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C-ALKYLATION OF β-DIKETONES WITH BENZYLPYRIDINIUM SALTS. EVIDENCE FOR CHAIN RADICAL MECHANISMS

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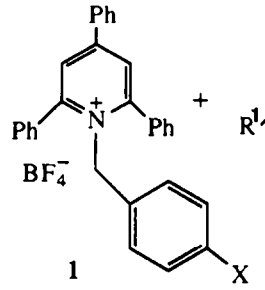
Abstract: 1-(p-Substituted benzyl)-2,4,6-triphenylpyridinium cations react with β-diketone anions by mechanisms which depend on the para-substituent. The p-methoxybenzyl derivative undergoes S_N1 displacement yielding O- and C-benzylated products. The p-nitrobenzyl compound reacts by a chain radicaloid mechanism and gives high yields of C-p-nitrobenzylated diketones. The parent benzyl compound forms some C- and some O-benzylated products, together with bibenzyl, probably by a radical chain reaction which was suppressed by radical traps.

INTRODUCTION.- Nucleophilic substitutions at saturated carbon atoms utilizing a neutral substituted pyridine ring as the leaving group have provided both useful synthetic methods[1] and a source of fundamental mechanistic information.[2,3] The spectrum of mechanisms operating in these reactions ranges from the classical S_N1 type, through classical S_N2 displacement, to an electron transfer from the nucleophile to the pyridinium ring followed by a non-chain radical-pair collapse. Examples at or near each of the possible borderlines have been reported.

Malonates and acetoacetates, but not hitherto β-diketones, have received some attention as nucleophiles in such reactions of pyridinium salts.[4] One of our groups has been involved in the study of the C-alkylation of β-dicarbonyl compounds in the form of their nickel(II)[5] and cobalt(II) [6,7,8] complexes both from the preparative[5-8] and from the mechanistic[9] viewpoints. We now present a synthetic study of the reactions of β-diketones with N-substituted pyridinium salts together with preliminary but informative experiments which indicate that the mechanistic spectrum of nucleophilic substitutions on pyridinium salts should be extended to include two radical-chain mechanisms (a) resulting from electron transfer to the pyridinium moiety and (b) of $S_{RN}1$ type[10] resulting from electron transfer to the aryl group of the benzyl moiety.

PREPARATIVE RESULTS.- Our attempts to use 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate, **1b**, as an alkylating agent towards $Co(acac)_2$ failed (refluxing chloroform, or chlorobenzene, or DMSO at 80ºC) showing that benzylpyridinium salts behave differently from benzyl halides.

β-Dicarbonyl compounds can be alkylated with benzyl halides in refluxing chloroform in the presence of potassium carbonate, and these alkylations are accelerated by the presence of cobalt(II) chloride bistriphenylphosphine which is assumed to initiate a chain



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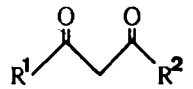

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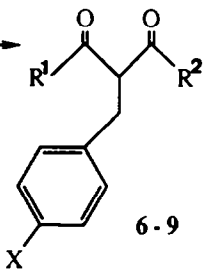

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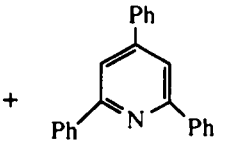

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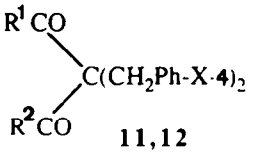

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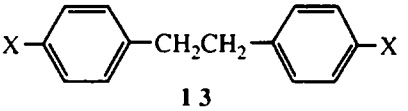

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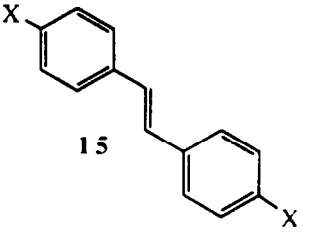

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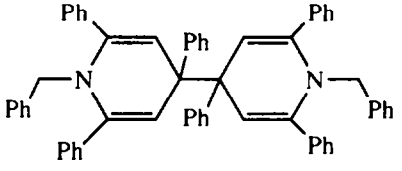

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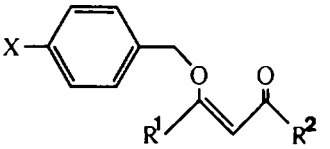

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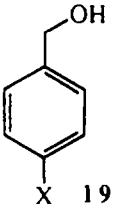

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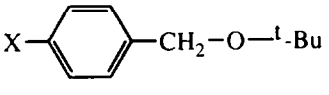
	X		R^1	R^2
a	CH_3O	**2, 6, 11, 16**	Me	Me
b	H	**3, 7, 12, 17**	Me	Ph
c	Cl	**4, 8, 18**	Ph	Ph
d	NO_2	**5, 9**	*t*-Bu	*t*-Bu

R^1 and R^2 could be interchanged in 17



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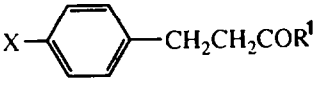

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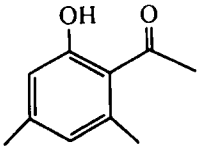

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mechanism by electron transfer.[11]. The results obtained in similar reactions with salts **1a**, **1b** and **1d** are collected in Table 1. These reactions of **1a** and **1d** were only slightly inhibited by 0.1 moles of the cobalt complex (Runs 1, 2, 6 and 7). However, the reaction of **1b** was completely prevented in the presence of the cobalt compound (Runs 3, 4 and 5). In no case was acceleration or enhancement of reactivity observed. In addition, the reaction of **1b** showed a strong dependence on the presence of light. Normal laboratory light was enough, but the reaction 3, carried out in the dark, led to the recovery of the starting material.

Important to the following discussion is the nature of the side products identified: 1,2-diphenylethane, **13b** (Run 4), which probably arises from benzyl radical dimerization, and structure **14** (Run 3) tentatively attributed on the basis of ^{1}H-NMR and MS spectroscopic evidence. Compound **14** exhibited singlets of equal intensity at 4.0 (showing long range coupling) and 5.5 which are assigned to the benzyl methylene and the enamine ring protons, respectively. The MS shows only intense peaks at 398(88) (which is exactly half of the molecular weight) and at 91(100). The small amount available prevented further characterization. The best hypothesis to explain the formation of **14** is again a radical dimerization.

Table 1. Reactions of **1** and **2** in refluxing chloroform[a]

Run	Pyridinium	2	$CoCl_2(PPh_3)_2$	Time	6 (%)	Other products[b] (%)
1	**1a** 0.2M	0.2M	-----	41 h	**6a** (29)	
2	**1a** 0.2M	0.2M	0.02M	41 h	**6a** (21)	
3	**1b** 0.29M	0.29M	-----	41 h	**6b** (30)	**14** (4)
4	**1b** 0.2M	0.6M	-----	69 h	**6b** (30)	**13b** (5)
5	**1b** 0.37M	0.37M	0.037 M	41 h	**6b** (traces)	
6	**1d** 0.2M	0.2M	-----	41 h	**6d** (7.5)	**11d** (20)
7	**1d** 0.2M	0.2M	0.02M	41 h	**6d** (7)	**11d** (11), **15d** (22)

[a] Potassium carbonate was introduced in a fourfold excess with respect to **2**. All the reactions were carried out under normal laboratory light.
[b] Triphenylpyridine, **10**, was isolated in more than 60% yield in Runs 1-4, 6 and 7. In Run 5 the isolated yield was 7%.

The C-dialkylated diketone **11d** is normally produced under radical mechanism conditions from 4-nitrobenzyl systems.[11] Stilbene **15d** (Run 7) can be interpreted as a consequence of the alkylation inhibition thus allowing the 4-nitrobenzyl moiety to be transferred to a different ionic reaction pathway. Moreover, qualitative results based on UV monitoring proved that 0.1 mole galvinoxyl practically stopped the reaction of **1b** with acetylacetone in DMSO at room temperature and in the presence of potassium carbonate.

The yields of products **6** under the conditions of Table 1 were too low for the

reactions to be synthetically useful, and we experimented to improve them. Surprisingly, the sodium salt of **2** in refluxing ethanol was inert towards **1b** both in the dark and under irradiation. However, salts **1a-d** reacted efficiently with diketones **2-5** in the dark in anhydrous t-butanol and in the presence of three equivalents of DBU, a base with electron transfer ability.[12,13,14] These results are gathered in Table 2.

The type of the reaction products is related to the electronic nature of the substituent in the benzyl moiety of the pyridinium salts **1a-d**. Thus, salt **1a** (X = OMe), carrying a 4-methoxy substituent, reacts with pentane-2,4-dione, **2**, with 1-phenyl-1,3-butanedione, **3**, and with 1,3-diphenylpropane-1,3-dione, **4**, to afford moderate yields of products **6a**, **7a**, and **8a** arising from monoreaction at the activated methylene groups of the diketones (Runs 1, 2 and 3). Significant amounts of products **16a** and **17a** from O-alkylation were also isolated, as well as alcohol **19a** and ether **20a**. The alcohol could originate by hydrolysis of **16a-18a** during the working up. The ether **20a** can arise from direct attack of the solvent or its conjugate base. No other products were detected in the reactions of **1a**.

Table 2.- Reactions of **1** with **2-5** in the presence of DBU[a]

Run	Salt	Diket.	T[a]	Time	C-Alkylated **6-9, 11-12**(%)	Dimer **13**(%)	O-Alkylated **16-18**(%),**19-20**(%)
1	**1a**	**2**	Refl.	0.5h	**6a**(38)		**16a**(33), **19a**(4), **20a**(15)
2	**1a**	**3**	Refl.	0.5h	**7a**(39)		**17a**(12), **19a**(19), **20a**(18)[c]
3	**1a**	**4**	Refl.	0.5h	**8a**(31)		**19a**(22), **20a**(24)[c]
4	**1b**	**2**	Refl.	7h	**6b**(40)	**13b**(11)	**16b**(17)[b]
5	**1b**	**3**	Refl.	7h	**7b**(21)	**13b**(10)	**17b**(16)
6	**1b**	**4**	Refl.	6h	**8b**(27)	**13b**(8)	**18b**(20)
7	**1c**	**2**	Refl.	3h	**6c**(60)	**13c**(6)	**16c**(15)
8	**1c**	**3**	Refl.	3h	**7c**(17)	**13c**(6)	**19c**(18)
9	**1c**	**4**	Refl.	3h	**8c**(13)	**13c**(2)	**18c**(21), **19c**(8)
10	**1c**	**5**	Refl.	3h	**9c**(0)	**13c**(14)	**19c**(16)
11	**1d**	**2**	R.t.	15m	**6d**(63), **11d**(31)		
12	**1d**	**3**	R.t.	1h	**7d**(84), **12d**(1)		
13	**1d**	**4**	R.t.	1h	**8d**(82)		
14	**1d**	**5**	R.t.	3h	**9d**(56)		
15[d]	**1b**	**2**	Refl.	7h	**6b**(19)	**13b**(32)	e
16[d]	**1d**	**2**	R.t	15m	---		

[a]Concentrations of **1**, **2** and DBU: 1M, 3M and 3M in anhydrous t-butanol. Yields of isolated products unless otherwise stated. [b]Products **21b**(28)[c] and **22**(13) also formed. [c]Yields calculated from 1H-NMR spectra. [d]In the presence of 0.2 mole of galvinoxyl. [e]Not investigated.

The array of products formed in the reactions of the salt **1b** (X = H) (Runs 4, 5 and 6) showed a significant difference. The C-alkylation products, **6b**, **7b** and **8b** were also isolated in reasonable yields. The O-alkylation products **16b-18b** were also formed. However, 1,2-diphenylethane, **13b**, the radical dimer was also formed. The phenol **22** is the result of aldol type condensations between two molecules of diketone **2**.

Salt **1c** (X = Cl) was used in Runs 7, 8, 9 and 10. The C-alkylation products **6c-8c** were again isolated except for Run 13 in the reaction with 2,2,6,6-tetramethylheptane-3,5-dione, **5**. However, in Runs 7 and 9 were the O-alkylated **16c** and **18c** isolated. In general, products of attack at the oxygen atoms of the diketones are now quantitatively less important. 1,2-Bis(4-chlorophenyl)ethane, **13c**, was isolated in each of the four experiments.

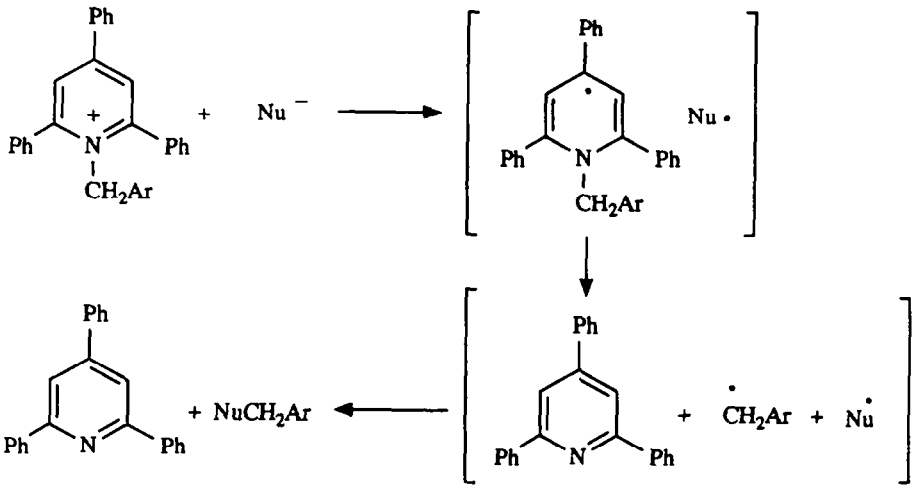
The reactions of salt **1d** with a 4-nitro substituent were clearly the fastest and afforded the highest yields of C-alkylated products **6d-9d** (Runs 11, 12, 13 and 14). They were also the cleanest reactions, the only by-products isolated being the C-dialkylation diketones **11d** and **12d**.

Reactions 15 and 16 (Table 2), carried out in the presence of Galvinoxyl (powerful radical scavenger) led to partial inhibition in the case of **1b** (exp. 15) and complete inhibition in the case of **1d** (exp. 16). In addition, an increase of the amount of the produced radical dimer **13b** was observed in exp. 15.

DISCUSSION.- Important changes in the nature of products, required times and temperatures and in colours are observed in the reactions of β-diketones **2-5** with N-benzyl-2,4,6-triphenylpyridinium salts in t-butanol and in the presence of DBU as a base (Table 2) which are related to the electronic features of the substituents in the aryl ring of the benzyl moiety of the pyridinium salts. Thus, Runs 1, 2, and 3 where the starting salt is **1a** (OMe substituent) show the typical array of products coming from a polar mechanism: similar amounts of C- and O-alkylation, benzyl alcohol, **19a**, t-butyl ether, **20a**. On the other hand none of the features typical of radical reactions are present (no strong colours, no dimers, no sensitivity to radical scavengers). Therefore we classify Runs 1, 2, and 3 of Table 2 as examples of S_N1 processes already well known in this field, when substituents in the group attached to nitrogen can help stabilize the positive charge.[15]

At the other end of the mechanistic spectrum we have the reactions of **1d** (NO_2 substituent) (Runs 11, 12, 13, and 14 of Table 2). These reactions are by far the cleanest and the fastest among the studied in the present work. Relevant features are the isolation of only the C-alkylation products in high yields, the no appearance of products of ionic origin (such as O-alkylation products, or the corresponding ether or alcohol), the fact that the reactions occur at room temperature, and the intense red colour that develops upon mixing of the reactants. We have compared these with the similar reactions using bromide as leaving group. The results are shown in Table 3. The reaction of 4-nitrobenzyl bromide (Run 3 in Table 3) under the identical conditions used for the corresponding

Scheme 1



Scheme 2

$$ArCR_2X \xrightarrow{e^-} [ArCR_2X]^{\pm}$$

$$[ArCR_2X]^{\pm} \longrightarrow ArCR_2^{\cdot} + X^-$$

$$ArCR_2^{\cdot} + Nu^- \longrightarrow [ArCR_2Nu]^{\pm}$$

$$[ArCR_2Nu]^{\pm} + ArCR_2X \longrightarrow ArCR_2Nu + [ArCR_2X]^{\pm}$$

pyridinium salt **1d** (Run 11 in Table 2) shows the very similar outcome of both reactions. No O-alkylation products are found, strong red colours were developed, and the required reaction times are of the same order.

One of our groups has reported[16] that N-(4-nitrobenzyl)-2,4,6-triphenylpyridinium tetrafluoroborate, **1d**, reacts with nitronates through a non-chain radicaloid mechanism (Scheme 1). This mechanism involves a single electron transfer from the nucleophile to the pyridinium ring followed by C-N bond homolytic breaking and radical pair collapse in the solvent cage.

Table 3. Reactions of benzyl halides with acetylacetone in the presence of DBU[a], or potassium carbonate[a].

					C-alkylated		O-alkylated
Run	Halide	Base	T[a]	Time	6(%)	11(%)	16(%)
1	$C_6H_5CH_2Br$	DBU	Refl.	2h	**6b**(23)	**11b**(15)	**16b**(31)
2[b]	$4\text{-}Cl\text{-}C_6H_4CH_2Br$	DBU	Refl.	2h	**6c**(35)	**11c**(9)	
3[b]	$4\text{-}NO_2\text{-}C_6H_4CH_2Br$	DBU	R.t.	15m	**6d**(48)	**11d**(14)	
4	$4\text{-}NO_2\text{-}C_6H_4CH_2Br$	K_2CO_3	R.t.	15m	—	—	—

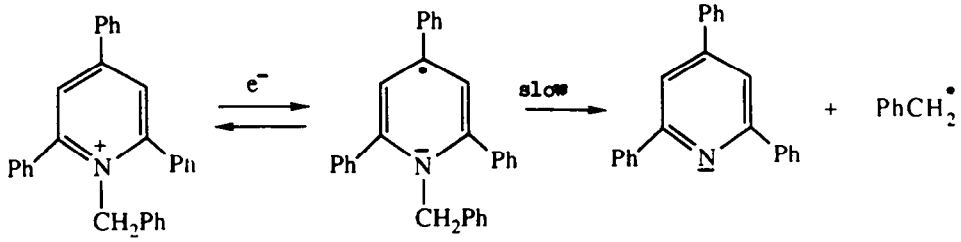
a) Concentrations of benzyl halide, acetylacetone and base: 1M, 3M and 3M in anhydrous t-butanol. For potassium carbonate an equimolar amount with respect to acetylacetone was suspended in the solvent. Yields of isolated products. b) Intense red colour.

In the case of Run 3, in Table 3 no electron transfer from the nucleophile to the leaving group is possible and the substract is known to react well through the radical chain $S_{RN}1$ mechanism[10] (Scheme 2). The similarity of Run 3 of Table 3 and Run 11 of Table 2 forces us to believe that, contrary to the nitronate case, electron transfer to the pyridinium ring in Run 11 of Table 2 does not operate: instead, electron transfer to the 4-nitrobenzyl substituent induces a radical chain mechanism of $S_{RN}1$ type. As expected complete inhibition is observed when the reaction is carried out in the presence of galvinoxyl (20% molar), (run 16, Table2). Another important feature of this type of mechanism is the possibility of entrainment[17] and we think the reaction of **1d** with diketones in the presence of DBU (Runs 11, 12, 13 and 14 of Table 2) constitute examples of it. This conclusion is reinforced by comparing these results with those obtained using potassium carbonate as a base (Run 6, Table 1). Although more than 70% of starting pyridinium had been consumed, the low C-alkylation yield obtained in Run 6 of Table 1 in a relatively slow reaction was not affected by the presence of radical scavengers such as cobalt(II) chloride bistriphenylphosphine (soluble in chloroform) and the run did not show any strong colour. These features correspond to a S_N mechanism, probably S_N2 considering the substrate. This interpretation is strongly supported by the results obtained with bromide as leaving group (Run 4, Table 3). The entrainment effect of DBU is evident since

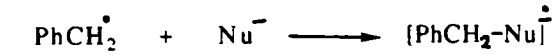
no reaction at all was achieved in this case. The electron donor properties of DBU are well established.[12, 13, 14] The corresponding reactions using N-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate, **1b**, show yet another distinct behaviour (Runs 4, 5, 6, and 15 Table 2). These reactions are slower than the preceding ones indicating a clear curvature in a hypothetical Hammett plot, but the reaction times are of the same order as those reported for related reactions using diethyl ethylmalonates[4] and nitronates[18] as nucleophiles which are believed to occur through the non-chain radicaloid mechanism (Scheme 1). The main features of our reactions are: the appearance of C- and O-alkylation products (the first predominating); the isolation in all the cases of the radical dimer 1,2-diphenylethane, **13b**; the absence of the corresponding ether and alcohol; the absence of strong colours; and the partial inhibition, with simultaneous yield increase of the radical dimer 1,2-diphenylethane, when the reaction is carried out in the presence of galvinoxyl. The parallel reaction using bromide as leaving group (Run 1, Table 3) shows a different behaviour. Thus, almost the same amount of O-alkylation (31%) and C-alkylation (38%) is obtained, and no radical dimer could be detected. Benzyl bromide is a well established S_N2 reactant and probably this is the operating mechanism with benzyl bromide (Run 1, Table 3). Considering the systematic differences and the similar cases previously described by one of our groups[4,16,19] we believe that **1b** reacts with diketones in the presence of DBU, in part (the O-alkylation product would come through a S_N2 mechanism), through the non chain radicaloid mechanism that includes electron transfer to the pyridinium moiety (Scheme 1). The difference in electronic affinity between the pyridinium and the benzyl moieties in this case must be too large to achieve enough benzyl radical anion to elicit the chain $S_{RN}1$ mechanism. Particularly interesting is the observed partial inhibition in this reaction in the presence of radical scavengers(run 15, Table 2), since similar results have been reported for the corresponding reactions with nitronates and this datum was considered important in proposing the non chain radicaloid mechanism (Scheme 1) for those reactions[19].

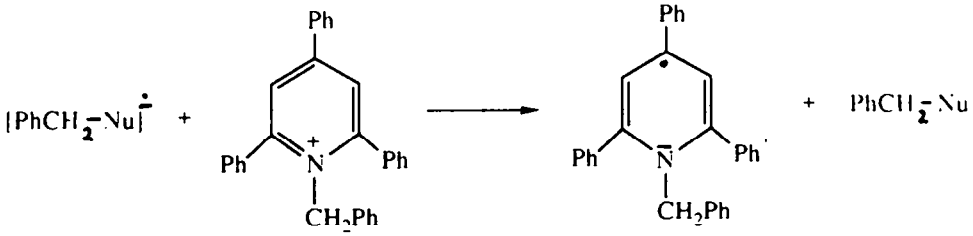
The results reported in Table 1 (Runs 3, 4, and 5) support the previous interpretation and add new data. Thus, reaction in the presence of potassium carbonate as a base is shown to be less efficient (reaction times in Table 1 are not optimized) but the difference was not so marked as in the $4\text{-}NO_2$ case. More relevant, the reaction showed a strong dependence on the presence of light, and its relative inefficiency allowed us to isolate in low yield a new dimer **14** most probably resulting from the combination of two pyridinium radicals and thus confirming the latter's existence in these reactions. The radical dimer **13b** was also obtained. Another interesting feature of this reaction (Runs 3 and 4 of Table 1) is the fact that it was completely supressed (Run 5 of Table 1) when it was carried out in the presence of a 10% molar amount of cobalt(II) chloride bistriphenylphosphine (radicaloid species with good electron transfer properties and soluble in chloroform).[11] Kornblum[20] has demonstrated that the electronically related cupric salts strongly inhibit radical chain processes like $S_{RN}1$. Our results suggest we have uncovered a new radical chain

mechanism via electron transfer to the pyridinium moiety (Scheme 3). In the present case the solvent is chloroform, and the solvent cage in it should be weaker than in polar and hydrogen bond forming solvents. The inefficiency of the process must be attributed to the difficult N-C bond homolytic breaking, and to the non particularly favoured combination between the poorly electrophilic benzyl radical and the nucleophile anion (probably leading to a ketyl radical anion). That, even makes the reaction through other pathways (S_N1 or S_N2) preferred in the cases both of a strong electron donor (OMe), and of a strong electron acceptor (NO_2) substituent in the aryl ring of the benzyl moiety.



Scheme 3





The reactions between N-(4-chlorobenzyl)-2,4,6-triphenylpyridinium tetrafluoroborate 1c and β-diketones in t-butanol and in the presence of DBU (Runs 7, 8, and 9, Table 2) show many similarities with the reactions of 1b just commented on. Nevertheless, reactions of 1c show strong red colours that probably indicate increased mechanistic complexity.

The results described in the present paper demonstrate the enormous mechanistic variety and complexity of the reactions involved (S_N1, S_N2, non chain radicaloid mechanism, radical chain mechanism through electron transfer to the pyridinium ring, radical chain mechanism through electron transfer to the aryl ring in the benzyl moiety), and the narrow borderlines involved. A deeper mechanistic study is now in progress.

EXPERIMENTAL.- 1-(4-X-Benzyl)-2,4,6-triphenylpyridinium tetrafluoroborates, **1a-d** were prepared as previously described.[16] The t-butanol solvent was dried by refluxing over calcium oxide.

Reaction of 1a with pentane-2,4-dione, 2. Typical procedure. (Run 1 of Table 2).

A mixture of DBU (2.74 g, 18.0 mmol), pentane-2,4-dione (1.80 g, 18.0 mmol) and t-butanol (6 mL) was stirred for five minutes. 1-(4-methoxybenzyl)-2,4,6-triphenylpyridinium tetrafluoroborate, **1a**, (3.09 g, 6.0 mmol) was then introduced. The mixture was refluxed for 30 minutes monitoring the disappearance of **1a** by tlc, diluted with chloroform (50 mL) and partitioned with 1M HCl (2 x 100 ml). The organic layer was washed with water, dried and evaporated. The residue was chromatographed through silica gel to afford the following products in order of elution: (i) 2,4,6-triphenylpyridine, **10**, (1.765 g, 96%). M.p. 137-9ºC (ethanol) (Lit. m.p. 139ºC).[21] (ii) t-Butyl 4-methoxybenzyl ether, **20a**, (0.178 g, 15%). 1H-NMR ($CDCl_3$): δ 1.31 (s, 9H), 3.67 (s, 3H), 4.10 (s, 2H), 6.60-7.34 (AA'BB' system, 4H); MS: m/e 194(M, 22), 121(100), 109(27), 43(22). (iii) 3-(4-Methoxybenzyl)pentane-2,4-dione, **6a**, (0.504 g, 38%). M.p. 65-8ºC (Lit. m.p. 69-70ºC);[22] IR(KBr): enol form 3430 (broad), 1610, 1585 cm^{-1}. 1H-NMR ($CDCl_3$): δ enol form 2.08 (s, 6H), 3.58 (s, 2H), 3.77 (s, 3H), 6.77-7.12 (AA'BB' system, 4H), 16.74 (s, 1H). The keto form presents signals at 2.15 (s, 6H), 3.09 (d, J = 7.1 Hz, 2H) and 3.95 (t, J = 7.1 Hz, 1H). (iv) 4-(4-Methoxybenzyl)oxy-3-penten-2-one, **16a**, (0.438 g, 33%). M.p. 75-6ºC (acetone-hexane); IR(KBr): 1666, 1579 cm^{-1}; 1H-NMR($CDCl_3$): δ 2.19 (s, 3H), 2.33 (s, 3H), 3.84 (s, 3H), 4.79 (s, 2H), 5.62 (s, 1H), 6.88-7.47 (AA'BB' system, 4H); 13C-NMR($CDCl_3$):δ 19.7, 31.9, 55.2, 69.9, 100.3, 114.0, 127.5, 129.3, 159.7, 171.5, 196.6; MS: m/e 121(82), 78(60), 52(21), 51(25), 43(100). Calcd. for $C_{13}H_{16}O_3$: C, 70.97; H, 7.33; Found: C, 71.08; H, 7.29. (v) 4-Methoxybenzyl alcohol, **19a**, (36 mg, 4%). It was compared with an independent sample.

Other experiments of Tables 2 and 3. All of them were run in the same manner. Some of the compounds were isolated in low amounts and their characterization was made by spectroscopic techniques. The O-alkylation products **16-18** were frequently unstable showing propensity to hydrolysis. The physical constants for the isolated products **6-22** or the literature references were as follows:

3-Benzylpentane-2,4-dione, **6b**. Oil, compared with an independent sample.[5]

3-(4-Chlorobenzyl)pentane-2,4-dione, **6c**. 1H-NMR($CDCl_3$): δ enol form 1.94 (s, 6H), 3.51 (s, 2H), 6.92-7.27 (AA'BB' system, 4H), 16.71 (s, 1H), δ keto form 2.05 (s, 6H), 3.00 (d, J = 7.0 Hz, 2H), 3.85 (t, J = 7.0 Hz, 1H). The 1H-NMR spectrum was coincident with the previously described.[23]

3-(4-Nitrobenzyl)pentane-2,4-dione, **6d**. M.p. 89-91ºC (ethanol) (Lit. m.p. 90-1ºC (24).

2-(4-Methoxybenzyl)-1-phenylbutane-1,3-dione, **7a**. M.p. 60-1ºC (acetone-hexane); IR(KBr): 1721, 1674 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 2.09 (s, 3H), 3.23 (d, J = 7.3 Hz, 2H), 3.70 (s, 3H), 4.72 (t, J = 7.3 Hz, 1H), 6.68- 7.15 (AA'BB' system, 4H), 7.4-7.7 (m, 3H), 7.85-8.0 (m, 2H); 13C-NMR($CDCl_3$): δ 28.4, 33.8, 55.0, 64.8, 113.9, 128.5, 128.6, 129.6, 130.2,

133.4, 136.4, 158.2, 195.7, 203.0; MS: m/e 282(M, 3), 239(38), 121(100), 77(32). Calcd. for $C_{18}H_{18}O_3$: C, 76.67; H, 6.43. Found: C, 76.42; H, 6.60.

2-Benzyl-1-phenylbutane-1,3-dione, **7b**. M.p. 51-3ºC (hexane) (Lit. m.p. 55-6ºC)[25]; IR(KBr): 1709, 1688 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 2.15 (s, 3H), 3.33 (d, J = 7.0 Hz, 2H), 4.78 (t, J = 7.0 Hz, 1H), 7.18 (s, 5H), 7.40-7.63 (m, 3H), 7.85-8.01 (m, 2H).

2-(4-Chlorobenzyl)-1-phenylbutane-1,3-dione, **7c**. M.p. 39-40ºC (acetone-hexane); IR(KBr): 1711, 1674 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 2.17 (s, 3H), 3.25 (d, J = 7.0 Hz, 2H), 4.71 (t, J 7.0 Hz, 1H), 7.13-7.60 (m, 7H), 7.8-8.0 (m, 2H); MS: m/e 288(0.2), 286(M, 0.7), 105(55), 77(69), 51(42), 43(100). Calcd. for $C_{17}H_{15}ClO_2$: C, 71.21; H, 5.27; Cl, 12.36. Found: C, 71.47; H, 5.31; Cl, 12.34.

2-(4-Nitrobenzyl)-1-phenylbutane-1,3-dione, **7d**. M.p. 81-2ºC (ethanol); IR(KBr): 1707, 1672, 1514, 1342 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 2.15 (s, 3H), 3.42 (d, J = 7.7 Hz, 2H), 4.79 (t, J = 7.7 Hz, 1H), 7.25-8.15(m, 9H); 13C-NMR($CDCl_3$): δ 28.6, 34.2, 63.8, 123.7, 128.6, 129.0, 129.8, 134.0, 136.1, 146.2, 195.0, 202.0; MS: m/e 298(9), 297(M, 4), 254(59), 105(100), 77(88), 43(46). Calcd. for $C_{17}H_{15}NO_4$: C, 68.75; H, 5.09; N, 4.72. Found: C, 68.68; H, 5.09; N, 4.64.

2-(4-Methoxybenzyl)-1,3-diphenylpropane-1,3-dione, **8a**. M.p. 97-9ºC (ethanol) (Lit. m.p. 95-6ºC)[26]; IR(KBr): 1688, 1670 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 3.40 (d, J = 7.0 Hz, 2H), 3.75 (s, 3H), 5.48 (t, J = 7.0 Hz, 1H), 6.74-7.99(m, 14H).

2-Benzyl-1,3-diphenylpropane-1,3-dione, **8b**. M.p. 102-4ºC (acetone) (Lit. m.p. 105-7ºC)[27]; IR(KBr): 1695, 1664 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 3.45 (d, J = 6.7 Hz, 2H), 5.50 (t, J = 6.7 Hz, 1H), 7.19-7.99 (m, 15H).

2-(4-Chlorobenzyl)-1,3-diphenylpropane-1,3-dione, **8c**. M.p. 117-8ºC (ethanol); IR(KBr): 1679 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 3.41 (d, J = 7.0 Hz, 2H), 5.46 (t, J = 7.0 Hz, 1H), 7.20-7.96 (m, 14H); 13C-NMR($CDCl_3$): δ 34.5, 58.8, 128.5, 128.6, 128.8, 130.3, 132.4, 133.5, 135.9, 137.4, 195.1; MS: m/e 350(0.1), 348(M, 0.5), 245(25), 243(77), 105(100), 77(88). Calcd. for $C_{22}H_{17}ClO_2$: C, 75.71; H, 4.91; Cl, 10.16. Found: H, 4.91 and 4.82; Cl, 10.32 and 10.18. No good carbon elemental analysis could be obtained.

2-(4-Nitrobenzyl)-1,3-diphenylpropane-1,3-dione, **8d**. M.p. 122-3ºC (ethanol) (Lit. m.p. 125ºC)[26]; IR(KBr): 1693, 1664, 1514, 1343 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 3.56 (d, J = 7.0 Hz, 2H), 5.51 (t, J = 7.0 Hz, 1H), 7.27-8.17 (m, 14H).

2,2,6,6-Tetramethyl-4-(4-nitrobenzyl)heptane-3,5-dione, **9d**. M.p. 117-8ºC (ethanol); IR(KBr): 1720, 1684, 1517, 1346 cm^{-1}; 1H-NMR($CDCl_3$): δ keto form 1.15 (s, 18H), 3.23 (d, J = 7.0 Hz, 2H), 4.73 (t, J = 7.0 Hz, 1H), 7.32, 7.41, 8.08, 8.18 (AA'BB' system, 4H); 13C-NMR($CDCl_3$): δ 27.0, 35.0, 44.5, 56.6, 123.6, 129.8, 146.6, 208.6; MS: m/e 319(M, 0.1), 57(100). Calcd. for $C_{18}H_{25}NO_4$: C, 67.77; H, 7.90; N, 4.39. Found: C, 67.96; H, 7.96; N, 4.31.

3,3-Dibenzylpentane-2,4-dione, **11b**. M.p. 110-2ºC (Lit. m.p. 112-4ºC).[5]

3,3-Bis(4-chlorobenzyl)pentane-2,4-dione, **11c**. M.p. 107-8ºC (ethanol); IR(KBr): 1717, 1690 cm^{-1}; 1H-NMR($CDCl_3$): δ 2.14 (s, 6H), 3.22 (s, 4H), 6.83-7.28 (AA'BB' system, 8H); 13C-

NMR($CDCl_3$): δ 28.1, 36.8, 71.8, 128.5, 130.9, 132.8, 134.2, 205.8. Calcd. for $C_{19}H_{18}Cl_2O_2$: C, 65.34; H, 5.20. Found: C, 65.23; H, 5.19.

3,3-Bis(4-nitrobenzyl)pentane-2,4-dione, **11d**. M.p. 226-30°C (Lit. m.p. 225-7°C).[11]

2,2-Bis(4-nitrobenzyl)-1-phenylbutane-1,3-dione, **12d**. M.p. 212-4°C (washed with ether); IR(KBr): 1712, 1669, 1518, 1346 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.92 (s, 3H), 3.51 (center of the signals of the diastereotopic methylene protons, 4H), 7.10-8.15 (m, 13H); MS: m/e 105(100), 77(46), 43(85). Calcd. for $C_{24}H_{20}N_2O_6$: C, 66.73; H, 4.69; N, 6.48. Found: C, 66.54; H, 4.75; N, 6.22.

1,2-Diphenylethane, **13b**. M.p. 48-50°C (Lit. m.p. 52°C).[28] 1H-NMR($CDCl_3$): δ 2.86 (s, 4H), 7.21 (s, 10H).

1,2-Bis(4-chlorophenyl)ethane, **13c**. M.p. 98-9°C (Lit. m.p. 100-1°C).[29]; 1H-NMR($CDCl_3$): δ 2.85 (s, 4H), 6.96-7.31 (AA'BB' system, 8H).

1,1'-Dibenzyl-2,2',4,4',6,6'-hexaphenyl-1,4,1',4'-tetrahydro-4,4'-bipyridine, **14**. M.p. 155-7°C; IR(KBr): 1650, 755, 740, 730, 690 cm^{-1}; 1H-NMR($CDCl_3$): δ 4.0 (s, 4H), 5.5 (s, 4H), 6.0-7.5 (m, 40H); MS: m/e 400(5), 399(29), 398(88), 307(22), 91(100).

4,4'-Dinitrostilbene, **15**. M.p. 297-300°C (Lit. m.p. 292.5-293.5°C)[30]; IR(KBr): 1600, 1510, 1350 cm^{-1}; 1H-NMR($CDCl_3$): δ 7.20 (s, 2H), 7.57 (d, J = 7.3 Hz, 2H), 8.20 (d, J = 7.3 Hz, 2H); MS: m/e 270(100), 165(30).

4-Benzyloxy-3-penten-2-one, **16b**. Oil; 1H-NMR($CDCl_3$): δ 2.15 (s, 3H), 2.32 (s, 3H), 4.85 (s, 2H), 5.55 (s, 1H), 7.34 (s, 5H); MS: m/e 91(54); 65(23), 43(100). This product could not be purified further.

4-(4-Chlorobenzyloxy)-3-penten-2-one, **16c**. Impure sample showed signals in the 1H-NMR($CDCl_3$) spectrum at δ 2.12 (s, 3H), 2.31 (s, 3H), 4.69 (s, 2H), 5.49 (s, 1H), 7.14 (s, 4H).

3-(4-Methoxybenzyl)oxy-1-phenyl-2-buten-1-one, **17a** or its isomer 4-(4-Methoxybenzyl)oxy-4-phenyl-3-buten-2-one, m.p. 107-9°C (acetone-hexane); IR(KBr): 1649, 1614, 1571 cm^{-1}; 1H-NMR($CDCl_3$): δ 2.45 (s, 3H), 3.82 (s, 3H), 4.90 (s, 2H), 6.28 (s, 1H), 6.88-8.01(m, 9H); MS: m/e 282(M, traces), 121(100). Calcd. for $C_{18}H_{18}O_3$: C, 76.67; H, 6.43. Found: C, 76.74; H, 6.67.

3-Benzyloxy-1-phenyl-2-buten-1-one, **17b** or its isomer 4-Benzyloxy-4-phenyl-3-buten-2-one. An impure sample exhibited signals in the 1H-NMR($CDCl_3$) spectrum at δ 2.38 (s, 3H), 4.96 (s, 2H), 5.10 (s, 1H), 7.1-7.6 (m, 10 H).

3-Benzyloxy-1,3-diphenyl-2-propen-1-one, **18b**. M.p. 92-3°C (acetone-hexane); IR(KBr): 1657 cm^{-1}; 1H-NMR($CDCl_3$): δ 4.68 (s, 2H), 6.86 (s, 1H), 7.34-8.08(m, 15H); MS: m/e 314(M, traces), 105(77), 91(100), 77(40). Calcd. for $C_{22}H_{18}O_2$: C, 84.15; H, 5.78. Found: C, 83.48; H, 5.78.

3-(4-Chlorobenzyl)oxy-1,3-diphenyl-2-propen-1-one, **18c**. M.p. 108-10°C (dichloromethane-hexane); IR(KBr): 1656 cm^{-1}; 1H-NMR($CDCl_3$): δ 4.67 (s, 2H), 6.81 (s, 1H), 7.25-8.08 (m, 14H); MS: m/e 350(0.9), 348(M, 2.8), 208(22), 127(54), 125(100), 105(35), 77(21). Calcd.for $C_{22}H_{17}ClO_2$: C, 75.71; H, 4.91; Cl, 10.16. Found: C, 75.02; H, 4.84; Cl, 9.97.

4-Methoxybenzyl alcohol, **19b**. Oil; IR(film): 3345 (broad) cm^{-1}; 1H-NMR($CDCl_3$): δ 3.75 (s, 3H), 4.49 (s, 2H), 6.72-7.30 (AA'BB' system, 4H).

4-Chlorobenzyl alcohol, **19c**. M.p. 70-72ºC (Lit. m.p. 75ºC).[28]

4-Phenyl-2-butanone, **21b**. Oil; 1H-NMR($CDCl_3$): δ 2.07 (s, 3H), 2.63-2.90 (m, 4H), 7.14 (s, 5H).

2-Acetyl-3,5-dimethylphenol, **22**. M.p. 54-7ºC (Lit. m.p. 55-6ºC)[31]; 1H-NMR($CDCl_3$): δ 2.27 (s, 3H), 2.55 (s, 3H), 2.63 (s, 3H), 6.55 (s, 1H), 6.65 (s, 1H), 12.57 (s, 1H).

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