Journal of Organometallic Chemistry, 241 (1983) 143–156
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE REACTION OF PHENYLLITHIUM WITH CARBON MONOXIDE *

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(Received July 10th, 1981; in revised form July 23rd, 1982)

Summary

Three main products are obtained from the reaction between phenyllithium and carbon monoxide, namely: benzophenone (I), benzoin (II) and α,α-diphenylacetophenone (III). Evidence is given for the existence of benzoyllithium as the first intermediate of the reaction and for the subsequent intermediates in the production of I, II and III. The basic sequences followed in the formation of those and of other minor products are outlined in the Scheme. Reaction conditions can be adjusted to obtain III in a high yield or to prevent further reaction of the first intermediate and obtain diarylalkylcarbinols, or substituted tetrahydrofurans.

Introduction

The addition of nucleophiles to carbon monoxide activated by coordination to metal ions forms the basis for a thoroughly explored and useful class of reactions [2]. Organolithium reagents and other organometallic derivatives of Group Ia and IIa metal ions do not provide the obvious activation provided by the coordinating transition metal ions and therefore their reactions with carbon monoxide are less well understood. The formation of acyl derivatives of Group Ia and IIa metal ions has been proposed in reactions between carbon monoxide and tert-butyllithium [3] and trimethylsilyllithium [4], but they were not well characterized as stable entities.

Although several mechanistic studies and synthetic applications of alkali aromatic ketyls [5–8] have been recently published, no further study of the mechanism of the reaction of phenyllithium with carbon monoxide has been reported since the work of one of us with Whitesides et alia [9]. In that paper the dilithium benzophenone dianion was proved to be an intermediate but several mechanistic questions remained unresolved. The present work was initiated with the objectives of finding

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* Presented in part at the XV Argentine Chemical Symposium [1].

0022-328X/83/0000-0000/$03.00

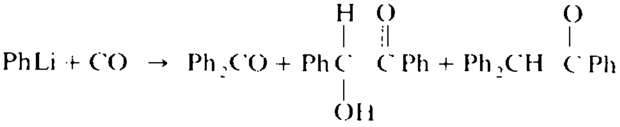
evidence for the stability of acyllithium compounds and for the mechanism of the reaction, and of finding new approaches to the generation of nucleophilic acyl groups and other applications of the reaction. The data that follow provide evidence for the existence of benzoyllithium as an intermediate and suggest applications of the reaction in the synthesis of useful compounds.

Results

Reaction of phenyllithium with carbon monoxide in ether solutions

Previous work [10] and preliminary runs in our laboratory showed that the reaction is very sensitive to the concentration of phenyllithium (Table 1) and to the solvent (Table 2). Benzene is presume to arise from ether cleavage and phenyllithium hydrolysis in the starting solution [11] and also from unavoidable traces of water in the reaction flask. Biphenyl can arise during the preparation and also from aryl coupling upon standing of the reagent solution [12]. In fact, an increase in the biphenyl concentration has been found in old phenyllithium solutions, thus solutions less than four days old were used, and the amount of biphenyl found in the reaction with carbon monoxide was always the same as present in the starting solution. When phenyllithium was prepared by metal–halogen interchange, no biphenyl nor benzene were detected when the reaction was complete (Tables 2–5). Consequently, since benzene and biphenyl are not products of the carbonylation reaction, they will not be considered in the discussion.

It can be observed in Table 1 that the production of benzophenone (I) (eq. 1) diminishes with increasing concentration of phenyllithium, while the amount of benzoin (II) remains almost invariant and the yield of diphenylacetophenone (III) increases.



$$\mathrm{PhLi + CO \rightarrow Ph_2CO + Ph\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}Ph + Ph_2CH-\overset{\displaystyle O}{\overset{|}{C}}Ph} \qquad (1)$$

(I) (II) (III)

TABLE 1

REACTION OF PHENYLLITHIUM WITH CARBON MONOXIDE IN DME AT 0°C [10] [a,b]

Products	[PhLi]		
	0.075 *N*	0.150 *N*	0.380 *N*
Benzene	13.0	9.6	7.0
Biphenyl	7.0	3.5	2.1
Benzophenone	20.5	18.0	13.0
Benzoin	36.6	39.0	33.0
Diphenyl-acetophenone	20.0	23.0	43.1

[a] PhLi prepared from diphenylmercury and lithium dispersion. [b] In all the tables yields are based in PhLi conversion.

TABLE 2

SOLVENT EFFECT ON THE REACTION OF PhLi WITH CARBON MONOXIDE AT 0°C

Products	Hexane [a] (suspension)	70% Hexane- [b,c] 30% DME 0.08 *N* PhLi	Diethyl ether [b] 0.5 *N* PhLi	THF [a] 0.25 *N* PhLi
Benzophenone	23	20.8	36.8	22.3
Benzoin	–	7.5	10.2	21.3
Diphenylacetophenone	41	65.5	11.0	13.3
Benzhydrol	4		–	2.7
1,1,2-Triphenylethyleneglcol	16	–	–	9.8
1-phenylbenzoin	6	–	1.0	26.1

[a] Present work. [b] Ref. 10. [c] Benzene is eluted together with the solvent in GLC; only relative yields are reported.

Table 2 shows the solvent effect. It can be observed that a more polar solvent considerably diminishes the formation of III. This result together with Table 1 and the observed temperature effect (there is a linear dependence of the yield of III on $1/T$ (°C) [13]) is interpreted as a consequence of the variable concentration of carbon monoxide relative to that of phenyllithium. A variable degree of association of the reagent in the different solvents is also expected: it is known from the work of Wittig et alia [14], confirmed by further determinations, [15,16] that phenyllithium is dimeric in ethyl ether solution, and a higher degree of aggregation is expected in hydrocarbon solutions assuming a behaviour similar to that of the alkyllithium reagents [17].

All the above results are consistent with a mechanism of formation of III which requires relatively high concentration of phenyllithium and they offer a synthetic application of the reaction for the preparation of this compound. Indeed, the best yield (94%) of III, is obtained in the heterogeneous reaction of solid PhLi at 110°C [13]. The previously reported preparations [18,19] involve several steps and the yield is less than 60%.

Quasi-kinetic measurements

In order to gain further insight into the mechanism, to find out if III is formed by subsequent reactions of other products, a quasi-kinetic determination of products as a function of time was performed. The results are summarized in Table 3. The relation between the yields is not obvious and it is evident from the data that the products are formed by independent reactions.

Formation of III has been observed to be highly dependent on the reaction conditions [13]. The possibility exists that III could be formed by a further reaction of an intermediate that has incorporated carbon monoxide at low temperature. Phenyllithium (suspended in hexane) was allowed to react with carbon monoxide at 0°C during 2 h. After substitution of carbon monoxide by the nitrogen atmosphere, the reaction mixture was heated at 50°C. The results summarized in Table 4 show that there is not an apparent thermal reaction in the absence of carbon monoxide.

TABLE 3

REACTION OF PHENYLLITHIUM IN HEXANE SUSPENSION WITH CARBON MONOXIDE AT 20°C

Products	Time (min)							
	0	15 [a]	35	55	115	225	370	1020
Benzene	100	100	65	44	22	4	0	0
Benzophenone	–	–	8	13	18	22	23	23
α,α-Diphenylacetophenone	–	–	18	29	41	51	53	53
Benzhydrol	–	–	1	2	3	3.5	4	4
1,1,2-Triphenylethane-1,2-diol	–	–	4.5	7.5	11	13	14	14
α-Hydroxy-α,α-diphenylacetophenone	–	–	1.2	2.5	3	4.5	5	5

[a] A faint coloration was observed but no reaction products were detected by GLC.

TABLE 4

REACTION OF PHENYLLITHIUM IN HEXANE SUSPENSION WITH CARBON MONOXIDE AT 0°C AND SUBSEQUENT HEATING AT 50°C

Products	Time of heating at 50°C (min)			
	0	50	115	355
Benzene	52.1	52.1	52.0	52.1
Benzophenone	11.1	11.2	11.1	11.2
α,α-Diphenylacetophenone	19.1	19.1	19.1	19.1
1,1,2-Triphenylethane-1,2-diol	14.0	14.1	14.0	14.1
α-Hydroxy-α,α-diphenylacetophenone	2.4	2.3	2.3	2.3
Benzhydrol	1.2	1.2	1.2	1.2

TABLE 5

REACTION OF PHENYLLITHIUM WITH CARBON MONOXIDE IN THF

Product	Quenching with water [a]			Quenching with acetic anhydride		
	−78°C	0°C	35°C	78°C	0°C	35°C
Benzophenone	15.4	22.3	17.6	18.1	25.0	20.0
Benzoin	39.8	21.2	16.0	40.1 [b]	22.0 [b]	16.1 [b]
α,α-Diphenylacetophenone	3.9	13.3	31.4	4.0 [c]	16.1 [c]	36.2 [c]
α-Hydroxy-diphenylacetophenone	32.1	26.1	17.5	36.2	28.1	22.3
1,1,2-Triphenylethane-1,2-diol	4.2	9.8	10.1			

[a] Small amounts of α-hydroxyacetophenone and benzhydrol were also detected. [b] Diacetate of the *cis*-enol of benzoin. [c] Acetate of the enol of α,α-diphenylacetophenone.

These results also confirm the fact that I is not present in the reaction mixture before hydrolysis since ca. 50% of phenyllithium remains unaltered and formation of triphenylcarbinol was not detected.

The effect of temperature on the reaction in solution (THF) was also studied. The reaction mixture was quenched with two different reagents to trap possible intermediates. It is again observed (Table 5) that higher temperatures favour formation of III; the acetate derivatives of the enolic forms of II and III are obtained when the reaction mixture is quenched with acetic anhydride.

Discussion

In spite of the complexity of the resulting product mixtures and their sensitivity to reaction conditions the following general conclusions could be drawn from the above results:

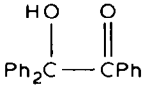
1) The main reaction products are I, II and III.
2) Formation of the three compounds follows parallel paths.
3) Processes leading to products I and III in DME and to II and III in THF are competitive.
4) The production of III increases with the phenyllithium concentration, the temperature and the "inertness" of the solvent.
5) No triphenylcarbinol (IV) and only small amounts of benzhydrol (V) and α-hydroxy-α α-diphenylacetophenone (VI) were detected.
6) Treatment of the reaction mixture with acetic anhydride produces the diacetate of the *cis*-enol of II (VII) and triphenylacetoxyethylene (VIII) as the only acetylated compounds.
7) The reaction run in the presence of alkyl bromide yields the corresponding diphenylalkylcarbinol (80% yield for R = C_4H_9 (IX)), and variable amounts of II; but not even traces of I were detected [20].
8) The dilithiumbenzophenone dianion does not produce IX under the same reaction conditions [20].

Ph_3COH

(IV)

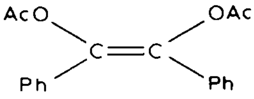
Ph_2CHOH

(V)

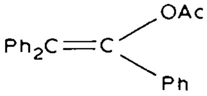


$Ph_2C(OH)-C(=O)Ph$

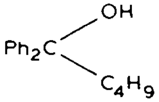
(VI)



(VII)

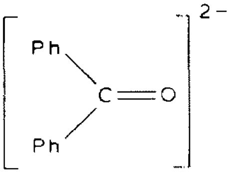


(VIII)

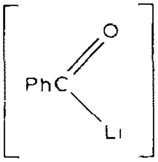


(IX)

Results 3 and 4 as well as a similar temperature effect found for the reaction in diethyl ether [9] suggest that formation of III is favoured by a ratio [PhLi] : [CO] ⩾ 1. A mechanism of formation of III has been previously proposed invoking the intermediation of dilithium benzophenone dianion (X) [9]. However, the most important unresolved mechanistic question was the implication of benzoyllithium (XI) in the entire process. Thus there was no way of distinguishing between e.g.



(X)



(XI)

conversion of monomeric phenyllithium to X by way of XI (eq. 2–3) and conversion of dimeric phenyllithium to X by a concerted insertion of carbon monoxide into an aggregate (eq. 4–5). Similarly, subsequent reactions of X may involve XI.

$$\text{PhLi} + \text{CO} \rightarrow [\text{PhCOLi}] \qquad (2)$$

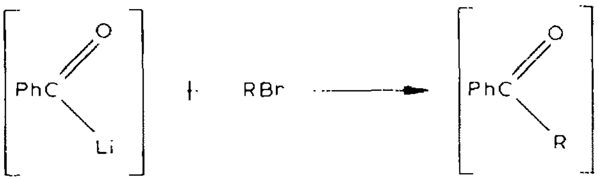
$$[\text{PhCOLi}] + \text{PhLi} \rightarrow [\text{Ph}_2\text{COLi}_2] \qquad (3)$$

$$2\ \text{PhLi} \rightarrow (\text{PhLi})_2 \qquad (4)$$

$$(\text{PhLi})_2 + \text{CO} \rightarrow [\text{Ph}_2\text{COLi}_2] \qquad (5)$$

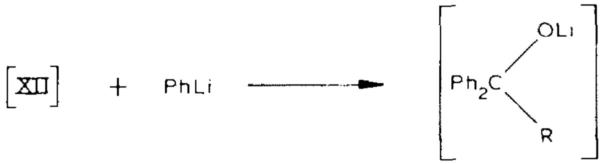
That X is an intermediate in the formation of II has been proved previously by labelling experiments [9] and is confirmed in the present study by the spectra of the reaction mixture at the outset of the reaction which is characteristic of the benzophenone dianion. Nevertheless, the absence of substantial amounts of V, even at the outset of the reaction (Table 3) indicates that the concentration of X is never high. Since the absorption of carbon monoxide is fast when the reaction is run in THF, it can be inferred that subsequent reactions of X must be even faster to account for its small concentration in the reaction mixture. Not even traces of benzaldehyde have ever been found in the product mixtures. Therefore it can be expected that reaction 3, if it exists, is faster than 2.

Result 7 could only be explained through the intermediation of XI (eq. 6, 7).



(6)

(XII)



(7)

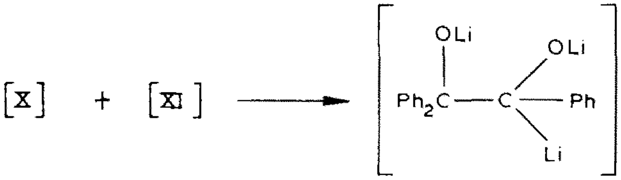
(XIII)

Although X could, in principle, react with RBr to produce XIII (eq. 8) it does not occur under the experimental conditions (result 8); furthermore, if X were present its subsequent reactions with (PhLi, CO) must be faster

$$[Ph_2COLi_2] + RBr \not\longrightarrow [XIII] \qquad (8)$$

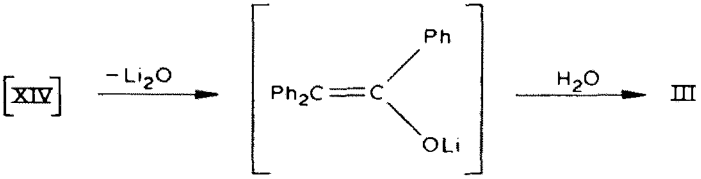
than its formation and even traces of I, III or the other reaction products should have been found. Only II is formed in small amounts [20] and can be explained as a dimerization product of XI (see below).

Once the existence of XI is indicated, the following mechanism of formation of III can be sketched (eq. 9, 10).



(9)

(XIV)

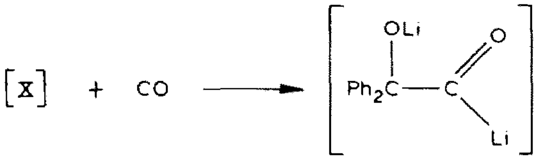


(10)

(XV)

That XIV and XV are intermediates is proved by the isolation of 1,1,2-triphenylethyleneglycol (Tables 2 and 4) and of triphenylacetoxyethylene (Table 5) when the reaction is quenched with water or acetic anhydride, respectively [9].

An alternative mechanism could involve the reaction of X with carbon monoxide followed by addition of phenyllithium to give XIV (eq. 11, 12). However, according with the above results, eq. 11 should be rate determining. This is not in agreement with the observed concentration ratio dependence.



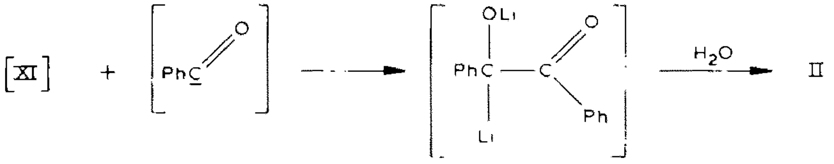
(11)

(XVI)

$$[XVI] + PhLi \longrightarrow [XIV] \qquad (12)$$

Since X is an intermediate in the formation of III, and X could also be formed by insertion of CO into dimeric phenyllithium (eq. 4), it is reasonable to expect that production of III would be preferred in those solvents in which the equilibrium of the eq. 4 lays to the right, as it is actually observed (Table 2).

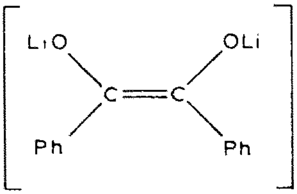
The production of II does not imply electron transfer and, in principle, it could be envisaged as a condensation of a benzoyllithium molecule with the resulting acyl anion of another molecule (eq. 13).



(13)

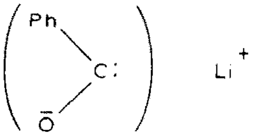
(XVII)

Nevertheless, this mechanism does not agree with result 6 which suggests that XVIII and not XVII is the real precursor of II. The stereospecificity of the reaction (only the *cis*-isomer is obtained) would exclude the equilibrium XVII ⇌ XVIII.



(XVIII)

An alternative possibility could be the intermediation of a carbene of anionic structure (XIX). There is relevant evidence for the nucleophilic character of an anionic carbene [21]. In addition, such a carbene has been proposed as an intermediate in the dimerization of formaldehyde [22]. Acyl-polycarbonyl-metallic compounds of transition metals have been demonstrated to have a carbene structure [23]. ESR studies of arylmethylenes have shown that such species have a diradical planar triplet structure [24,25]. Assuming XIX is also in its triplet state, its dimerization could occur in the plane of the molecule: approach of both molecules in a *cisoid* transition state would allow each lithium atom to coordinate with both oxygens simultaneously. This would explain the absolute stereospecificity of the coupling reaction.

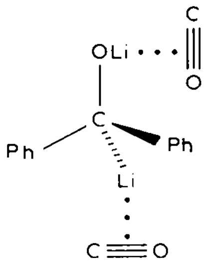


(XIX)

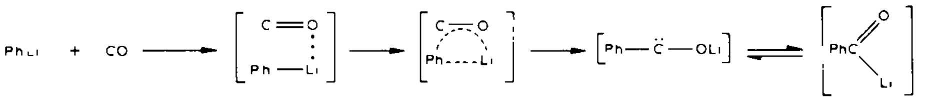
Formation of I implies an oxidative process of the intermediate X. Carbon monoxide is an effective oxidant toward a variety of aromatic radical ions and dianions [26] and it has been shown to oxidize X to I in diethyl ether solution [9]. Nevertheless, I cannot be free in the reaction mixture before hydrolysis since no triphenylcarbinol has been detected even when the reaction was quenched when considerable amounts of phenyllithium still remain unreacted (Table 3). The same conclusion was confirmed by running the reaction in the presence of lithium hydride: no change in the product mixture was observed.

The absence of V in yield comparable to that of I precludes the intermediation of a lithium benzophenone ketyl. Similarly, other possible intermediates whose disproportionation or partitioning could render I and other products should be disregarded on the same grounds, since the reported yields account for the total fate of phenyllithium.

Inasmuch as the most obvious oxidation pathways failed to gain experimental support, the process is inferred to occur during the solvolytic work-up procedure. It is reasonable to assume that X is not free in the reaction media (at least not in high concentration) but coordinated to two carbon monoxide molecules through the lithium atoms (XX). The work-up procedure should favour the elimination of the elements of lithium carbonyl, producing the oxidation product I. Although no evidence for lithium carbonyl has been observed in the present study, it can be obtained by the reaction of carbon monoxide with lithium metal [27]. Indirect signs of such a coordination are: a) in the reaction of *o*-anisyllithium (in which the lithium atoms are intramolecularly coordinated with the *ortho*-methoxy groups) *o,o*-dianisylketone and *o,o*′-dianisylcarbinol are obtained in comparable yields (33 and 32%, respectively) [28]; and b) the effect of donor-bases: when the reaction is performed in the presence of DABCO or TMEDA a five-times decrease in the rate of reaction is observed [1], although it is known that these amines usually increase the reactivity of organolithium reagents by coordination to the metal atom [29]. This last result could indicate that the first step in the whole reaction is the coordination of the lithium atom, and subsequent attack on the carbanion producing a four-centre cyclic transition state (XXI) and further rearrangement to give the benzoyllithium (eq. 14).



(XX)

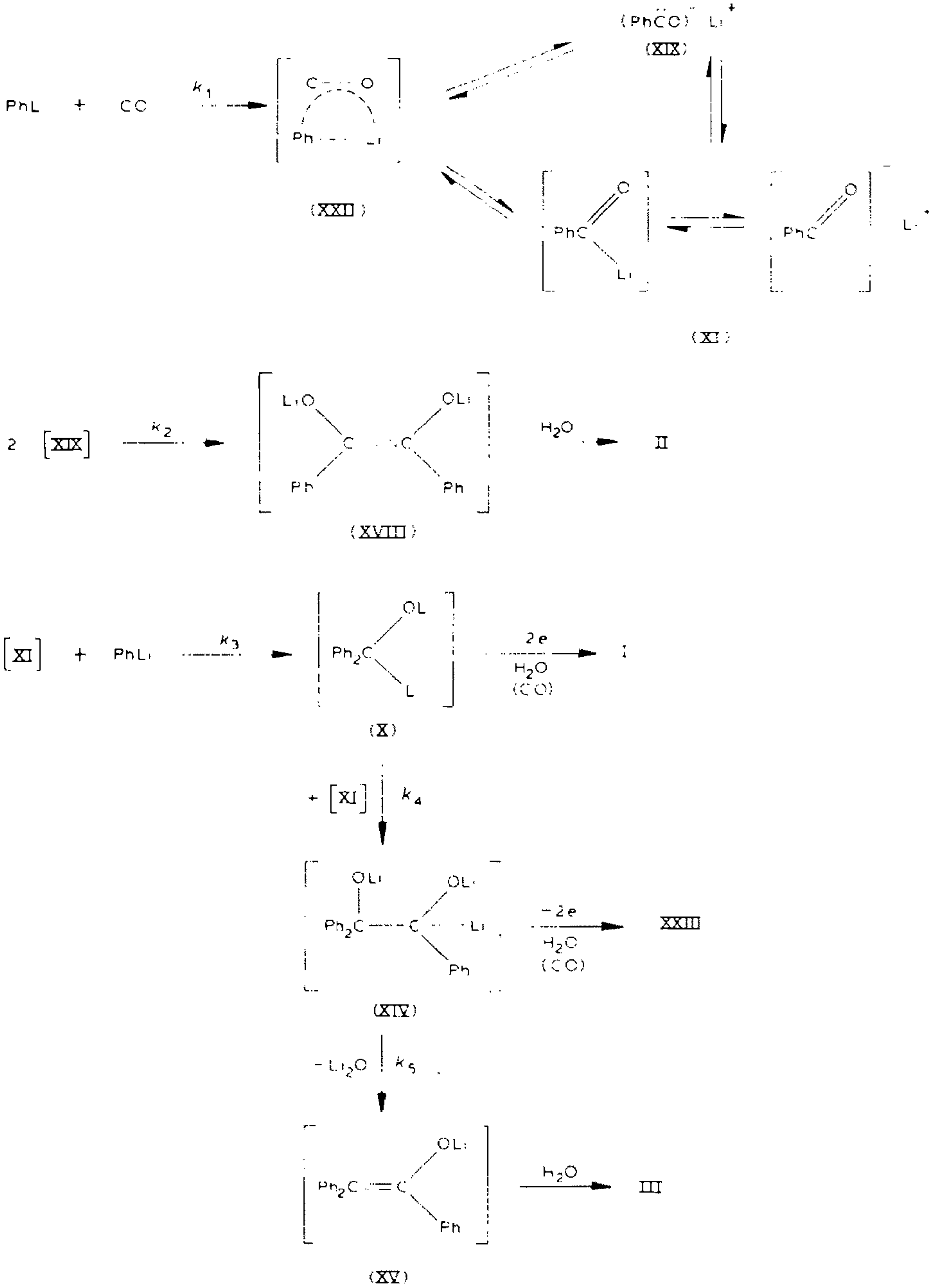


(XXI)

(14)

The fourth in importance reaction product (α,α-diphenyl-α-hydroxyacetophenone, (XXII)), also results from an oxidation process which could proceed in a way similar to the formation of I. Again, the oxidative process should not occur before the work up. The whole mechanism implied by all the above data is summarized in Scheme 1.

SCHEME 1



No kinetic determination of the various rate constants, k, was attempted because of the complexity of the reaction and its sensitivity to the geometry of the reaction flask, stirring speed, dissolution rate of the carbon monoxide, etc. However, the empirical facts suggest that k_1 is not likely to be rate determining in the formation of III (except, probably, when the reaction is performed between crystals of phenyllithium and gaseous carbon monoxide), k_2 and k_3 are higher than k_4 and only in the case in which the ratio [PhLi]:[CO] is high, production of III is important. It has been also established that step k_5 has a high energy of activation. In addition, the concentration of carbon monoxide is important in the production of I and XXIII. This can be interpreted on the basis of coordination of carbon monoxide to the lithium atoms of the intermediates X and XIV.

The identification of the different organic anions involved as intermediates has provided methods for the generation of useful compounds [30] and suggests further uses of the reaction in synthesis.

Experimental

General methods

All reactions involving organolithium reagents were carried out using standard techniques for the manipulation of air- and water-sensitive compounds [31]. All compounds reported here were fully characterized by mass spectrometry (using a Varian Mat CH 7A spectrometer), infrared spectroscopy (determined on a Perkin Elmer 137 spectrometer), ultraviolet spectroscopy (recorded on a Beckman DK 2A spectrophotometer) and nuclear magnetic resonance spectroscopy (determined on a Varian A-60 spectrometer) and showed spectral characteristics consistent with the spectra of authentic samples. The GLC analyses were carried out on a 5830 Hewlett-Packard gas chromatograph, GC-MS were performed on a Varian 1440 gas-chromatograph coupled to the Varian Mat CH 7A mass spectrometer equiped with a Varian Mat Data System 166 computer. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Hexane and THF were purified as previously described [9] and were distilled from dark blue solutions of benzophenone ketyl under nitrogen immediately before using. Carbon monoxide was generated by standard procedures [32] and was purified by passing through a column of potassium hydroxide and then bubbling through a solution of benzophenone ketyl in toluene. In general, phenyllithium was prepared by metal-halogen exchange between butyllithium and iodobenzene by the method previously described [13]. However, the phenyllithium used in the experiments of Table 1 was prepared from diphenylmercury by transmetallation [9]. Triphenylcarbinol was prepared by standard procedures [32b], m.p. 162–163°C. 1,1,2-triphenyl-ethyleneglycol was prepared from α-hydroxy-α,α-diphenylacetophenone as previously described.

α-Hydroxy-α,α-diphenyl-acetophenone was prepared in 40% yield by the procedure of Greene and Zook [33], m.p. 84–85°C (lit. [33] 84.5–85°C).

1-Phenyl-1-acetoxy-acetophenone, prepared in 90% yield according to the procedures of Francis and Keane [34], had a m.p. of 80–81°C (lit. [34] 80.5–81°C).

α,α-Diphenylacetophenone was prepared in 40% yield after Polansky, Schinzel and Wessely [18], m.p. 136–137°C (lit. [18] 136°C).

α-Hydroxyacetophenone

To a solution of 1.3 g (9 mmol) of benzoyl chloride in 50 ml of diethyl ether was

added a solution of 18 mmol of diazomethane in 50 ml of diethyl ether. After 48 h at room temperature, a 3 *N* aq. solution of perchloric acid was added and the mixture stirred for 6 h. The reaction mixture was neutralized with sodium bicarbonate. The solvent was distilled off at reduced pressure. The product was crystallized from ligroin, m.p. 82–83°C (lit. [35] 84°C, yield 42%).
IR (KBr): 3450, 2960, 1730, 1480, 1420, 740, 670 cm^{-1}.
NMR (CCl_4): δ 3.5 (s, 1), 4.9 (s, 2), 7.6 (m, 3), 8.0 ppm (m, 2).
MS, *m/e* (rel. ab.): 136 (M^+, 10%), 106 (12%), 105 (100%), 77 (90%).

cis-1,2-Diphenyl-1,2-diacetoxyethylene

A mixture of 3 g (14 mmol) of benzil and 35 g of 2% sodium amalgam in 25 ml of diethyl ether and 25 ml of benzene was allowed to stir under a dry atmosphere. A violet solid was immediately formed. After 3 h stirring an orange precipitate of disodium benzil formed. The flask was cooled at 0°C and 5 g of acetic anhydride was added. The solvent was removed by distillation. The excess acetic anhydride was removed by treatment with hot water, extraction with diethyl ether and neutralization with sodium bicarbonate. The ether solution was dried and concentrated to give the product which was crystallized from methanol, m.p. 116–117°C (lit. [36] 116°C). According to Fieser [37] it is the *cis* isomer.
IR (KBr): 3050, 1800, 1390, 1200, 760, 690 cm^{-1}.
NMR ($CDCl_3$): δ 2.72 (s, 6), 7.20 ppm (s, 10).
MS *m/e* (rel. ab.): 296 (M^+, 7%), 254 (27%), 212 (100%), 105 (49%), 77 (11%).

Diphenyl-n-butyl-carbinol

0.6 g (5 mmol) of methyl pentanoate was added dropwise to a solution of 10 ml of PhLi in diethyl ether. The white precipitate formed was poured into ice and treated with a solution of ammonium chloride. The product was extracted with diethyl ether, dried ($MgSO_4$) and the solvent distilled to yield a yellow oil that was purified by preparative TLC on silica gel (yield 76%).
IR (film) 3350, 2850, 1450, 760, 700 cm^{-1}.
NMR (CCl_4): δ 0.9 (t, 3), 1.25 (m, 4), 2.15 (t, 2), 1.95 (s, 1), 7.2 ppm (m, 10).
MS *m/e* (rel. ab.) 240 (M^+, 1.2%), 183 (100%), 105 (71%), 77 (36%).

Dilithium benzophenone dianion (X)

Benzophenone (4.06 g, 22 mmol), was dissolved in 30 ml of THF. Lithium wire (1 g, 140 mg-atom, cut into 0.25 inch pieces) was added. The mixture was allowed to stir for 1 day at room temperature. A pale blue precipitate of lithium benzophenone ketyl formed initially, which was subsequently reduced to a purple solution characteristic of X. Vigorous stirring is required to keep the precipitate from settling. An aliquot of the solution was quenched with degassed water, ligroin was added and the organic layer analyzed by GLC using a NPGS column, the yield of benzhydrol was 95%.

Reaction of X with butylbromide in THF at −78°C

The flask containing the solution of X (10 ml 0.5 *M*) was put into a dry ice-acetone bath and 1.5 ml (15 mmol) of butylbromide was added. The mixture was allowed to react for 30 min. The reaction was quenched with degassed water and processed as described before. Only benzhydrol (95% yield) was detected.

Reaction of phenyllithium with CO: general procedures

0.840 g of solid PhLi (10 mmol) contained in a tube capped with a no-air stopper was dissolved in 20 ml of the desired solvent and exposed to CO (1 atm pressure). The colorless solution immediately turned pink and when the gas absorption had ceased was brownish purple. n-Undecane was added as internal GLC standard. The reaction was then quenched with water or acetic anhydride, extracted with ether and dried ($MgSO_4$). The ether layer was analyzed by GLC. The time for CO absorption varies from 14 h in hexane suspension to 15 min in THF. The total amount absorbed was always nearly 1.5 eq. of the PhLi.

Isolation and characterization of the products

The reaction mixture was worked up in a similar way. The ether layer was distilled off at reduced pressure. When the production of III was high, a white residue was obtained. This residue was treated with methanol and the crystals collected. In other cases a viscous oil was obtained. This oil was subjected to column chromatography on silica gel with benzene-methanol mixtures as the eluent. Fractions containing I, II and III were collected and characterized by their melting points, spectra and TLC behaviour. The other compounds are produced only in small amounts and were identified by GC-MS and TLC behaviour.

Product balance by GLC

The reaction mixture was analyzed by GLC on a 3% SE 30 on Chromosorb W column at 50–250°C. On this column benzoin and benzil have the same retention time, but only benzoin was isolated by column chromatography and fully characterized. The same happens with benzophenone and benzhydrol, but they can be separated on a NPGS 10% on Chromosorb G column.

Acknowledgements

The authors are indebeted to SECYT (Science and Technology Secretariat), to the CONICET (National Research Council of Argentina) and to the Organization of American States for financial support. A.A.V. is a grateful recipient of a fellowship from the CONICET. The spectroscopic determinations were performed by UMYMFOR (FCEN-CONICET).

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