of 1, 2, and 3 with Nonamalgamated Zinc[a]

				products, %					
entry	substr	reactn system	convn, %	Ph_2CHCl **2**	Ph_2CHOAc **4**	Ph_2CH_2 **5**	$(Ph_2CH)_2$ **6**	Ph_3CCOPh **7**	$Ph_2C{=}CPh_2$ **8**
1	**1**	AcOH[b]	52		32	3	6	1	
2	**1**	AcOD	53		7[c]	40[d]	2[d]	1	3
3	**1**	AcOH/HCl	100		4	23	3	65	5
4	**1**	AcOH/TFA	69		13[e]	19		34	3
5	**2**	AcOH	100		3	71	24	1	1
6	**2**	AcOH/HCl	100			58	38	3	1
7	**3**	AcOH[f]	100			45	2	13	39
8	**3**	AcOH/HCl[f]	100			46	3	21	29
9	**1**	AcOH/HCl[g]	68	3	6	52	3	1	1
10	**1**	AcOH/TFA[g]	11		5	4			

[a] Entries 1–8 refer to reactions run in refluxing AcOH for 2 h. Entries 9–10 refer to reactions run at 10 °C for 1 h. [b] Benzhydryl alcohol was also present in 10% yield. [c] Monodeuteriated. [d] Dideuteriated. [e] This includes both Ph_2CHOAc and $Ph_2CHOCOCF_3$. [f] The reaction also afforded 1% 1,1,1,2-tetraphenylethane (**9**). [g] The reaction also afforded 2% tetraphenyloxirane (**10**).

Table II. Product Distribution in the Reduction of 1, 2, and 3 with Amalgamated Zinc[a]

				products, %				
entry	substr	reactn system	convn, %	Ph_2CHOAc **4**	Ph_2CH_2 **5**	$(Ph_2CH)_2$ **6**	Ph_3CCOPh **7**	$Ph_2C{=}CPh_2$ **8**
1	**1**	AcOH[b]	71	25	25	7	3	8
2	**1**	AcOH[b,c]	59	23	30	2		1
3	**1**	AcOH/HCl	100	16	28	4	27	25
4	**1**	AcOH/TFA	100	9	58		30	3
5	**2**	AcOH	96	45	48	2	1	
6	**2**	AcOH[c]	98	47	50	1		
7	**2**	AcOH/HCl	100		73	24	3	
8	**2′**	AcOH/HCl	100	4[d]	90[d]	3[e]	3	
9	**3**	AcOH	100		25	5	51	19
10	**3**	AcOH[c,f]	72[g]	5	28	6	14	17
11	**3**	AcOH/HCl	100		34	4	18	44

[a] General experimental conditions: 2 h in refluxing AcOH. [b] Ph_2CHOH was also formed in 3% yield. [c] Reaction run at 25 °C for 1 h. [d] Monodeuteriated. [e] Dideuteriated. [f] The reaction also afforded 2% 1,1,1,2-tetraphenylethane (**9**). [g] The recovered material was 26% **1**, 2% **3**.

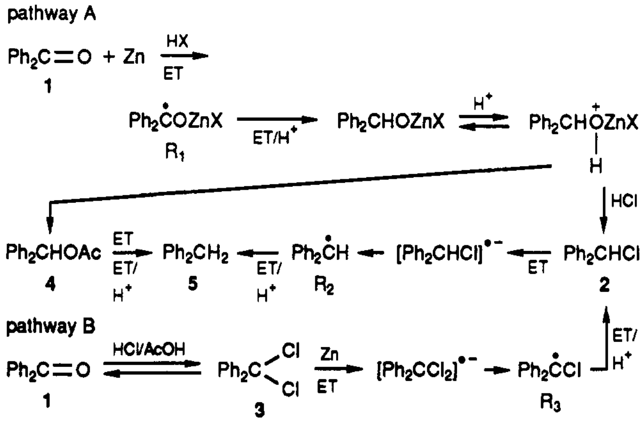
to the substrate involve the formation of organozinc intermediates with the metal bound to the carbonyl oxygen. It is apparent that both ionic and nonionic reactions contribute to the global reductive process. As for the nonionic reactions, preliminary ESR study indicates that the radical species involved in the reduction either are formed in amounts too low or their lifetimes are too short to be detected. The occurrence of radical species in the chemical reduction of a diaryl ketone, however, is out of the question. Unequivocal evidence that unstable radical intermediates occur also in the electrochemical reduction of aromatic carbonyl compounds are available.[16]

As a whole, our data and their rationale support the mechanistic pattern summarized in Scheme I. It shows the four electron transfers (ET) required by the elementary process $>CO \rightarrow >CH_2$ (every ET is followed by an ET/H$^+$ step) involving radical species R_1, R_2. Scheme I does not account for the intimate mechanism by which the CH bonds are formed in the final hydrocarbon. This will be considered in the last section of the discussion.

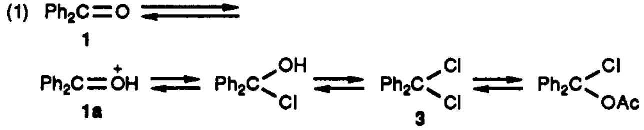
Pathways A and B have in common the intermediacy of chloride **2**. The comparison between the reactions performed at 10 °C in the AcOH/HCl and AcOH/TFA systems (items 9 and 10 in Table I) points to the conclusion that **2** (identified among the products in AcOH/HCl) is indeed an intermediate in the Clemmensen reduction of **1**. This is also supported by the reduction of Ph_2CDCl, which afforded 90% Ph_2CDH and some Ph_2CDOAc.

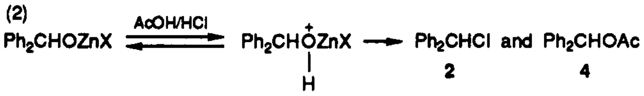
Pathways A and B are concurrent and mediated by a series of ionic reactions. Their relative importance must depend on the nature—and consequently the strength—of the acid involved in the series of equilibria (1) and (2).

Scheme I[a]



[a] X = OAc, Cl.





Pathway A. The occurrence of pathway A becomes evident if one compares the product distributions obtained

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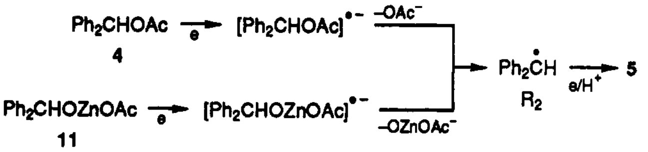
[16] Feoktistov, L. G.; Lund, H. In *Organic Electrochemistry*; Baizer, M. M., Ed.; Marcell Dekker: New York, 1973; Chapter 8, 372–375.

in neat AcOH to those in the presence of a stronger acid. Independently from the use of the amalgamated metal, the reduction of 1 in neat AcOH (in contrast to those in the presence of HCl or TFA) results in small amounts, if not in the absence, of dimeric products 6–8. According to pathway A, in the absence of HCl, the main product is benzhydryl acetate (4), which may arise from the solvolysis of $Ph_2CHOZnOAc$ (11), formed after the two initial SETs. Attempts to synthesize 11 have been unsuccessful.

We have ascertained that 4 can undergo the reduction to 5, albeit very slowly, in refluxing AcOH. This reduction might be initiated by SET, followed by formation of benzhydryl radical R_2, which is reduced to 5 or dimerized. However, the reduction of 4 cannot be the only pathway to diphenylmethane. In fact, 1, but not 4, was reduced at 25 °C in neat AcOH (entry 2 in Table II). These results suggest that in the absence of HCl or TFA, diphenylmethane forms mainly through a mechanism involving the reduction of the organozinc intermediate 11.

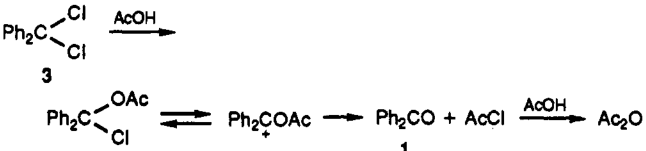


A different situation is encountered in the presence of HCl. In this case, the reaction must proceed mainly through chlorinated intermediates, such as 2 and 3. This point is supported by the results obtained from the reduction of 1 with HCl or TFA at 10 °C. The two acids were shown to have practically the same pK_a in glacial AcOH.[17] In spite of this, the reduction with TFA gave a much lower yield of 5. The above results are easily explained if we consider that a byproduct such as 4 can be more easily reduced to 5 in the presence of HCl, due to its conversion into chloride 2.

The destiny of radical anions such as $[Ph_2CHCl]^{\bullet-}$, $[Ph_2CCl_2]^{\bullet-}$, $[Ph_2CHOCOCH_3]^{\bullet-}$, and $[Ph_2CHOZnOAc]^{\bullet-}$, is determined by their conversion into the radical $Ph_2\dot{C}H$ through elimination of stable anions (Cl^-, AcO^-, $AcOZnO^-$).

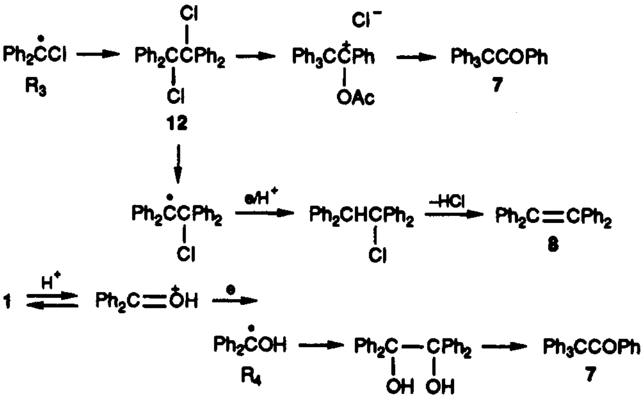
The poor yield of dimeric compounds in the reduction of 1 in AcOH indicates that dimer formation requires an efficient protonation of the ketone, which brings us to pathway B.

Pathway B. The relative importance of pathways A and B depends on the nature and the concentration of the acid. In refluxing AcOH, dichloride 3 was rapidly converted into 1. This reaction reasonably occurs through the partial solvolysis of 3, followed by an intramolecular process, probably involving tight ion pairs:



The presence of Ac_2O in the reaction mixture has been recognized. A strong common ion rate depression has been established. No such effect has been encountered with added $ZnCl_2$.[18,19] The fast solvolysis of 3 in refluxing AcOH might suggest that pathway B does not take part in the reduction of 1. However, product distributions clearly indicate that the reduction of 3 is competitive with its conversion into benzophenone. In fact, the results from the reduction of 1, 2, and 3 in refluxing AcOH/HCl (with amalgamated or nonamalgamated zinc) showed the following: (i) with 2 only traces of 7 and 8 were formed, at most; (ii) with dichloride 3, 7 and 8 were obtained in overall yields ranging from 50 to 62%; (iii) 7 and 8 accounted altogether for 52–70% of the product in the reduction of 1 in the presence of HCl (where 3 can form) and only 1–11% in neat AcOH. The above results allow the conclusion that 3 takes part in the reduction of 1 performed in the presence of HCl. Notice that the *gem*-dichloride was shown to form by treating 1 with AcOH/HCl.

Mechanisms of Dimer Formation. Products 7 and 8 must derive from dimerization of radical species intermediately formed. However, R_1 (X = Cl, OAc) cannot be responsible for all the dimer formation, since reduction of 1 occurred also in neat AcOH, i.e., under conditions that lead to little or none of the various dimeric compounds. This is consistent with the view that, in presence of HCl, the high yields of 7 and 8 (entries 3 in Tables I and II) occur via radical species R_3 and R_4 rather than R_1. The formation of 7 and 8 from these radicals can be interpreted according to the following mechanism.



The results in AcOH/TFA are in line with the above hypotheses, since under these conditions practically the only dimer was benzopinacolone, reasonably formed via R_4. Accordingly, in neat AcOH the first SET involves mainly the ketone, while in the presence of a stronger acid it concerns mainly the protonated substrate. The dimerization of $(C_6H_5)_2\dot{C}Br$, eventually leading to 8, has been reported.[20] Reduction of an authentic sample of 12 yielded 7 and 8 in approximately a 1:9 ratio, which is far from the one observed with ketone 1. Notice that the reduction of both 1 and 3 afforded 7 and 8 in ratios ranging from 1:1 to 1:3. This suggests that 7 is formed predominantly through R_4, rather than through R_3.

The formation of tetraphenylethene cannot be ascribed to a single mechanism, since it may originate from several routes, including the interaction of carbenoid species with 1 itself.

Role of HCl. Similar, but structurally different, species might be involved in the reductive process, depending on the nature of the counter ion of the protic acid. This hypothesis is consistent with the observation that significant amounts of 7 were formed in the presence of HCl or TFA but only traces in neat AcOH. In neat AcOH the covalent nature of the bond linking the metal to the acetoxy group might be responsible for the low tendency

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(17) Shkodim, A. M.; Karkuzaki, L. I. *Zh. Fiz. Khim.* **1959**, 2795. Fialkov, Yu. Ya.; Borovikow, Yu. Ya. *Ukr. Khim. Zh.* **1964**, *30*, 119.

(18) The observed S_Ni reaction, apparently, is to some extent analogous to the halo-dehydroxylation of alcohols with $SOCl_2$ and to the decomposition of alkyl chloroformated into alkyl chlorides and CO_2, all involving a four-membered cyclic TS.[19]

(19) Lee, C.-C.; Finlayson, A. J. *Can. J. Chem.* **1961**, *39*, 260. Lewis, E. S.; Herndon, W. C.; Duffey, D. C. *J. Am. Chem. Soc.* **1961**, *83*, 1959.

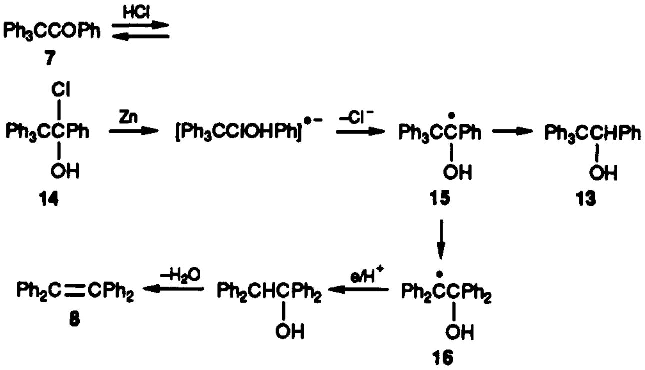
(20) Murray, W.; Trozzolo, A. M. *J. Org. Chem.* **1962**, *27*, 3341.

of R_1 (X = OAc) to dimerize. In the presence of HCl or TFA, due to the different ionic character of Zn–Cl and Zn–OCOCF$_3$ bonds, the following equilibria might be considered:

$$\underset{R_1}{\mathrm{Ph_2\dot{C}OZnX}} \rightleftarrows \mathrm{Ph_2\dot{C}OZn^{+}X^{-}} \overset{HX}{\rightleftarrows} \underset{R_4}{\mathrm{PH_2\dot{C}OH}} + \mathrm{ZnX_2}$$

$$X = \mathrm{Cl, CF_3CO_2}$$

The main species responsible for the production of benzopinacol should be R_4. The pinacol is known to undergo acid-catalyzed rearrangement to 7 in AcOH.[21] Incidentally, 7 was found to be completely inert in the reduction in the absence of HCl. In the Zn(Hg)/AcOH/HCl system, however, the ketone was partially reduced, giving 38% 8, 15% 1,2,2,2-tetraphenylethanol (13), and traces of 1,1,1,2-tetraphenylethane (9). Due to the steric hindrance, the carbonyl group of ketone 1 cannot be easily approached by zinc metal, the preferred process being protonation, ultimately resulting in HCl addition. Adduct 14 may then be reduced to radical 15, the precursor of carbinol 13. Alternatively, 15 may undergo a radical rearrangement to the more stable benzhydryl-type radical 16, followed by reduction and H_2O elimination to afford 8.



Free radical rearrangements, involving a 1,2 shift of an aryl radical, have been reported.[22] Alternatively, 8 might originate from 13 through an ionic pathway involving an HCl-catalyzed rearrangement.

In the reduction of 1 in AcOH, the role of HCl is determinant in (i) the production of the chlorinated intermediates; (ii) the protonation of 1 leading to the radical species R_3 and R_4; (iii) the depression of the acetolysis. In the moderate ionizing solvent, a high concentration of Cl^- may depress the ionization of 2 and, hence, its solvolysis. This point was confirmed by the reduction of chloride 2 in Zn(Hg)/AcOH/LiCl, which resulted in a considerably higher yield (85 vs 48%) of 5.

Role of Amalgamated Zinc. In principle, the pretreatment of Zn with a $HgCl_2$ solution may influence any of the reactions involved in the reductive process. Modification of the metal surface might have a great influence. Investigations on this subject, however, did not lead to any definite conclusion.[8] In our opinion, the use of amalgamated zinc may result in a kinetic effect favorably influencing the reductive processes. Notice that the use of Zn(Hg) in the reduction of 2 resulted in a lower yield of 6, while reduction of deuteriated chloride 2′ gave an almost quantitative yield of 5. This behavior might tentatively be ascribed to a somewhat lower tendency of $\mathrm{Ph_2\dot{C}D}$ to undergo dimerization with respect to $\mathrm{Ph_2\dot{C}H}$.

Role of Carbenoid Species. The possibility that carbenes might be intermediates in the Clemmensen reduction of ketones has already been considered,[7,8,11] but their role was not emphasized and little evidence was provided. A zinc–carbene, formed on the surface of bulk zinc, was claimed to be an intermediate in the reduction of acetophenone.[23] The relevance of carbenoid species in our reductions is certainly of minor importance, but it cannot be accurately weighed, since in the presence of styrene, as carbene scavenger, the reduction of 1 did not match the normal reduction. In this context the following facts should be considered: (i) 5 obtained in 90% yield from Ph_2CDCl was 100% monodeuteriated, while the reduction of Ph_2CHCl gave only 5% 1,1,2-triphenylcyclopropane; (ii) only 3% of the above cyclopropane was formed in the reduction of dichloride 3 in the presence of styrene; (iii) the reduction of 1 in the presence of styrene gave 9% of the above cyclopropane, along with 14% tetraphenyloxirane (reasonably formed by the reaction of diphenylcarbene with ketone 1[24]) and 3% 8. These facts call for a number of separated observations. In the reduction of Ph_2CDCl, the combined absence of Ph_2CH_2 and 8 proved that diphenylcarbene is not formed in this reaction, while the reduction of Ph_2CHCl indicates that diphenylcarbene formation represents a minor process. Analogously, the poor yield of cyclopropane derivative in the reduction of 3 suggests that also in this reduction diphenylcarbene plays a relatively unimportant role. As to the reduction of 1 in the presence of styrene, if one takes into consideration the total yield of the triphenylcyclopropane and tetraphenyloxirane (23%), the conclusion can be drawn that diphenylcarbene is certainly formed in the reaction with the scavenger. This, however, does not necessarily mean that in the absence of the scavenger the role of carbenoid species is equally important.

Reductive Process. The data presented here do not allow definitive conclusions as to the intimate mechanism of the four SETs involved in the process $Ph_2CO \rightarrow Ph_2CH_2$. In its ultimate essence, the fundamental issue concerns the source of the methylene hydrogen atoms in the final hydrocarbon. In principle, two events may account for the zinc-promoted reduction of any of the radical species formed in the reductive process: a direct attack by $H^{\bullet}$ or a SET from the metal to the carbon radical, resulting in a carbanion, quenched by the acid present. The first event is contrasted by the very fact that zinc, as well as the amalgamated metal, does not produce molecular hydrogen in neat AcOH, i.e., under conditions that allow reduction. As for the second event, if one considers the initial formation of a radical species like $\mathrm{Ph_2\dot{C}OZn^{\bullet}}$, another question arises: is the second electron donated to the carbon radical by the free metal or, intramolecularly, by the zinc atom bound to the oxygen, in a sort of a three-membered TS?[25] Apparently, so far there is no experimental way to distinguish between these two possibilities. The problem, however, is perhaps more complicated, since the radical reduction might well occur through a complex mechanism in which one electron is transferred by the bound metal to a near proton coordinated to the oxygen of the alkoxy–zinc moiety. This event

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(21) Bachmann, J. G. St. C. In *Organic Syntheses*; John Wiley; New York, 1943; Collect. Vol. II, p 73.

(22) For reviews, see March, J. ref. 4, p 955.

(23) Burdon, J.; Price, R. C. *J. Chem. Soc., Chem. Commun.* 1986, 893.

(24) Tomioka, H.; Miwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* 1980, *53*, 753.

(25) The possibility that the destiny of $\mathrm{Ph_2\dot{C}{-}O{-}\dot{Z}n}$ might involve a SET by the bound metal to a second molecule of 1 can be excluded; in fact, the resulting diradical $\mathrm{Ph_2\dot{C}{-}O{-}Zn{-}O{-}\dot{C}Ph_2}$ should easily undergo an intramolecular coupling reaction ultimately leading to the dimeric compounds 7 and 8. Indeed, such dimers were formed only in traces in the reduction of 1 in the absence of HCl.

might be concerted with the interaction of the thus formed $H^{\bullet}$ with the nearby carbon radical, in a process involving a four-membered TS. In this connection, one should recall that in neat AcOH (i.e., in the presence of a low H^+ concentration) the reduction of 1 is very inefficient, while no molecular hydrogen is evolved.

Possible evidence for the above mechanism was sought by investigating the reduction in neat AcOD. Since the D^+ reduction potential (E_0 = 0.0034)[26] is higher than that of the proton, the reduction in AcOD was expected to give a higher yield of the final hydrocarbon, along with lower yield of 4, in view of the lower "proton" donating ability of AcOD.[27] These expectations were verified by the experiment, as shown by the comparison of entries 1 and 2 in Table I. Therefore, at the present stage of the research, the above mechanism represents the best rationale of all the data available.

Whatever the real mechanism dealing with the reduction of the radical species might be, the results reported in this paper suggest that in the reduction of 1 the zinc bulk transfers the first electron to the substrate, but then a single zinc atom becomes bound to the carbonyl oxygen. In this regard zinc behaves like magnesium. The mechanisms discussed so far afford a tool for interpreting literature data not understood hitherto, concerning other zinc-promoted reactions.[28]

Experimental Section

GC analyses were carried out with a Carlo Erba HRGC 5300 Mega Series apparatus on a 2 m, 3% OV-17, 80/100 Chromosorb WHP column. GMS analyses were performed with a Hewlett-Packard 5970B system on a 12 m × 0.2 mm i.d. × 0.33 µm film thickness, HP-1 cross-linked methylsilicone column. ^{1}H NMR spectra were recorded on a Bruker WP-80 spectrometer with $CDCl_3$ as the solvent. HPLC analyses were performed with a Philips apparatus, equipped with a PU4020 UV detector on a 100 × 3 mm i.d., Lichrosorb Si 60 (7 µm) column. Isolation of the products were carried out by preparative HPLC on a 250 × 10 nm i.d., Lichrosorb Si 60 (7 µm) column.

Materials. Anhydrous AcOH was prepared according to a standard procedure. Stock solutions of approximately 0.3 M anhydrous HCl in AcOH were prepared by bubbling HCl gas in the solvent. TFA (99%) (Aldrich) was used, without further purification, in 5% concentration. Starting materials 1, 2, and 3 were commercial reagents (Aldrich) of 99% purity. Deuteriated 2 was prepared by $LiAlD_4$ reduction of 1, followed by chlorination of the resulting alcohol with $SOCl_2$. 1,2-Dichloro-1,1,2,2-tetraphenylethane (12) was prepared according to the literature.[29]

General Procedure for the Clemmensen Reductions. The reactions were performed in anhydrous AcOH in different systems, normally at the refluxing temperature, occasionally at 10 °C and 25 °C, using an approximately 1:7 molar ratio of substrate and zinc. A 3 mM substrate was generally employed. The amalgamated zinc was prepared according to the literature[30] and repeatedly washed with anhydrous AcOH before use. The general workup was the following: the final mixture was diluted with three volumes of CH_2Cl_2, filtered from unreacted zinc, and repeatedly washed with H_2O and then with a saturated $NaHCO_3$ solution, to remove AcOH; the residual solution, after drying over Na_2SO_4, was evaporated to dryness. GC and GMS analyses of the residue were performed. Isolation of the products, when necessary, was accomplished by known procedures.

Product Distribution Analysis. Identification of the products and their distribution were accomplished by GC, NMR, and GMS analyses. The mass balance of each reaction was determined. GC response factors for all the products were determined from different mixtures of pure samples. Retention times, obtained for each product under standard operating conditions, and mass spectra are given as supplementary material.

Reduction of Benzhydryl Chloride (2) in the Presence of LiCl. The reaction was carried out with amalgamated zinc, using a standard 3 M solution of anhydrous LiCl in AcOH at the refluxing temperature for 2 h. The product distribution was: 7% 4, 8% 6, 85% 5. When the reaction was performed as above, but in the presence of TFA (5%), the result was 10% 6, 90% 5.

Reduction of Benzhydryl Acetate (4). The reduction performed with Zn(Hg) in neat AcOH (refluxing temperature for 2 h) gave only a 10% conversion into 5. In the presence of anhydrous HCl a 74% conversion of the substrate was obtained, 5 being the only product.

Reduction of Benzopinacolone (7). The substrate was recovered unchanged after 2 h of reflux in AcOH in the presence of Zn(Hg). In the presence of anhydrous HCl, a 53% conversion was obtained after being refluxed for 2 h, the product distribution being 38% 8, 15% 13, and traces of 6.

Reduction of 1,2-Dichloro-1,1,2,2-tetraphenylethane (12). The compound was reduced with amalgamated zinc in a AcOH/HCl system after being refluxed for 2 h. The product distribution was 10% 7, 90% 8.

Reduction of 1, 2, 2′, and 3 in the Presence of Scavenger. The reactions were performed with amalgamated zinc in AcOH/HCl at refluxing temperature for 2 h, in the presence of 0.5 mol of styrene. The results were the following. With 1: 2% 4, 18% 5, 21% 7, 3% 8, 9% 1,1,2-triphenylcyclopropane, 14% tetraphenyloxirane, 25% 1,3,3-triphenylpropene, 2% 1,1,3-triphenylpropane, 2% styrene, 3% styrene dimers. With 2: 27% 5, 2% 6, 5% 1,1,2-triphenylcyclopropane, 32% 1,3,3-triphenylpropene, 27% 1,1,3-triphenylpropane, 5% styrene, 2% styrene dimers. With 2′: 5% 4, 31% 5, 2% 6, 12% 1,3,3-triphenylpropene, 27% 1,1,3-triphenylpropane, 5% styrene, 18% styrene dimers. With 3: 2% 1, 2% 4, 24% 5, 4% 6, 16% 7, 26% 8, 3% 1,1,2-triphenylcyclopropane, 3% styrene, 20% styrene dimers.

Acetolysis of Dichlorodiphenylmethane (3). The reaction was performed in neat AcOH and in the presence of 3 mol LiCl or $ZnCl_2$. After 5 min at the refluxing temperature, the amounts of the starting dichloride were 3% in AcOH, 50% in AcOH/LiCl, 3% in AcOH/$ZnCl_2$. At 25 °C the figures were in the order 75%, 95%, 75%. The equilibrium between 1 and 3 was proved by an independent experiment. After 2 h of standing at 25 °C, a solution of 1 in AcOH/0.3 M HCl gave 3% of 3.

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Supplementary Material Available: Complete MS and GC data for all the compounds (2 pages). Ordering information is given on any current masthead page.

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