Role of Alkali Halides in the Synthesis of Nitrogen Containing Heterocycles by Reductive Carbonylation of Aromatic Nitro-Derivatives Catalysed by $Ru_3(CO)_{12}$

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The presence of alkali halides as co-catalysts in the reductive carbonylation of *o*-nitrobiphenyl **1** catalysed by $Ru_3(CO)_{12}$ strongly increases the rate of reactions and selectivity towards heterocyclization products [carbazole **2** and 5*H*-phenanthridin-6-one **3**]. With sodium halides, depending on the anion, the selectivity for carbazole is in the order $Cl^- > Br^- \approx F^- \gg I^-$; whereas the selectivity for 5*H*-phenanthridin-6-one is the reverse $I^- > Br^- \approx F^- > Cl^-$. The influence of the cation can be explained with the polarization of a CO ligand of the ruthenium cluster, due to the interaction of the alkali cation with the oxygen lone pair. In fact high yields (>80%) of heterocyclization products are obtained when the alkali cation is free to coordinate the CO. When this interaction is reduced, by sequestering the cation with crown-ethers, or better with cryptands, the yield of heterocyclic products is 14% and 0% respectively. The role of the anion and cation in the catalytic mechanism are discussed. The attempted extension of this reaction to other nitro-derivatives for the potential synthesis of aromatic heterocycles with larger rings are also reported.

Reductive carbonylation of aromatic nitroso and nitro compounds in the presence of transition metal complexes has been widely investigated in these last years.[1] Particularly appealing from the synthetic point of view is the reductive carbonylation catalysed by $Ru_3(CO)_{12}$ which has been successfully used for the preparation of important organic compounds such as carbamates,[2a] amines, [2b] ureas [2a] and so on.

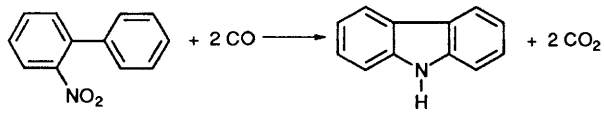
Reductive carbonylation of aromatic nitro compounds bearing suitable substituents in the *ortho* position has been shown to be a promising route for the synthesis of nitrogen heterocyclic derivatives like indoles,[3] benzotriazoles,[4] benzimidazoles [5] and benzoxazines.[6]

The preparation of carbazole by reductive carbonylation of *ortho*-nitrobiphenyl catalysed by $Ru_3(CO)_{12}$ showed the possibility of heterocyclization involving nitrene insertion on a rather stable aromatic C–H bond. It has been proposed that in this reaction the intermediate is $Ru_3(\mu_3\text{-}NC_6H_4\text{-}o\text{-}C_6H_5)_2(CO)_9$ cluster in which the nitrene ligand is triply bridged with the ruthenium atoms. This intermediate species is quite stable and its decomposition at 220 °C affords the reaction products. Unfortunately under catalytic conditions the main product is, in any case, the *ortho*-aminobiphenyl while the best yield of carbazole obtained was 30% in acetonitrile as solvent.[7]

We have now found, and it is the object of this paper, that addition of catalytic amounts of alkali halides strongly affects both the reaction rate and selectivity, by favouring the formation of heterocyclic products. The possible extension of this catalytic system to the synthesis of related aromatic heterocyclic derivatives with more than five membered ring has been also investigated.

Results and Discussion

Reductive carbonylation of *ortho*-nitrobiphenyl **1** catalysed by $Ru_3(CO)_{12}$ is a good model of catalytic heterocyclization reaction occurring through a nitrene insertion on an aromatic C–H bond (Scheme 1). However even under optimum reaction conditions (CH_3CN as solvent, 50 bar* of CO, 220 °C and a substrate/catalyst ratio of 25) carbazole **2** was obtained in less than 30% yield, together with 50% of *ortho*-aminobiphenyl **4**.[7]



1 **2**

Scheme 1

Table 1 Influence of sodium halides (Na^+X^-) on the product distribution of reductive carbonylation of *o*-nitrobiphenyl catalysed by $Ru_3(CO)_{12}$[a]

	Product (%)[b]		
X^-	Carbazole	*o*-Aminobiphenyl	5*H*-Phenanthridin-6-one
c	28	50	—
F	43	11	37
Cl	60	12	28
Br	46	13	40
I	12	15	52

[a] 100% Conversion, for reaction conditions see Experimental. [b] Yields are based on isolated products by column chromatography. [c] Data from ref. 7, reaction time 5 h.

The known chemical inertness of aromatic C–H bond towards nitrene insertion[8] and the stabilization of the intermediate aryl nitrene, which is triply coordinated in the ruthenium cluster, are probably responsible for the poor yield of heterocyclic products. The presence in the reaction of other species capable of coordinating the ruthenium atom with the consequent opening of at least one Ru–N bridge should increase the reactivity of the intermediate. As a consequence, since the reaction occurs on the coordination sphere of the metal, the intramolecular insertion, leading to heterocyclic products, should be also enhanced.

In agreement with this latter assumption, the introduction in the reaction mixture of catalytic amounts of dry sodium halides

* 1 bar = 10^5 Pa.

Table 2 Influence of alkali chlorides (M^+Cl^-) on the products distribution of reductive carbonylation of *o*-nitrobiphenyl catalysed by $Ru_3(CO)_{12}$[a]

	Products (%)[b]		
M^+	Carbazole	*o*-Aminobiphenyl	5*H*-Phenanthridin-6-one
Li	15	14	71
Na	60	12	28
K	48	18	34
Cs	42	28	—[c]
[K⊂Crown][d]	14	54	—[c]
[K⊂2.2.2][e]	0	35	—[c]

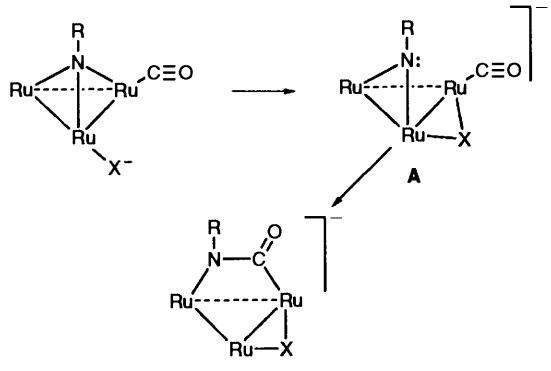
[a] 100% conversion, for reaction conditions see Experimental. [b] Yields are based on isolated products by column chromatography. [c] The difference to 100% are mixtures of unidentified products. [d] Dicyclohexane–18-crown-6 in stoichiometric amounts with respect to KCl; [e] (2.2.2)-Cryptand in stoichiometric amounts with respect to KCl.

strongly affects the rate of reaction and product distribution (Table 1).

In the presence of halides yields of the heterocyclization products [carbazole **2** and 5*H*-phenanthridin-6-one **3**] are 88% for Cl^-, 86% for Br^-, 80% for F^- and 74% for I^- with the preference for carbazole in the order $Cl^- > Br^- \approx F^- \gg I^-$; whereas the selectivity for 5*H*-phenanthridin-6-one is the reverse $I^- > Br^- \approx F^- > Cl^-$

The yield of *o*-aminobiphenyl **4**, probably derived from the protonation of the intermediate nitrene complex, is strongly decreased.

Following the evidence produced by G. L. Geoffroy *et al.*[9] and others[10] we believe that the anions X^- promote the formation of a doubly bridged nitrene, by breaking one bridge of the Ru–N cluster. This latter species can more easily undergo aromatic C–H insertion as such (**A**) or after carbonylation to isocyanate (**B**) thus affording carbazole and 5*H*-phenanthridin-6-one respectively as the major products (Scheme 2).



Scheme 2

The amounts of species **A** and **B** depend on the nature of X^-, the former being favoured by Cl^- whereas the latter is prevalent in the presence of I^-. An interesting aspect, up to now never evidenced, is the role played by the cation in driving the reaction towards **A** or **B**.

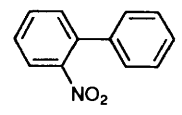
Results are reported in Table 2 for alkali chlorides as co-catalysts.

It turned out that small cations promote heterocyclization reactions; yields being 86, 88 and 82% for Li^+, Na^+ and K^+ respectively, the complement to 100% is the amine side product. By increasing the size of cation the amount of isolated carbazole decreases, being: 42% for Cs^+, 14% for [K⊂dicyclohexano-18-crown-6]$^+$ and 0% for [K⊂2.2.2]$^+$, while the 5*H*-phenanthridin-6-one is not formed at all. It is worth noting that with these cations the amounts of amine increase and mass balance of isolated products becomes very poor due to very low selectivity and the formation of many products whose separation and identification is very difficult. Particularly interesting is the case of Li^+ which afforded 71% of the 5*H*-phenanthridin-6-one, the remainder being carbazole and *o*-aminobiphenyl, 15% and 14% respectively.

With the aim of understanding the role played by the cation, reductive carbonylation of *o*-nitrobiphenyl was carried out under conditions identical to those reported in Table 1, but in the presence of $NaBF_4$ as co-catalyst. In this case the role of the anion is minimized due to low coordinating capability of BF_4^- in comparison with that of halide anions, and thus the influence of Na^+ should be better evidenced. Results showed a complete conversion of the substrate with 80% yield of heterocyclization products: carbazole and 5*H*-phenanthridin-6-one being 48% and 32% respectively. Although it is very difficult to distinguish between the effect of the cation and that of the anion on the catalytic cycle, these data seem to indicate that the role of the cation is predominant. It is known for instance that, in homologation reactions catalysed by transition-metal carbonyls, the insertion of CO on to a metal coordinated substrate is favoured by the presence of alkali cations which polarize the CO group through coordination with the oxygen lone pair.*[11] This effect, which is directly related to the polarizing capability of the cation, is in agreement with the results here reported. In fact the small and highly polarizing Li^+ cation drives the reactive intermediate towards **B** (Scheme 2) thus leading to high yield of the 5*H*-phenanthridin-6-one. The effect of other cations such as Na^+ and K^+ is no less important, as they cause the amount of heterocyclization products to be increased and inhibit formation of the amine. On the other hand, in the presence of crown ethers, or better of cryptands, the cation is sequestered and cannot interact with the CO groups of the ruthenium cluster, thus explaining the very poor yield of heterocyclized products; amine being again the main product (Table 2). In agreement, when the 1,1-biphenyl-2-isocyanate **5** was used as substrate instead of *o*-nitrobiphenyl, under the conditions reported in Table 1, the conversion was complete and 75% of the 5*H*-phenanthridin-6-one was the isolated product, the remainder being a mixture of unidentified products, and carbazole was absent. This same experiment was repeated in the absence of $Ru_3(CO)_{12}$ and again there was complete conversion of the isocyanate with formation of 80% of the 5*H*-phenanthridin-6-one and 19% of *o*-aminobiphenyl.

It is likely that the role of $Ru_3(CO)_{12}$ in the reductive carbonylation of nitro-derivatives is to form the triply bridged ruthenium nitrene, but at least in the case of 5*H*-phenanthridin-

* As suggested by a referee, we cannot exclude the possibility that the cation can also interact with NO_2 oxygen atoms. This latter type of interaction promotes the loss of oxygen and formation of nitroso (RNO) and then nitrene (RN), enhancing the reaction rate. However, this does not explain the increased selectivity towards heterocyclization products.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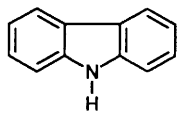
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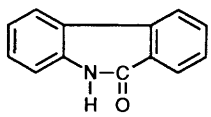
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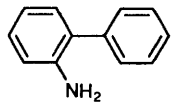
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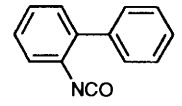
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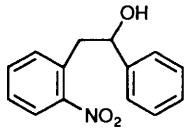
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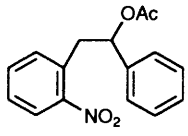
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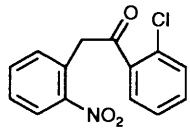
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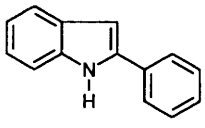
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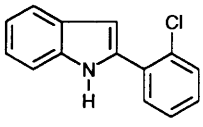
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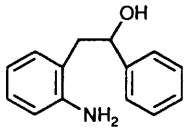
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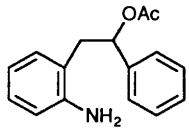
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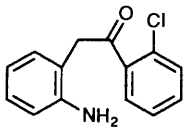
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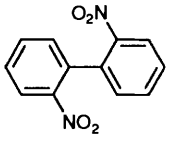
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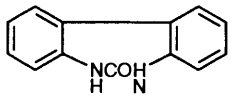
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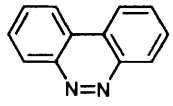
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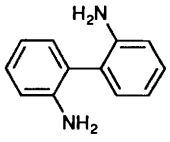
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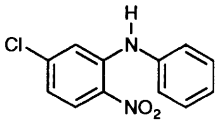
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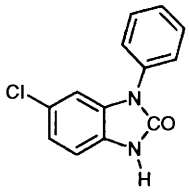
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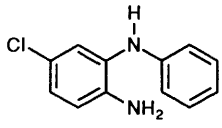
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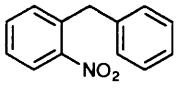
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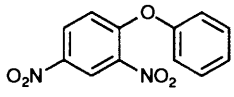
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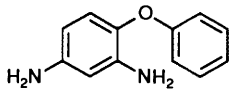
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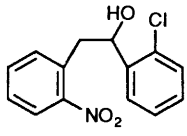
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Table 3 Reductive carbonylation of *o*-nitroaromatic derivatives catalysed by $Ru_3(CO)_{12}$[a]

		With NaCl		Without NaCl	
Entries	Substrate	Conv. (%)	Products (%)[d]	Conv. (%)	Products (%)[b]
1	**6**	100	Indole **9** 90	100	Indole **9** 54 Amine **11** 40
2	7	100	Indole **9** 40 Amine **12** 45	20	Indole **9** 40 Amine **12** 60
3	**8**	100	Indole **10** 94	100	Indole **10** 85 Amine **13** 5[c]
4	**14**	100	Urea **15** 67	100	Azo **16** 25 Urea **15** 50
5	**18**	100	Urea **19** 90 Amine **20** 10	100	Amine **20** 60
6	**21**	90	*d*	< 10	*d*
7	**22**	100	Diamine **23** 55	—	—

[a] For reaction conditions see experimental. [b] Calculated on converted product. [c] Identified by GC–MS of the reaction mixture. [d] Mixture of products difficult to identify.

6-one and ureas, the following reactions do not depend very much upon the catalyst (see later).

In order to extend the applications of this reaction, we used a variety of *o*-nitroderivatives as substrates, which should afford heterocyclic compounds with larger rings. The results are reported in Table 3.

We can observe that, with all substrates, the conversion was quantitative, whereas in the absence of NaCl, longer reaction times (5 h) were required and in some cases incomplete conversion was observed even after this time. With substrates **6**–**8** (runs 1–3) the only products were the 2-phenylindoles **9** and **10**, in greater than 80% yield, the remaining product being the amines **11** and **12**. These reactions do not occur *via* elimination of H_2O or CH_3CO_2H with formation of an alkene bridge which undergoes cyclization through the known nitrene attack,[3] they more likely occur through a direct attack of nitrene on the CHOH, CHOAc and CO groups with subsequent elimination. In fact, when benzyl phenyl ketone was used as substrate, under the same conditions, the starting material was recovered quantitatively thus confirming that the nitrene is necessary to promote the reaction.

When 2,2-dinitrobiphenyl **14** (run 4) was used as substrate, in the presence of NaCl, 70% of the corresponding cyclic urea **15** was isolated. Without NaCl, 50% of **15** and 25% of the diazo-derivative **16** were obtained, in agreement with results reported by Liu *et al.*[12] It appears that in this latter case the coupling of two nitrene intermediates directly or *via* CO insertion, occurs more easily than the usually easy reduction to diamine **17**. This is rather unexpected on the basis of previous results, although it is known that ruthenium complexes carrying two nitrene moieties can be formed under our reaction condition.[13,14] However when the two nitrenes are not in the same molecule, the coupling to azo or urea does not occur.

The polarizing effect of Na^+ on a CO ligand is better evidenced with **18** as substrate (run 5). In fact, in this case, the corresponding cyclic urea **19** was obtained in 90% yield; while without NaCl only traces of **19** were observed, the amine **20** being the main product (60% yield). When the substrate bears no reactive substituents, as in the case of *o*-nitrodiphenylmethane **21** (run 6), the selectivity of the reaction decreases giving a mixture of products difficult to identify. With 2,4-dinitrophenyl phenyl ether **22**, where nitrene insertion on an aromatic C–H bond is the only possible intramolecular reaction, diamine **23** was the isolated product and no traces of heterocyclic products were observed (run 7).

In conclusion we would like to stress the following points. (i) A clear separation of the co-catalytic effects of anion and cation does not seem possible. However, the anion appears to influence the opening of at least one bridge of the ruthenium nitrene cluster, while the cation polarizes a CO ligand, thus promoting its insertion through an isocyanate intermediate. The outcome of the reaction depends on the balance between the co-ordinating capability of anion and the polarizing power of the cation. (ii) The amine side product is strongly minimized in the presence of alkali halides. We can speculate that the formation of the amine under these conditions is kinetically disfavoured with respect to that of heterocyclized compounds. (iii) It is well known that the insertion of aryl nitrene, even when it is generated by classical procedures (photodecomposition of aryl azides, reduction of aromatic nitrocompounds by triethylphosphite, and so on), on a C–H aromatic bond is very difficult, especially when rings with more than five members have to be formed.[8] However, there are examples of formation of six and seven membered ring heterocycles by this reaction.[15] In our case we could observe mainly the easy formation of indoles through nitrene insertion on an aliphatic C–H bond by insertion–elimination concerted mechanism. With the exception of *o*-nitrobiphenyl, which afforded nitrene C–H insertion allowing carbazole, in some cases with good yields, we observed only the insertion of –NCO group allowing the formation of the phenanthridinones or cyclic ureas. We can then speculate that direct comparison between the reactivity of metal coordinated nitrenes with that of nitrenes generated by classical route is not straightforward, the reactivity of the former being also strongly influenced by other factors, probably geometrical, induced by coordination to the metal centre, as is the case of 2,2-dinitrobiphenyl in which azoderivative and cyclic urea are the main products.

Experimental

General Methods.—Dry solvents and alkali halides were used and stored under nitrogen atmosphere; the water content was checked by Karl–Fischer titration before use. $Ru_3(CO)_{12}$ was prepared by literature method[16] and purified from some ruthenium metal by dissolving in hot toluene and filtering the resulting solution through Celite 577. Of the compounds used as substrate **1**, **14**, **18** and **22** are commercially available, **6** and **24** were kindly prepared by Dr Piccoli of Recordati S.p.A. Company, while the preparation of **5**, **7**, **8** and **21** are reported in the present paper.

Reaction products **2**, **3**, **4**, **9** and **16** were identified by comparison with commercially available pure samples; **10**,[17] **15**,[12] **17**,[18] **19**,[19] **20**[19] and **23**[20] showed physical, chemical and spectroscopic properties in agreement with those reported in the literature. Previously known compound **11**[21] and the unknown **12** were synthesized by Dr. A. Manfredi of *Dipartmento di Chimica Organica e Industriale dell'Università di Milano* (Italy) by reduction with $SnCl_2$ of the corresponding nitro-derivatives following a procedure reported in the literature.[22] All the attempts to prepare compound **13** by reduction of the corresponding nitro-derivative **8** failed, giving the indole **10** as the only isolated product.

2-(2-*Aminophenyl*)-1-*phenylethanol* **11**. White solid, m.p. 96 °C (hexane) (Found: C, 78.75; H, 7.05; N, 6.5. $C_{14}H_{15}NO$ requires C, 78.83; H, 7.10; N, 6.56%); $\delta_H(CDCl_3)$ 2.85–3.05 (m, 2 H), 3.60 (br, s, 3 H, D_2O exchange), 4.95–5.00 (m, 1 H), 6.70–6.80 (m, 2 H), 7.00–7.10 (m, 2 H) and 7.20–7.40 (m, 5 H); *m/z* (EI) 213 (M^+, 20%), 107 (100), requires M^+, 213.

2-(2-*Aminophenyl*)-1-*phenylethyl acetate* **12**. Light brown, solid m.p. 75 °C (hexane) (Found: C, 75.1; H, 6.5; N, 5.4. $C_{16}H_{17}NO_2$ requires C, 75.26; H, 6.72; N, 5.48%); $\delta_H(CDCl_3)$ 2.10 (s, 3 H), 2.85–2.95 (m, 1 H), 3.20–3.30 (m, 1 H), 3.70 (br s, 2 H, D_2O exchange), 5.80–5.90 (m, 1 H), 6.55–6.70 (m, 3 H), 6.95–7.05 (m, 1 H) and 7.20–7.40 (m, 5 H); *m/z* (EI) 255 (M^+, 30%), 195 (45), 106 (100), requires M^+, 255.

General Procedure.—The reactions under high pressure were conducted in a glass liner inside a stainless steel hastelloy autoclave. The autoclave was charged with a solution of substrate (1 mmol) in acetonitrile (20 cm^3), $Ru_3(CO)_{12}$ (0.04 mmol; 25 mg) and alkali salt (0.24 mmol). The air in the autoclave was replaced with dinitrogen by three freeze–pump–thaw cycles, before the introduction of carbon monoxide (50 bar). The autoclave was heated at 220 °C by a thermoregulated oven, and the reaction mixture was magnetically stirred. The reaction was stopped after 2 h, unless otherwise specified. At the end of the reaction the autoclave was cooled by an ice bath, and then it was blown off. The solvent was evaporated under reduced pressure, and products were isolated by column chromatography (SiO_2, eluted with CH_2Cl_2, CH_2Cl_2–CH_3OH, 95 : 5). Compounds were analysed by GC–MS, using a Hewlett–Packard 5890 gas-chromatograph coupled with a 5971A Mass Selective Detector. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC300 spectrometer.

Biphenyl 2-Isocyanate **5**.—A solution of 1.48 g of bis(trichloromethyl) carbonate (triphosgene; 5 mmol) in dichloroethane [$(CH_2Cl)_2$; 20 cm^3] was slowly added into a stirred solution of *o*-aminobiphenyl (15 mmol; 2.55 g) in dichloroethane (50 cm^3) at room temp. The reaction is slightly exothermic and the temperature rose to 30 °C. The reaction

mixture was then stirred at room temp. for a further 2 h, filtered, and the solvent evaporated affording a deep brown oil (2.4 g). Column chromatography (SiO_2, CH_2Cl_2–light petroleum, 70:30) afforded a slightly yellow oil (1.5 g, 51%) (Found C, 79.8; H, 4.5; N, 7.1. $C_{13}H_9NO$ requires C, 79.98; H, 4.66; N, 7.17%); $\delta_H(CDCl_3)$ 7.00–7.50 (m, 4 H) and 7.50 (s, 5 H); ν_{max}(neat)/cm^{-1} 2260vs (N–C=O); GC–MS (Calc. for $C_{13}H_9NO$) single peak, *m/z* 195.

2-(2-*Nitrophenyl*)-1-*phenylethyl Acetate* **7**.—A solution of acetyl chloride (2.22 g; 28 mmol) in anhydrous CH_2Cl_2 (10 cm^3) was added slowly to a magnetically stirred solution of 2-(2-nitrophenyl)-1-phenylethanol **6** (4.86 g; 20 mmol) in anhydrous CH_2Cl_2 (50 cm^3) and triethylamine (3.03 g; 30 mmol) cooled at 0 °C with an ice bath. During the addition the temperature was maintained at 0–5 °C. After the addition was complete, the reaction mixture was stirred at 0 °C for further 2.5 h and then stored in the refrigerator for 20 h. The reaction mixture was transfered into a separatory funnel, diluted with CH_2Cl_2 (100 cm^3) and washed with H_2O and brine (100 cm^3 each). The organic phase was dried ($MgSO_4$) and the solvent evaporated to afford a slightly yellow thick oil (6.5 g). Column chromatography (SiO_2, Et_2O–light petroleum, 8:2) afforded a colourless thick oil (4.56 g; 80%) (Found: C, 67.4; H, 5.0; N, 4.9. $C_{16}H_{15}NO_4$ requires C, 67.37; H, 5.26; N, 4.91%); $\delta_H(CDCl_3)$ 1.95 (s, 3 H), 3.30–3.60 (m, 2 H), 5.90–6.20 (m, 1 H), 7.00–7.60 (m, 8 H) and 7.80–8.00 (m, 1 H); ν_{max}(neat)/cm^{-1} 1749 (CO), 1523 (NO_2 asym) and 1370 (NO_2 sym); *m/z* (EI) 226 (M^+ – CH_3COO, 20%), 149 (70), 107 (100), requires M^+, 285.

2-*Chlorophenyl* α-(2-*Nitrobenzyl*) *Ketone* **8**.—A 250 cm^3 three-necked round bottomed flask fitted with condenser, pressure equalizing dropping funnel and thermometer was charged with 1-(2-chlorophenyl)-2-(2-nitrophenyl)ethanol **24** (12.16 g; 44 mmol), CH_2Cl_2 (80 cm^3), KBr (0.6 g; 5 mmol) dissolved in H_2O (2.5 cm^3), and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (0.156 g; 1 mmol). The mixture was magnetically stirred and cooled to 0 °C with an ice bath, then aqueous sodium hypochlorite (NaOCl) (0.3 mol dm^{-3}; 180 cm^3; 54 mmol) at pH 8.6 was added over 1 h. The pH (12.7) of the aqueous NaOCl was adjusted to 8.6 by addition of sodium hydrogen carbonate (4.5 g per 100 cm^3 of solution) immediately before use. After the addition was complete, the reaction mixture was stirred at 0 °C for further 30 min. The organic phase was separated and washed initially with 10% aqueous HCl (50 cm^3) containing KI (2 g), then 10% aqueous sodium thiosulphate (80 cm^3), dried ($MgSO_4$) and the solvent evaporated under reduced pressure, affording a yellow thick oil (12.2 g). Column chromatography (SiO_2, CH_2Cl_2) afforded a white solid (11.0 g, 91%), m.p. 59–60 °C (hexane) (Found: C, 61.1; H, 3.6; N, 5.1. $C_{14}H_{10}ClNO_3$ requires C, 60.98; H, 3.66; N, 5.07%); $\delta_H(CDCl_3)$ 4.66 (s, 2 H), 7.20–7.80 (m, 7 H) and 8.00–8.25 (m, 1 H); ν_{max}(Nujol)/cm^{-1} 1696 (CO), 1516 (NO_2 asym) and 1344 (NO_2 sym); *m/z* (EI) 277 (M^+ + 2, 30%), 275 (10), 242 (25), 229 (30), 214 (100), requires M^+, 275.

2-*Nitrodiphenylmethane* **21**.[23]—A solution of 2-nitrobenzyl bromide (2.16 g; 10 mmol) in anhydrous benzene (50 cm^3) was stirred at room temp. with crushed $AlCl_3$ (4.0 g; 30 mmol). The reaction mixture showed a deep red colour. After 15 h, H_2O (10 cm^3) and Et_2O (100 cm^3) were added. The organic phase was separated, washed with H_2O (100 cm^3), dried ($MgSO_4$) and the solvent evaporated under reduced pressure to afford a red brown oil (2.53 g). Purification by column chromatography (SiO_2, Et_2O–light petroleum = 9:1) afforded a colourless oil (1.70 g; 80%) $\delta_H(CDCl_3)$ 4.32 (s, 2 H), 6.90–7.70 (m, 8 H) and 7.80–8.00 (m, 1 H); ν_{max}(neat)/cm^{-1} 1523 (NO_2 asym) and 1350 (NO_2 sym); *m/z* (EI) 213 (M^+, 10%), 212 (20), 196 (100), 165 (75), requires M^+, 213.

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