N,O-Heterocycles. Part 18.[1] Regiochemistry and Site Selectivity of *N*-Alkylhydroxylamine Addition to 2,3-Diphenylcyclopropenone

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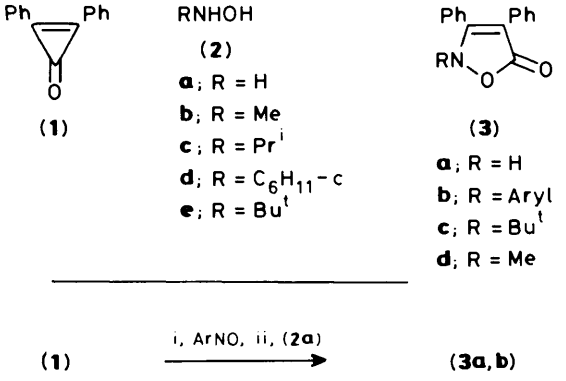
This paper evaluates the reactivity of 2,3-diphenylcyclopropenone [CPO, (**1**)] towards *N*-alkylhydroxylamines and 2,2-dimethylnitrosoethane (**4**). CPO preferentially affords 2-methyl-4,5-diphenylisoxazol-3(2*H*)-one when it is treated with *N*-methylhydroxylamine, while treatment with higher homologues gives rise to acyclic products. 3,4-Diphenyl-2-t-butylisoxazol-5(2*H*)-one is formed when substrate (**1**) reacts with (**4**). The formation of the products is strongly affected by the oxidizing power of the α-nucleophiles which drive the population of the observed reaction channels from the 1,2 or 1,4 adducts initially formed. A general mechanism is proposed whereby isoxazolones are formed from CPO and both nitroso compounds and hydroxylamine.

Diphenylcyclopropenone (CPO), (**1**) reacts with hydroxylamine (**2a**)[2] and nitrosoarenes[3,4] to give 3,4-diphenylisoxazole-5-(2*H*)-ones (**3a,b**). For the isomers of type (**3b**), the five-membered ring thus obtained undergoes skeletal rearrangement *via* either a neutral[5] or an ionized precursor[4] to give aziridine systems (Scheme 1).



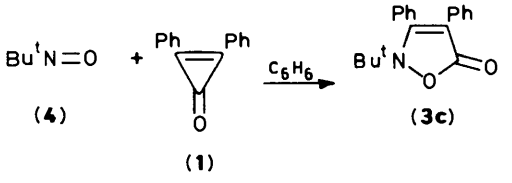
Scheme 1.

The use of CPO as a substrate in the large-scale preparation of compounds (**3b**) is a valuable and clean one-pot procedure. In order to extend the scheme to obtain *N*-alkyl isomers, nitrosoalkanes would have to be used. Unfortunately these compounds are extremely unstable under the experimental conditions adopted and, consequently, it is likely that this procedure could only be used to prepare *N*-t-alkyl substituted isoxazol-5(2*H*)-ones. It is, in fact, well established that nitrosoalkanes bearing α-protons readily undergo isomerization to the more stable oxime tautomers.[6] However, the results obtained by using hydroxylamine[2] would seem to suggest that, by choosing suitable *N,O*-α-nucleophiles at different oxidation states (*e.g.* nitroso and hydroxylamino compounds), CPO may prove to be a useful substrate in obtaining the five-membered systems (**3**).

Results

CPO reacted in benzene with 2,2-dimethylnitrosoethane (**4**) under the same experimental conditions reported for nitrosoarenes[3,4] to give 3,4-diphenyl-2-t-butylisoxazol-5(2*H*)-one (**3c**) in good yield (Scheme 2). The structure has been assigned on the basis of i.r., ^{1}H n.m.r. and m.s. data.

The m.s. spectrum in particular was typical for that of ionized



Scheme 2.

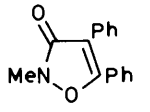
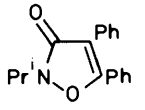
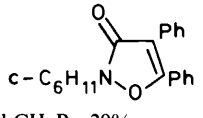
species of type (**3**) which undergo little degradation of the heterocyclic nucleus.[4] The nitroso compound (**4**) used in the synthesis of (**3c**) was stable under the experimental conditions adopted for the reaction. The stable tautomer of 2-methyl-nitrosoethane, *i.e.* acetone oxime, Me_2CNOH, (**5**), afforded neither isoxazolones nor appreciable amounts of any other compounds when it was allowed to react with CPO in the same way.[4]

The investigation of the formation of isoxazolones *via* CPO by the hydroxylamino approach focuses on the reactivity of *N*-alkyl monosubstituted species. *N*-Methylhydroxylamine (**2b**) was allowed to react with (**1**) under the same conditions reported for the parent hydroxylamine, *i.e.* aqueous/alcoholic buffered solution, with (**2b**) and (**1**) in the ratio 2:1. Two reaction products were obtained, a pale yellow solid (**6b**), and deoxybenzoin (**7**) which was isolated by t.l.c. from the crude mixture and characterized from its spectral data and R_F value. Although compound (**6b**) showed a melting point very close to that reported for 2-methyl-3,4-diphenylisoxazol-5(2*H*)-one (**3d**), all the physical parameters differ significantly from those obtained from an authentic sample of (**3d**) synthesized according to a known procedure.[7] The strong i.r. absorption of (**6b**) at 1 660 cm^{-1} showed that an amide-type functionality was present in the molecule, while the entire spectrum of (**6b**) was clearly distinct from that of (**3d**). Additional evidence was obtained from tandem mass spectrometry experiments[4,8] by matching the m.i. spectra of both (**6b**) and (**3d**), which can be used to finger-print the molecules under investigation.[8] Compound (**6b**) does, in fact, undergo competitive carbon monoxide elimination which gives rise to daughter ions at *m/z* 223, while the ionized isomer (**3d**) exhibited the expected CO_2 loss leading to fragments at *m/z* 207. Spectrometric data are, therefore, consistent with the hypothesis that the heterocyclic molecule (**6b**) obtained from CPO and *N*-methylhydroxylamine is 2-methyl-4,5-diphenylisoxazol-3(2*H*)-one (Scheme 3). No appreciable amounts of the isomeric 5(2*H*)-nucleus (**3d**) have been detected by t.l.c. and MS/MS on the final reaction mixture.

Table.

CPO + RNHOH ⟶ (6), (7), (8), (9)
(1) (2)

Scheme 3.

Compd.	Reaction time (h)	Products*
(**2b**; R = Me)	2	(**6b**),  75% (**7**), $PhCH_2Bz$, < 10%
(**2c**; R = Pr^i)	6	(**6c**),  < 5% (**7**), $PhCH_2Bz$, 13% (**8c**), Bz(Ph)CHCONPr^i, 41.3% (**9c**), $PhCH_2$(Ph)CHC(O)ONHPr^i, 27.5%
(**2d**; R = C_6H_{11}-c)	5	(**6d**),  < 5% (**7**), $PhCH_2Bz$, 20% (**8d**), Bz(Ph)CHCONH(C_6H_{11}-c), 65% (**9d**) $PhCH_2$(Ph)CHC(O)ONH-(C_6H_{11}-c)
(**2e**; R = Bu^t)	72	(**7**), $PhCH_2Bz$, 30% (**8e**), Bz(Ph)CHCONHBu^t, 70%

* The figures correspond to isolated yields

The formation of all these products requires an oxidation step which was considered abnormal[9] when (**3a**) was obtained.[2] Whereas the oxidation of CPO with hydrogen peroxide afforded a good yield of deoxybenzoin,[10] the dihydroisoxazolones (**3a**) and (**6b**) formally derive from a 1:1 adduct which has lost a hydrogen molecule. In order to eliminate the possible effect of atmospheric oxygen in driving the processes observed, CPO and (**2b**) were allowed to react in benzene in a closed system by following the general procedure for handling and transferring air-sensitive compounds. Soon after the reagents were mixed an exothermic reaction started which caused the separation of water from the reddish solution thus obtained.

When a 1:1 ratio of (**1**) and (**2b**) was used, the reaction was not completed even when the reaction time was prolonged: it could be seen from t.l.c. and i.r. on the crude reaction mixture that appreciable amounts of starting CPO were present. On the other hand, when the same reaction was carried out in the presence of a 2:1 molar ratio of (**2b**) with respect to (**1**), the experiment was completed after 2 h at room temperature. The dihydroisoxazolone (**6b**) thus obtained was isolated in 75% yield while deoxybenzoin (**7**), characterized as previously described, was formed in less than 10% yield as estimated by ^1H n.m.r. on the crude mixture.

The same products were obtained in almost the same yield by running the experiment in the presence of atmospheric oxygen. It is, therefore, clear that the population of the reaction pathways observed is strongly affected by the relative ratios of the α-nucleophile and substrate (Scheme 3).

When α-nucleophiles (**2c—e**) were allowed to react with CPO under similar experimental conditions structurally distinct acyclic molecules were obtained. Two molecular equivalents of (**2c**) reacted with (**1**) to give a complex mixture which by t.l.c. was shown to contain deoxybenzoin (**7**), Bz(Ph)CHCONPr^i (**8c**), and $PhCH_2$(Ph)CHC(O)ONHPr^i (**9c**) the isolated yields being 13, 41.3, and 27.5% respectively. Straightforward information on the structures of the last two compounds has been obtained by mass spectrometry. The spectra of the stable ions of (**8c**), in fact, displayed abundant species due to the elimination of isopropylamine and isopropyl isocyanate and an intense fragment corresponding to the benzoyl cation. The latter was completely suppressed in the m.i. spectra where the elimination of the amine moiety was the preferred reaction pathway.

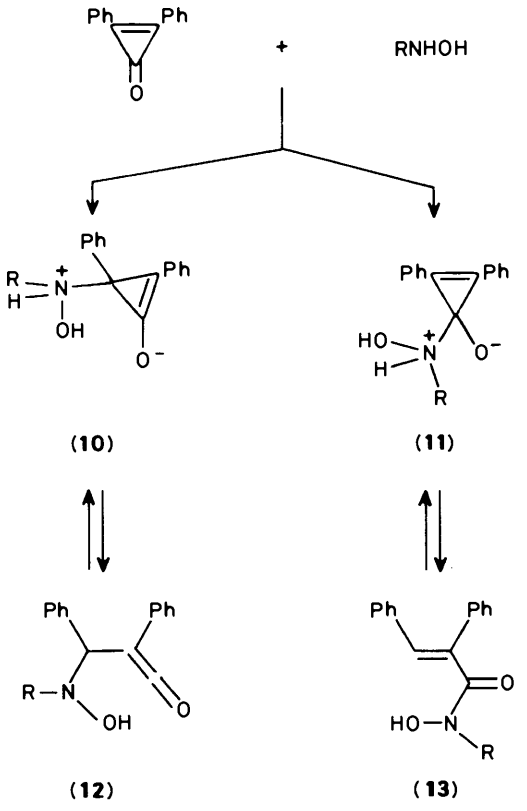
The benzoyl cation structure was also assigned to *m/z* 105 which was the base peak of the spectrum of the stable ions produced by the hydroxylamine (**9c**) after electron ionization, while other major transitions were the elimination of the hydroxylamine moiety, to give *m/z* 223, and the formation of *m/z* 118 which may have a phenylketene structure. The peak at *m/z* 223 in more than 92% relative yield arose from the preferred elimination of *N*-isopropylhydroxylamine.

N-Cyclohexylhydroxylamine (**2d**) and CPO afforded two main products corresponding to deoxybenzoin (**7**) and (**8d**) (Scheme 3). Traces of (**9d**) were also formed in the course of the reaction as suggested by a very weak peak in the m.s. subspectrum of the crude mixture at *m/z* 337. Although the results obtained from low eV spectra suggest that this peak corresponds to the molecular ion of the expected compound, all attempts to isolate and characterize it proved unsuccessful. The t-butyl isomer (**2e**) reacted with (**1**) to give a mixture of (**7**) and (**8e**) only (Scheme 3); the latter crystallized directly from the crude mixture. The hydroxylamines (**2c—d**) afforded compounds whose chemical purity prevented accurate physicochemical analyses also in low yields (3—5%). Their MS/MS spectra and i.r. carbonyl stretching frequencies suggested the isoxazolone (**6c—d**) structure (Scheme 3). The aforementioned data concerning the reactivity of *N*-alkylhydroxylamines towards diphenylcyclopropenone indicate that the substituent present at the nitrogen atom plays a key role. No reaction products were obtained when freshly prepared phenylhydroxylamine was allowed to react in benzene with (**1**). Starting materials were detected by t.l.c. when the reaction was carried out at room temperature whereas only decomposition products originating from the α-nucleophile were present when the same experiment was repeated at 80 °C.

Discussion

CPO may act as an ambident electrophile with a harder carbonyl carbon site and a softer β-position than other unsaturated ketones as has been verified with hard and soft nucleophiles. The former gave rise to 1,2-additions,[2,11] while the latter provided initial adducts at C-2 (C-3). These often collapse into products *via* an open ketene structure, which in some cases was trapped[12] or isolated.[13] *N*-Nucleophiles exhibit a rather complex reactivity[11,14,15] which becomes more puzzling in the case of hydroxylamine due to the occurrence of an oxidation step as yet undefined[9].

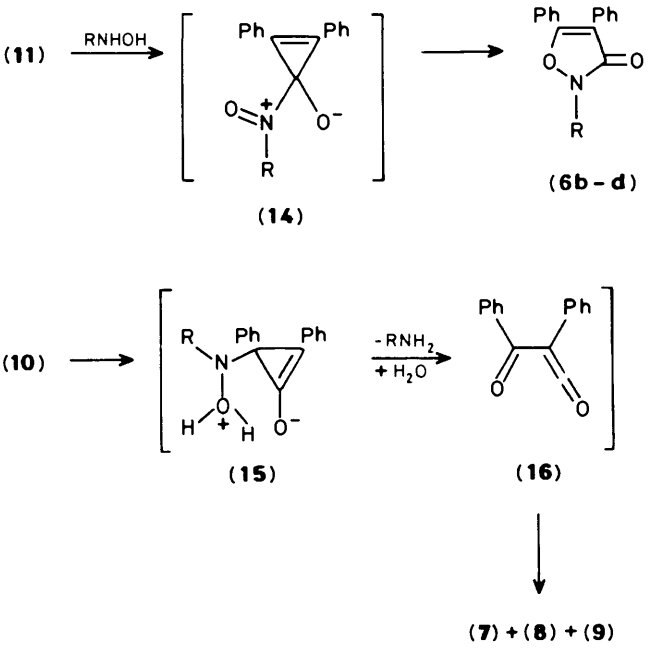
An initial Michael-type adduct (**10**) and a 1,2 carbonyl addition intermediate (**11**) (Scheme 4) could be responsible for the formation of (**3a**) and (**6b**) respectively. This interpretation is in agreement with the HSAB principle,[16] since the hardest nucleophile, *i.e.* methylhydroxylamine, preferentially approaches the carbonyl moiety of cyclopropenone, the hardest electrophilic site in the molecule. These adducts, once formed, could have populated the ring-opening pathways typical of cyclopropenone chemistry[9,17] to give the intermediates (**12**) and (**13**) (Scheme 4). However, hydroxamic acids of type (**13**) afford substituted isoxazolidinones under similar conditions.[18]



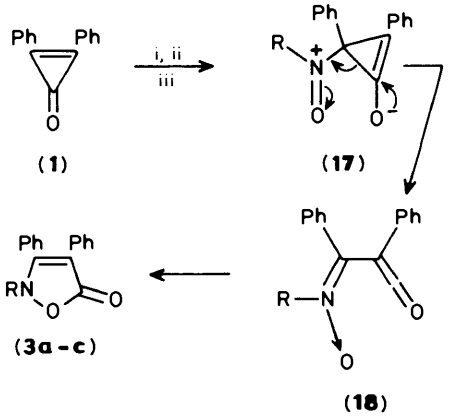
Scheme 4.

The experimental results discussed above clearly show that a 2:1 ratio of (**2b**) to (**1**) is necessary to drive the reaction to its completion. Disproportionation[19,20] of either (**2b—d**) before addition to CPO, or of intermediate (**11**) (Scheme 4) prior to cyclization can be ruled out since no isoxazolones of type (**3**) (Scheme 2) or acyclic amides[17] were obtained from the reaction mixture. The mechanism whereby the isoxazolones (**6b—d**) are formed requires therefore that (**11**) (Scheme 5), is first oxidized[21] to (**14**) by means of the excess of nucleophile used and then rearranged to (**6**) *via* a cyclization process similar to that undergone by nitrosocarbonyl alkenes.[22] The redox process is strongly affected by the oxidizing power of the α-nucleophile employed. In fact, the conversion of CPO into (**6a**) occurred in yields of less than 40% on treatment with an equimolar mixture of *N*-methyl-(**2b**) and *N*-t-butyl-(**2e**) hydroxylamines at room temperature.

The Michael adduct (**10**), which represents the thermodynamic product[23] in the nucleophilic addition to CPO, can also populate a competing reaction path which leads to the benzoylphenylketene intermediate (**16**) *via* the oxidative ring opening of the rearranged intermediate (**15**) (Scheme 5). A similar mechanism is in operation in the oxidation of CPO with hydrogen peroxide.[10] Under the experimental conditions used, ketene (**16**) can undergo hydrolysis and decarboxylation to deoxybenzoin (**7**), or can react both with the amine produced in the redox step and with the excess of hydroxylamine to give compounds (**8**) and (**9**) respectively (Scheme 5). The data obtained from the reaction between hydroxylamines and CPO enable an alternative mechanism to be suggested whereby the heterocyclic system (**3**) is formed from 2-methyl-2-nitrosopropane and nitrosoarenes.[3-5] A common intermediate (**17**) is populated by a 1,4 addition of either nitroso compounds or hydroxylamine which then rearranges into a 3,4-diphenyl-substituted isoxazolinone system probably *via* the nitronic intermediate (**18**) (Scheme 6).



Scheme 5.



Scheme 6. *Reagents:* i, NH_2OH, ii, oxidation; iii, RNO

Conclusions

The regiochemistry of *N*-alkylhydroxylamine addition to CPO is affected either by the basic strength of the nitrogen moiety according to the HSAB principle, or by steric hindrances at the site of the approaching hydroxylamines. The formation of the isoxazolone (**6b**) requires that the initially formed 1,2-adduct be oxidized by the excess hydroxylamine used, while the acyclic products (**7**), (**8**), and (**9**) are obtained by a competitive oxidative ring-opening process undergone by the Michael adducts.

Experimental

I.r. spectra were recorded on a Perkin-Elmer spectrophotometer 1330. ^1H N.m.r. spectra were recorded on either a Varian EM 360 (60 MHz) or XL-100 (100 MHz) spectrometer with tetramethylsilane as the internal standard and deuteriochloroform as solvent. Mass spectra were measured on either Varian Mat CH-5 DF or VG ZAB 2F mass spectrometer. M.p.s were measured on a Kofler hot-stage apparatus and are uncorrected. Oxygen-free experiments were performed in an atmosphere of nitrogen, which was purified by passing it through a column of R3-11 BASF deoxygenating catalyst and then dried over

molecular sieves. The work-up of the reaction mixture was carried out in air.

CPO was prepared as previously reported.[24] Commercially available *N*-cyclohexyl-, *N*-methyl- (HCl salt) and *N*-isopropyl- ($C_2O_4^{2-}$ salt) hydroxylamine were used.

Salt-free bases were obtained by treatment with diethylamine.[18] *N*-t-Butylhydroxylamine and 2,2-dimethylnitrosopropane were synthesized according to literature procedures.[25] Merck silica gel pre-coated plates were used for t.l.c. and Merck Kieselgel 60 H without gypsum was used for short column chromatography. Benzene was dried over sodium and stored on 4A molecular sieves. The yield of the isolated products refers to CPO.

3,4-*Diphenyl*-2-*t*-*butylisoxazol*-5(2H)-*one* (**3c**).—CPO (512 mg, 2 mmol) and 2,2-dimethylnitrosopropane (191 mg, 2 mmol + 10% excess) were heated in benzene (10 ml) at 80 °C in a tube sealed under nitrogen, for 70 h. The nitrosoalkane showed no appreciable decomposition. Evaporation of the solvent afforded a pale yellow solid, which was recrystallized twice from methanol to give 3,4-*diphenyl*-2-*t*-*butylisoxazol*-5(2H)-*one* (**3c**) (352 mg, 60%) as colourless needles, m.p. 164—165 °C (Found: C, 77.85; H, 6.55; N, 4.70. $C_{19}H_{29}NO_2$ requires C, 77.79; H, 6.53; N, 4.77%); $\nu_{max.}$ (1% KBr disc), 1 725 (C=O), 1 605, 1 580, 1 450, 1 400, 1 370, 1 230, 1 205, 1 190, 980, 785, and 705 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.25 (9 H, s, 2-Bu^t), 7.2—7.6 (10 H, m, ArH); *m*/*z* 293 (M^+, 13%) 237 (100), 178 (12), 165 (15.5), 104 (17.5), and 57 (51).

2-*Methyl*-4,5-*diphenylisoxazol*-3(2H)-*one* (**6b**).—*Method A*. A solution of CPO (2.06 g, 10 mmol) in benzene (15 ml) and a suspension of freshly prepared *N*-methylhydroxylamine (0.94 g, 20 mmol) in benzene (5 ml) were flushed separately for 15 min with dry oxygen-free nitrogen. The CPO solution was then transferred, under nitrogen, *via* a double-tipped needle, into the reaction flask containing the hydroxylamine. The initial exothermic reaction reached completion after 2 h at room temperature as monitored by t.l.c.; water then separated from the reddish benzene solution. The dried organic layer gave a pale red viscous oil corresponding, by ^1H n.m.r., to a mixture of deoxybenzoin (**7**), (14%) and 2-*methyl*-4,5-*diphenylisoxazol*-3(2H)-*one* (**6b**). Chromatography with diethyl ether–pentane (1:9) as eluant, yielded (**6b**) (1.88 g, 75%), m.p. 108—110 °C (Found: C, 76.55; H, 5.20; N, 5.5. $C_{16}H_{13}NO_2$ requires C, 76.48; H, 5.21; N, 5.57%); $\nu_{max.}$ (1% KBr disc), 1 660 (C=O), 1 410, 1 225, 1 160, 1 050, 1 030, 940, 780, 765, 740, and 690 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 3.65 (3 H, s, 2-Me), 7.0—7.6 (10 H, m, Ar); *m*/*z* 251 (M^+, 60%), 180 (8), 166 (9), 165 (29), 135 (13), 118 (43), 105 (100), 77 (53), and 51 (13).

Method B. The same ratio of (**6b**) and (**7**) was obtained by running the experiment in the presence of atmospheric oxygen.

Method C. To the solution obtained from *N*-methylhydroxylamine hydrochloride (1.77 g, 0.02 mol) in water (15 ml) and 20% aqueous sodium acetate (6 ml), was added 50 ml of ethanolic solution containing CPO (2.06 g, 0.01 mol). After 2 h of refluxing, the ethanol was evaporated off and the residue partitioned between diethyl ether and water. The same reaction products as in Method A were obtained in similar relative yield.

CPO and N-*Isopropylhydroxylamine*.—*N*-Isopropylhydroxylamine (0.375 g, 5 mmol) and CPO (0.510 g, 2.5 mmol) were allowed to react in benzene (10 ml) at reflux temperature until the disappearance of (**1**) (6 h). Solvent evaporation gave crude product (0.861 g) chromatography of which with diethyl ether–pentane (1:9) as eluant yielded deoxybenzoin (**7**) (63.7 mg, 13%), 2-*benzoyl*-N-*isopropyl*-2-*phenylacetamide* [**8c**) (290 mg, 41.3%), m.p. 182—184 °C and *O*-[*benzoyl*(*phenyl*)*acetyl*]-N-*isopropylhydroxylamine* (**9c**) (204 mg, 27.5%), m.p. 152—154 °C.

(**8c**) (Found: C, 76.8; H, 6.85; N, 4.90. $C_{18}H_{19}NO_2$ requires C, 76.84; H, 6.81; N, 4.98%); $\nu_{max.}$ (1% KBr disc), 3 295 (sharp, enolic OH), 3 100 , 2 995, 1 660 (C=O, amide), 1 570, 1 470, 1 370, 1 330, 1 285, 1 245, 1 220, 1 180, 1 030, 950, 900, 780, 740, and 715 cm^{-1}; δ_H (100 MHz; $CDCl_3$) 1.05 (3 H, d, *J* 7 Hz, Pr^i), 1.35 (3 H, d, *J* 7 Hz, Pr^i), and 3.6—4.2 (1 H, m, Me_2CH); *m*/*z* 281 (M^+, 15%), 222 (17), 196 (42), 118 (16), 105 (100), and 77 (26).

(**9c**) (Found: C, 72.65; H, 6.45; N, 4.65. $C_{18}H_{19}NO_3$ requires C, 72.71; H, 6.44; N, 4.71%); $\nu_{max.}$ (1%, KBr disc), 3 255 (sharp, enolic OH), 2 940, 1 640 (C=O, amide), 1 430, 1 410, 1 350, 1 255, 1 150, 1 080, 1 030, 1 020, 930, 905, 820, 760, 720, 690, 670, and 640 cm^{-1}; δ_H (100 MHz; $CDCl_3$) 1.36 (6 H, d, Pr^i), 4.13 (1 H, s, 2-H), 4.4—4.8 (1 H, m, Me_2CH), and 7.0—7.5 (10 H, m, ArH); *m*/*z* 297 (*M*, 14), 224 (6), 223 (41), 132 (4), 118 (23), 106 (11), 105 (100), 90 (10), and 77 (21).

An impure compound which could correspond to the isoxazolone (**6c**) was isolated by t.l.c. from the crude mixture as a pale yellow oil (20 mg, 3%); $\nu_{max.}$ (neat) 1 665 (C=O) cm^{-1}; *m*/*z* 279 (M^+, 100), 264 (30), 237 (76), 221 (19), 166 (50), 91 (30), and 77 (78).

CPO and N-*Cyclohexylhydroxylamine*.—CPO (0.206 g, 1 mmol) and *N*-cyclohexylhydroxylamine (0.23 g, 2 mmol) dissolved in benzene (5 ml) were heated at 80 °C for 5 h. Evaporation of the solvent gave an oily residue which showed three main spots by t.l.c., corresponding to deoxybenzoin and the two tautomeric forms of 2-*benzoyl*-N-*cyclohexyl*-2-*phenylacetamide* (**8d**). Chromatography with diethyl ether–pentane (1:9) as eluant yielded (**8d**) (208 mg, 65%), m.p. 164—165 °C (Found: C, 78.5; H, 7.30; N, 4.30. $C_{21}H_{23}NO_2$ requires C, 78.47; H, 7.21; N, 4.36%); $\nu_{max.}$ (1% KBr disc), 3 315 (OH), 2 920, 1 690 (benzoyl), 1 635 (amide), 1 530, 1 450, 1 335, 1 230, 1 205, 1 010, and 750 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.9—2.4 (11 H, m, C_6H_{11}), 5.60 (1 H, s, 2-H), and 7.6—8.3 (10 H, m, Ar); *m*/*z* 321 (M^+, 18%), 222 (24), 196 (71), 105 (100), and 77 (29). T.l.c. on the crude mixture was isolated a compound which could correspond to (**6d**) (20 mg, 6%) as thick oil, $\nu_{max.}$ 1 665 (C=O) cm^{-1}; *m*/*z* 319 (M^+, 17%), 237 (100), 222 (16), 165 (9), 104, (31), and 77 (21).

CPO and N-*t*-*Butylhydroxylamine*.—CPO (0.206 g, 1 mmol) and *N*-t-butylhydroxylamine (0.178 g, 2 mmol) in benzene (5 ml) were refluxed for 72 h. Evaporation of the solvent gave a pale yellow solid corresponding, by ^1H n.m.r., to a mixture of deoxybenzoin (30%) and the tautomeric mixture of 2-*benzoyl*-2-*phenyl*-N-*t*-*butylacetamide* (**8e**) (70%). Crystallization from diethyl ether yielded (**8e**) (150 mg, 51%), m.p. 199—200 °C (Found: C, 77.30; H, 7.25; N, 4.60. $C_{19}H_{21}NO_2$ requires C, 77.26; H, 7.17; N, 4.74%); $\nu_{max.}$ (1% KBr disc), 3 300 (OH), 3.080, 2 980, 1 690 (benzoyl), 1 660 (amide), 1 550, 1 390, 1 245, 730, and 705 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.33 (9 H, s, Bu^t), 5.45 (1 H, s, 2-H), 7.6—8.2 (10 H, m, Ar); *m*/*z* 295 (M^+, 8%), 239 (2), 222 (12), 196 (100), 118 (14), 105 (53), and 77 (18).

Acknowledgements

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