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THE REACTIONS OF N-BENZOYLPEROXYCARBAMIC ACID WITH AZINES AND IMINES

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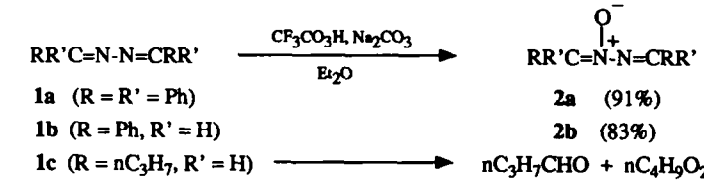
Abstract - N-Benzoylperoxycarbamic acid (BPC) was found to react generally with imines and azines to form oxaziridines rather than N-oxides. The imine products were stable, but those found from azines apparently were unstable and converted to ketones or aldehydes plus diazo compounds.

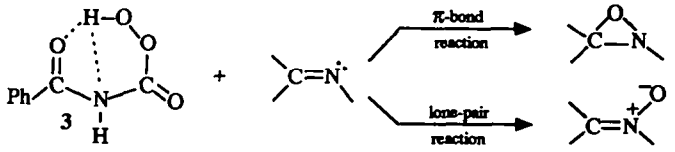
N-Benzoylperoxycarbamic acid (**BPC**) has been reported by Rebek et al. to be an effective epoxidation agent, with an advantage over typical peracids that it yielded as co-products only neutral moieties.[1] This made it a potentially very useful reagent when dealing with acid-sensitive systems.

We have in the past been interested in the thermal reactivity and photochemistry of azine monoxides[2] and thus have been interested in new, potentially useful oxygen transfer reagents for the synthesis thereof. In this regard, we found that buffered trifluoroperacetic acid was useful in the preparation of a number of phenyl-substituted azine monoxides, i.e. **2a** and **2b**, while for the alkyl-substituted analogues, only decomposition products could be obtained.[2] Other workers, before and since, have also attempted peroxyacid oxidations of azines with similar results.[3,4]



Although no intermediate azine monoxide was able to be detected in the latter case, it was considered reasonable that one might have formed and then undergone acid catalyzed decomposition to the products observed. Indeed H_2SO_4-catalyzed decomposition of **2b** resulted in analogous product formation. It was anticipated that use of BPC as the oxidizing agent might lead to a reaction mixture more conducive to the isolation of azinemonoxide products.

BPC, like other hydroperoxy oxygen-transfer agents, is very sensitive to the medium of reaction, being 200 times more reactive in an aprotic solvent such as $CHCl_3$ than it is in hydrogen-bonding solvents such as THF or alcohols.[1] Therefore most of our reactions were carried out in $CHCl_3$, generally reacting the azines with aliquots of crystalline BPC until reaction was complete (no further gas evolution).

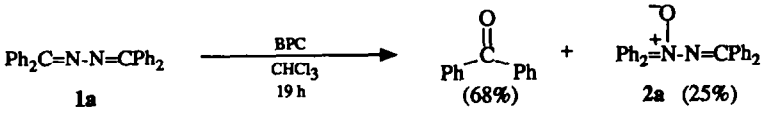


The oxygen-transfer action of peracids such as BPC is thought to be facilitated by intramolecular H-bonding,[1,5,6] such as in the BPC structure **3**. Usually there is competition in the oxidation of C=N double bonds between π-bond reaction to form oxaziridines and nitrogen lone-pair reaction to form N-oxides.

It was found in the present study that azine monoxide formation surprisingly was <u>not</u> the prevalent pathway followed for <u>any</u> of the azines studied, even for **1a** and **1b**. Nevertheless, a careful examination of the products actually formed provided considerable insight into the nature of the BPC reagent and how it compared with other peracids, in its reactions with C=N systems.

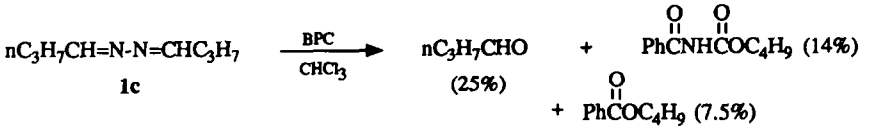
RESULTS AND DISCUSSION

The reaction of benzophenone azine with BPC gave isolated yields of 68% and 25% for benzophenone and benzophenone azine monoxide, respectively, with the reaction proceeding slowly at room temperature and being complete after 19 hours.



Reaction of benzaldehyde azine with BPC was rapid and exothermic, with benzaldehyde and benzaldehyde azine monoxide being formed in 62% and 20% isolated yield respectively.

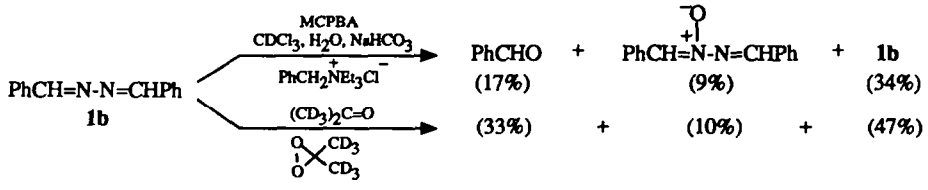
Reaction of butanal azine **1c** with BPC in chloroform gave 25% butanal (NMR yield using internal standard) in addition to 14% butyl N-benzoylcarbamate, and 7.5% butyl benzoate, but no azine monoxide product. It is interesting to note that the unstable carbamic acid produced from



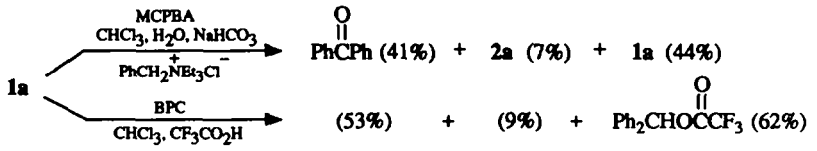
reaction of BPC was apparently stable enough to be trapped by diazobutane before it could decarboxylate.

Under these conditions it seemed unlikely that the ketone and aldehyde major products could have derived from azine monoxide decompositon. Indeed it was found that both **2a** and **2b** were stable to the reaction conditions. To explicitly rule out the possibility that trace amounts of HCl often present in chlorinated solvents like $CHCl_3$ might have catalyzed the conversion of azine monoxide to carbonyl compound, the reaction of benzaldazine with BPC was carried out in benzene wherein the reaction proceeded similarly although with reduced yields: benzaldehyde (40%) and azine oxide (4%).

In related experiments benzaldazine was allowed to react with buffered meta-chloroperbenzoic acid, a more classical oxygen atom donor, and with dimethyl dioxirane, a recently exploited oxygen-atom donor which has no acidic properties,[7] with the result that similar ratios of benzaldehyde and azine oxide were formed in each case.



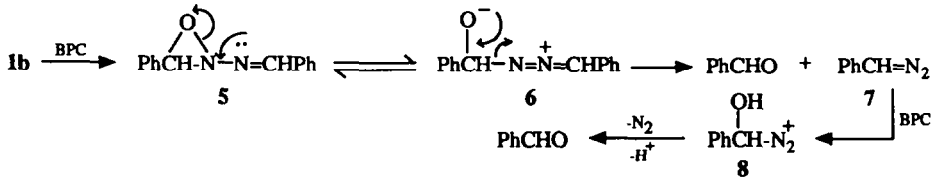
Likewise benzophenone azine was oxidized with various reagents with similar results. It was found moreover in a separate experiment that the product, benzophenone azine oxide, was relatively



stable to acid and converted to benzophenone and benzhydryl trifluoroacetate only slowly when treated with trifluoroacetic acid/CH_2Cl_2 (34% conversion after 15 hours). In conclusion, it does not appear that a mechanism involving conversion of azine oxide to carbonyl product can be involved in these reactions.

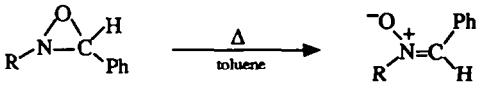
Mechanism of Aldehyde and Ketone Formation - The likely pathway for carbonyl formation in these reactions involves initial formation of an unstable oxaziridine intermediate (5) as shown below in Scheme I for **1b**.

Scheme I

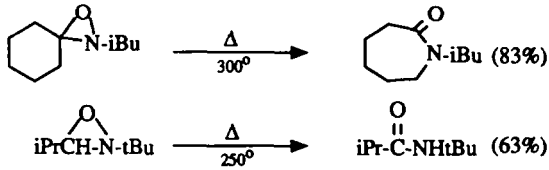


Oxaziridine 5 apparently decomposes largely via N-O bond cleavage to form a dipolar species such as 6 which can convert easily to benzaldehyde and diazospecies 7. Phenyldiazomethane (7), in the presence of excess BPC would be expected to be oxidized to benzaldehyde, probably via hydroxydiazonium species 8.

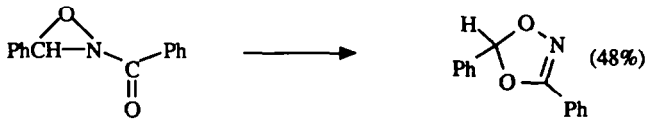
The thermal behavior of oxaziridines has been of interest since the initial report of their synthesis and chemical behavior by Emmons.[8] In his classic study, Emmons reported that 3-phenyloxaziridines rearrange in a general process to nitrones, i.e. via C-O bond cleavage, while



alkyl oxaziridines behaved quite differently, undergoing preferential N-O bond cleavage.[8]

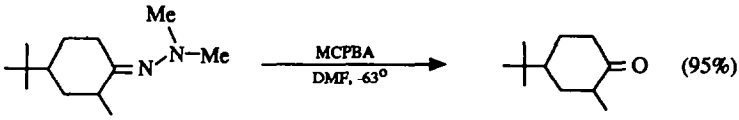


Finally, Schmitz and Schramm found that when electron withdrawing substituents were placed on the oxaziridine nitrogen, C-N cleavage occurred:[9]

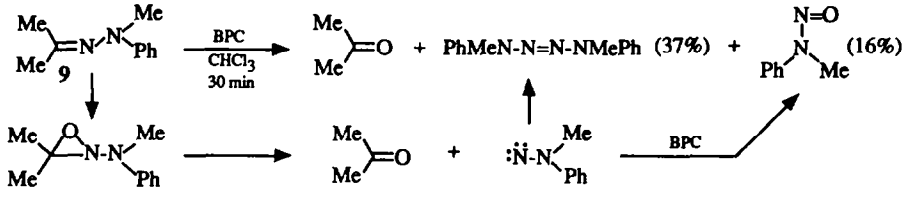


Therefore, there are published examples of thermal rearrangements of oxaziridines wherein any one of the different bonds in the three-membered ring can be seen to be preferentially cleaved. Interestingly there have been no reports of oxaziridines having been synthesized with donor heteroatoms such as O, N or S bound to nitrogen. It might be expected that such species would be reactive with respect to N-O bond cleavage for the reason implied in Scheme I.

Indeed Walborsky discovered that dimethyl hydrazones could be converted to their respective carbonyl species upon treatment with MCPBA.[10] It seems likely that this process would have proceeded via an intermediate oxaziridine. In order to test this and perhaps have the chance of



isolating such an oxaziridine, hydrazone 9 was treated with BPC. While no oxaziridine could be detected, products which might have been expected to have derived from the oxaziridine via a

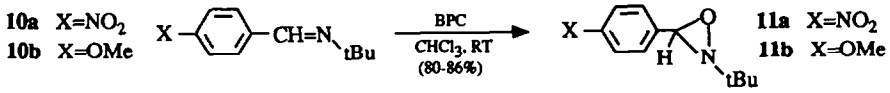


possible nitrene extrusion were clearly observed. There are a number of other examples of peracid or hydrogen peroxide oxidations of hydrazone species which lead to carbonyl formation.[11-13]

In conclusion it seems probable that, as depicted in Scheme I, the carbonyl products which are formed from peracid oxidation of azines derive from precursor oxaziridines such as 5 which undergo N-O bond cleavage leading to subsequent extrusion of a diazoalkane coproduct.

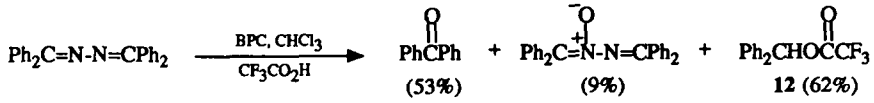
Azine Oxide Formation - None of the results which we have obtained give particular insight as to whether the azine oxide product which is usually formed in competition with the carbonyl product derives from direct formation via reaction with the nitrogen lone pair, or via competitive C-O cleavage of the intermediate oxaziridine.

One result which favors the latter explanation is that treatment of imines **10a** and **b** with BPC leads only to oxaziridine products **11a** and **b**. It was found, using a 10-fold excess of each imine,



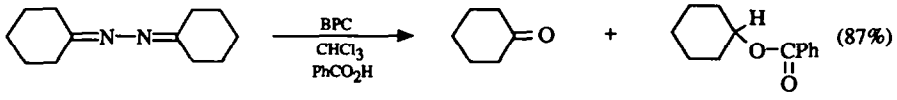
that **10b** reacted at a rate 1.8 times that of **10a**, a result consistent with the rate-determining step being an electrophilic attack on the imine. Whether oxaziridines **11a** and **b**, or for that matter the proposed unstable oxaziridines such as **5**, are formed directly via one-step, epoxidation-type addition[14] or via an addition-elimination (Baeyer-Villiger type) mechanism such as that proposed by Ogata and Sawaki[6] cannot be inferred from the present work.

Fate of the Diazoalkane Coproduct - It would be expected that BPC should convert any diazoalkane to a second equivalent of carbonyl product as shown in Scheme I. There is precedent for the conversion of diazo compounds to carbonyl species upon treatment with peracids.[15] The intermediacy of diazoalkanes in our reactions was moreover demonstrated by carrying out the oxidations in the presence of excess carboxylic acid which is known to react rapidly to trap diazo species. Thus ester **12** is formed in a yield comparable to that of benzophenone when BPC



oxidation of benzophenone azine is carried out in the presence of trifluoroacetic acid.

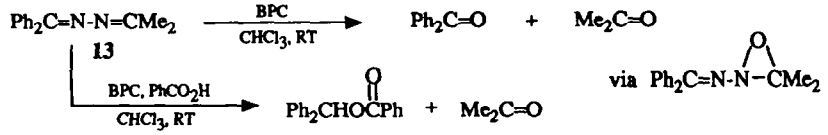
Similarly, cyclohexanone azine was treated, in the presence of excess benzoic acid, with 1.2 equivalents of BPC with the result that cyclohexyl benzoate was formed in 87% yield (%23 of



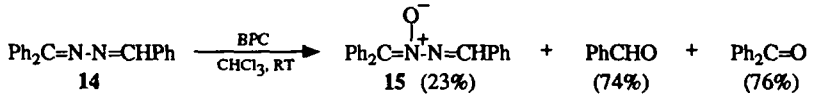
unreacted azine was also recovered).

Reaction of BPC with Unsymmetrical Azines - Interestingly, when the unsymmetrical azine **13** is treated with BPC in the presence of benzoic acid the only carbonyl product is acetone, a result which clearly indicates specific oxidation at the azine nitrogen most proximate to the dimethyl-substituted carbon, with the result that diphenyldiazomethane would be specifically formed and

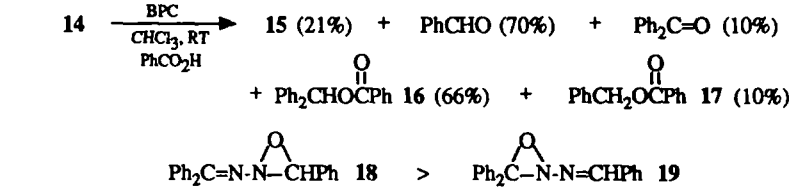
trapped as shown below.



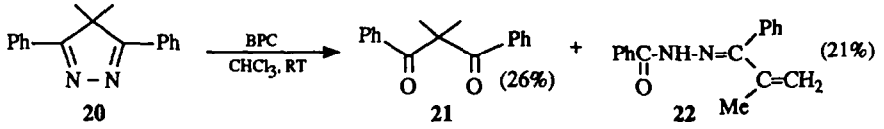
In a more subtle test of the selectivity of azine oxidation, unsymmetrical azine **14** was treated with BPC. Again carbonyl production dominated, but some azine oxide (**15**) was formed.



When the reaction was carried out in the presence of excess benzoic acid, the ratio of carbonyl products and ester products clearly indicated a preferential oxidation of nitrogen closest to the monophenyl-substituted end of the azine, such that oxaziridine **18** was by inference formed preferentially over oxaziridine **19**.

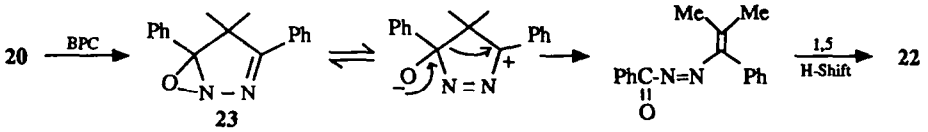


Reaction of BPC with a Cyclic Azine - When cyclic azine **20** was treated with excess BPC, 26% of the expected diketone **21** was formed along with 21% of a new type of cleavage product (**22**).



Formation of **22** can be rationalized as occurring via oxaziridine **23** by a process such as that depicted in Scheme II.

Scheme II



When this reaction was carried out in THF, the yields of **21** and **22** were 60% and 30%, respectively, with some azine oxide (7%) also being observed.

CONCLUSION

The results presented above are all consistent with oxaziridines being involved as the primarily-formed, short-lived intermediates in the oxidation of azines with N-benzoylperoxycarbamic acid. The major products observed in these reactions, presumably resulting from the decomposition of such oxaziridines, were aldehydes or ketones and diazoalkanes. Azine oxides were formed, but never as major products, in contrast to expectations.

While the use of BPC as an oxygen-transfer agent with azines did not provide us with a synthetic entry into new azine monoxide systems, the observed chemistry provided considerable insight into the nature of this reagent vis-a-vis other hydroperoxy and peroxy oxygen-transfer agents. The differences in regioselectivity, i.e. oxaziridine vs. N-oxide formation, between various oxygen-transfer agents is an area worthy of further investigation, both from a mechanistic and a synthetic point of view.

EXPERIMENTAL SECTION

Benzophenone Azine (**1a**) Reaction with BPC - Into a 25-mL round-bottom flask equipped with magnetic stirrer and glass stopper were added 744 mg (2.06 mmol) **1a**,[16] 10 mL $CHCl_3$, and 2.298 g (12.7 mmol) BPC. The yellow mixture was allowed to stir at ambient temperature for 19 h. The reaction mixture was filtered to give a white solid and a yellow filtrate. The solid was washed with two 2-mL portions of $CHCl_3$. The combined filtrates were concentrated to give a yellow solid

which was then subjected to flash chromatography on silica gel, eluting with 20% ethyl acetate/80% hexane.

The first eluted compound (R_f=0.73), a pale amber oil, was benzophenone. The yield was 509 mg (68%). The second eluted compound (R_f=0.46), an amber solid, was identified as benzophenone azine monoxide (**2a**). The yield was 195 mg (25%). Recrystallization from chloroform/hexane gave mp 148-151° (lit.[17] mp 157°): IR (KBr) 3060w, 3030w, 2480w, 1590w, 1565m, 1525m, 1490m, 1440s, 1315m, 1295w, 1240s, 1130m, 1075m, 970m, 960m, 760s, 690vs cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (m, 2H), 7.47-7.36 (m, 6H), 7.33-7.24 (m, 10H), 7.08 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0 (C=N), 135.8 (quat), 134.3 (quat), 133.6 (quat), 133.1 (quat), 131.8 (CH), 130.8 (CH), 130.5 (CH), 129.9 (CH), 129.7 (CH), 129.1 (CH), 128.7 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH); MS (m/e) 376(M^+, 5), 360(13), 283(28), 196(11), 180(50), 165(100), 105(34), 77(69), 51(19).

Benzaldehyde Azine (**1b**)[18] Reaction with BPC, NMR Yield - Into a 10-mL beaker were added 55 mg (0.264 mmol) **1b** and 2 mL $CDCl_3$. To the pale yellow solution were carefully added 259 mg (1.43 mmol) BPC a little bit at a time. The exothermic reaction liberates CO_2. The reaction had a short induction period. After addition was completed, 27.5 mg (0.376 mmol) DMF were added as an internal standard. Integration of the 60 MHz NMR spectrum gave 5.12 for the benzaldehyde proton and 35.4 for the DMF methyls. This translates to an NMR yield of 62% for the benzaldehyde.

Benzaldehyde Azine (**1b**) Reaction with BPC - Into a 25-mL round-bottom flask equipped with magnetic stirrer were added 800 mg (3.84 mmol) **1b**[18] and 10 mL $CHCl_3$. To the stirred solution were carefully added 2.50 g (13.8 mmol) BPC a little at a time. Gas was evolved and the flask became warm. After completion of addition, the solution was allowed to cool to ambient temperature and benzamide precipitated. The mixture was filtered and the solid washed with 2 mL chloroform.

The combined filtrates were subjected to flash column chromatography using silica gel and eluting with 20% $CHCl_3$/80% hexane, then switching to 50% $CHCl_3$/50% hexane, and finally pure $CHCl_3$. The first compound to elute was benzaldehyde (R_f=0.32). The second compound to elute was an amber semi-solid (R_f=0.12). A total of 175 mg (20%) of this compound was obtained. It was identified as benzaldehyde azine monoxide (**2b**) by comparison with an authentic sample. A second flash chromatrography using $CHCl_3$, followed by recrystallization from hexane gave colorless needles mp 127-128° (lit.[17] mp 130-131°): IR (KBr) 1660, 1610, 1580, 1555, 1450, 1410, 1210, 1095, 1070, 820, 755, 690s cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.40 (1H, s), 8.28 (2H, dd, J=2.1 and 7.3 Hz), 7.86 (3H, m), 7.44 (6H, m); MS (e/m) 224 (M^+, 1), 207(3), 131(6), 103(100), 90(3), 76(43), 51(20); Mean of 8 scans is 224.0977±0.00235 (±10.5 ppm); Calc. mass for $C_{14}H_{12}N_2O$ is 224.09496 dev + 0.002824 (+12.6 ppm).

Nitrobenzaldehyde-t-butyl Imine (**10a**) Reaction with BPC - Into a 25-mL round-bottom flask equipped with magnetic stirrer were added 812 mg (3.94 mmol) **10a** and 10 mL $CHCl_3$. To the solution were carefully added 876 mg (4.84 mmol) BPC a little bit at a time. Gas was evolved upon addition of the BPC and the flask became slightly warm. After addition was completed, the mixture was allowed to stir for 20 minutes, then it was filtered and the insoluble solids were washed with 1 mL $CHCl_3$. The combined filtrates were concentrated to give a yellow solid which was dissolved in a minimum of ethyl acetate and purified by flash chromatography using 10% ethyl acetate/90% hexane. A total of 755 mg (86%) white solid oxaziridine (**11a**) (R_f=0.53) were obtained: mp 63.8-64.8° (lit.[8] mp 64-65°); IR (KBr) 3120w, 2970m, 2870w, 2490w, 1940w, 1805w, 1610m, 1520s, 1470m, 1350s, 1315m, 1290m, 1255m, 1245m, 1210m, 1185m, 1105m, 1010w, 915w, 865w, 835s, 820m, 750m, 720m, 690m cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 8.3 (2H, d, J=8.5 Hz), 7.7 (2H, d, J=8.5 Hz), 4.7 (1H, s), 1.2 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9 (quat), 142.8 (quat), 128.6 (CH), 123.6 (CH), 72.3 (CH), 58.9 (quat), 25.2 (CH_3).

Methoxybenzaldehyde-t-butyl Imine (**10b**) Reaction with BPC - Into a 25-mL round-bottom flask equipped with magnetic stirrer were added 805 mg (4.21 mmol) of **10b** and 10 mL $CHCl_3$. To the stirred solution were carefully added 1.008 g (5.56 mmol) BPC a little bit at a time. Evolution of CO_2 was immediate and the flask became warm. After addition of the BPC was completed, the mixture was allowed to stir for 20 minutes, then filtered and the white solids washed with 2 mL $CHCl_3$. The combined filtrates were concentrated to give a pale yellow semi-solid which was dissolved in a minimum of ethyl acetate and purified by flash chromatography on silica gel, eluting with 5% ethyl acetate/95% hexane. A total of 699 mg (80%) clear, pale amber liquid was obtained (R_f=0.54) which was the oxaziridine (**11b**):[6] IR 2980m, 1615m, 1515m, 1390w, 1360w, 1250s, 1170m, 1035m, 830m cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.4 (2H, d, J=9 Hz), 6.9 (2H, d, J=9 Hz, 4.65 (1H, s), 3.75 (3H, s), 1.15 (9H, s).

After several months at ambient temperature in a clear glass vial, **11b** had rearranged completely to N-t-butyl-p-methoxybenzamide: IR (film) 3410m (br), 3080w, 2980m, 2940w, 2840w, 2500w, 1680w, 1603s, 1580w, 1560w, 1508s, 1463m, 1408m, 1363m, 1323m, 1304m, 1255vs, 1196m, 1170s, 1122s, 1109m, 1030s, 910w, 840s cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (2H, d, J=9.1 Hz), 7.48 (1H, s, NH), 6.91 (2H, d, J=9.0 Hz), 3.80 (3H, s, OCH_3), 1.58 (9H, s, t-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8 (quat), 130.7 (CH), 124.1 (quat), 113.7 (CH), 70.0 (quat), 55.2 (OCH_3), 28.3 (t-Bu).

Competition Experiment Reaction of BPC with Imines - Into a 10-mL flask were added 191 mg (1.00 mmol) **10b**, 205 mg (1.00 mmol) **10a**, and 0.5 mL $CDCl_3$. To the solution were carefully added 20 mg (0.11 mmol) BPC. Gas was vigorously evolved and a clear solution was formed. The solution was analyzed by 60 MHz ^1H NMR and the products identified by their methine chemical shift. Integration gave 3.7 for the nitrophenyl oxaziridine (**11a**) and 6.7 for the methoxyphenyl oxaziridine (**11b**). This translates to 64% for **11b** and 36% for **11a**. The methoxy derivative **11b** reacts 1.8 times faster than the nitro derivative **11a**.

Benzaldehyde Azine (**1b**) Reaction with BPC in Benzene, NMR Yield - Into a 5-mL round-bottom flask equipped with magnetic stirrer and glass stopper were added 100 mg (0.480 mmol) **1b**,[18] 2 mL benzene-d_6, and 261 mg (1.44 mmol) BPC. The yellow mixture was allowed to stir for 46 hours at ambient temperature. To the mixture were added 57 mg (0.780 mmol) DMF. The mixture was filtered and the 60 MHz ^1H NMR of the filtrate was taken. The integration for the benzaldehyde proton was 5.8 and the DMF methyl groups were 70.0. This works out to an NMR yield of 40% for benzaldehyde.

Benzaldehyde Azine (**1b**) Reaction with BPC in Benzene - Into a 100-mL round-bottom flask equipped with magnetic stirrer and glass stopper were added 800 mg (3.84 mmol) **1b** and 10 mL benzene. To the clear, yellow solution were carefully added 2.50 g (13.8 mmol) BPC. Only a little

BPC was added at first and since no reaction occurred over a 20-minute period, the flask was heated gently with a hot air gun. Gas was evolved as the reaction proceeded. Heating was discontinued and addition of BPC was maintained to keep the reaction going. The reaction was strongly exothermic. After addition was completed, the reaction mixture was allowed to stir at ambient temperature for 46 hours. The mixture was filtered and the white solid washed with 2 mL benzene.

The combined filtrates were subjected to flash column chromatography on silica gel eluting with 50% $CHCl_3$/50% hexane. The product was eluted when the solvent was switched to pure $CHCl_3$. A total of 97.7 mg (11%) yellow solid was obtained. The yellow solid was determined to be benzaldehyde azine monoxide (**2b**) by comparison with an authentic sample.[17]

Butanal Azine (1c) Reaction with BPC - Into a 100-mL round-bottom, three-necked flask equipped with magnetic stirrer, thermometer, nitrogen inlet and nitrogen outlet were added 800 mg (5.70 mmol) butanal azine[19] and 10 mL $CHCl_3$. The flask was cooled in an ice bath to 10°. To the flask were carefully added 1.138 g (6.28 mmol) BPC over a period of 10 minutes. The temperature remained below 15°. A gas was evolved. After addition was completed the mixture was allowed to warm to room temperature and the solvent was removed by rotary evaporation at reduced pressure. The reaction mixture was subjected to flash chromatography using silica gel and eluting with 30% ethyl acetate/70% hexanes. A total of 76.6 mg (7.5%) clear, colorless liquid, which was butyl benzoate, were obtained (R_f=0.45): IR 3310w, 3060w, 2955s, 2870m, 1630s, 1555m, 1445m, 1395m, 1325s, 1160m, 1070s, 780m, 690m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (2H, dd, J=1.7 and 8.0 Hz), 7.42 (3H, m) 4.26 (2H, t, J=6.6 Hz), 1.80 (2H, m), 1.51 (2H, m), 0.99 (3H, t, J=7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6 (C=O), 133.0 (quat), 130.8 (CH), 128.4 (CH), 126.7 (CH), 65.9 (CH_2O), 30.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3); MS e/m 178 (M^+, 5), 122(88), 105(100), 77(48), 51(23).

In addition, 175 mg (14%) N-benzoylcarbamic acid, butyl ester were obtained as a colorless solid which was recrystallized from hexane/$CHCl_3$ to give a colorless solid mp 55-59° (R_f=0.25): IR (KBr) 3250s(br), 2970m, 2880w, 2410w, 1755s, 1685m, 1520s, 1200s, 1155w, 1055m, 1020m, 955m, 777m, 705m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.86 (1H, s), 7.90 (2H, d, J=7.0 Hz), 7.55 (1H, t, J=7.5 Hz), 7.44 (2H, t, J=7.4 Hz), 4.18 (2H, t, J=6.7 Hz), 1.62 (2H, m), 1.37 (2H, m), 0.90 (3H, t, J=7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (C=O), 151.6 (C=O), 133.1 (quat), 132.9 (CH), 128.7 (CH), 127.9 (CH), 66.0 (CH_2O), 30.6 (CH_2), 18.9 (CH_2), 13.6 (CH_3); MS e/m 221 (M^+, 5), 193(2), 166(52), 149(3), 121(4), 105(100), 77(54), 56(14), 51(19).

Butanal Azine (1c)[19] Reaction with BPC, NMR Yield - Into a 10-mL beaker were added 100 mg (0.713 mmol) butanal azine and 1.0 mL $CDCl_3$. To the solution were carefully added 194 mg (1.07 mmol) BPC. The reaction was exothermic and gas was evolved. After cooling to ambient temperature, 50 mg (0.331 mmol) p-nitro-benzaldehyde were added as internal standard. The solution was drawn up in a syringe and separated from solid benzamide. The 300 MHz ^1H NMR was taken and the resonances of the aldehyde protons were integrated to determine the yield. Integrations of 1.4280 for p-nitrobenzaldehyde and 1.5683 for butanal were obtained, indicating a yield of 0.363 mmol butanal (25%).

4,4-Dimethyl-3,5-diphenyl-4[H]-pyrazole (**20**) Reaction with BPC in Chloroform - Into a 100-mL round-bottom flask equipped with magnetic stirrer were added 800 mg (3.22 mmol) **20**[2] and 10.0 mL $CHCl_3$. To the stirred solution were carefully added 1.751 g (9.67 mmol) BPC a little bit at a time. There was a slight induction period before reaction occurred. A red-brown color appeared which faded at the end of addition. A gas was evolved and the flask became warm. After 30 minutes at ambient temperature, the excess BPC and benzamide were removed by suction filtration. The white solid obtained was washed with 1.0 mL $CHCl_3$. The pale yellow filtrate was concentrated by rotary evaporation at reduced pressure to give a mixture of yellowish solid and oil. Purification by flash chromatography gave 215 mg (26%) 2,2-dimethyl-1,3-diphenylpropane-1,3-dione (**21**) (R_f=0.59) as a white solid mp 75-92°. Recrystallization from hexane gave colorless crystals mp 96.0-97.8° (lit.[20] mp 99°): IR (CCl_4) 3060w, 2980w, 2920w, 1660s, 1590m, 1580m, 1250m, 1225m, 940m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (4H, d, J=7.3 Hz), 7.38 (2H, t, J=7.3 Hz), 7.28 (4H, t, J=7.5 Hz) 1.66 (6H, s).

There were also obtained 183 mg (21%) 1-(2-methyl-1-phenyl)propenylidenebenzoic acid hydrazide (**22**) (R_f=0.21) as a white solid mp 116.5-117.7°. Recrystallization from hexane/$CHCl_3$ gave fine white needles mp 110.0-111.0°: IR (CCl_4) 3350w, 3310w, 3070w, 3030w, 2930w, 1695s, 1665s, 1475s, 1450m, 1320s, 1250m, 1140m, 900m, 700s cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.56 (1H, s), 7.82 (4H, m), 7.47 (3H, m), 7.37 (3H, m), 5.72 (1H, s), 5.23 (1H, s), 1.96 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (C=O), 156.45 (C=O), 137.8 (quat), 134.5 (quat), 133.5 (quat), 132.0 (CH), 130.0 (CH), 128.9 (CH), 128.5 (CH), 127.3 (CH), 127.1 (CH), 119.7 (=CH_2), 21.2 (CH_3); MS e/m 264 (M^+, 5) 223(4), 159(42), 105(100), 77(50), 51(11).

There were also obtained 44 mg white solid (R_f=0.28) mp 91-100°. Analysis by ^1H NMR indicated this to be a mixture of compounds even though it gave only one TLC spot. Recrystallization from hexane gave white solid mp 100-105.3°, however no improvement in the purity was observed by ^1H NMR.

Reaction of N-Isopropylidene-N'-diphenylmethyleneazine (**13**)[21] with BPC in Chloroform - Mixed azine **13** was dissovled in $CDCl_3$ in an NMR tube and BPC was added in small portions to the solution. Reaction was immediate with the liberation of gases. The reaction was monitored by NMR with the result that as the methyl hydrogen signals of **13** disappeared, the methyl hydrogen signals of acetone appeared. Sufficient BPC was added to consume all the azine and then the $CHCl_3$ and the acetone were taken off in vacuo. The residue was taken up in CCl_4 and the benzamide was removed by centrifugation. NMR analysis of the solution showed the presence of benzophenone. The only products formed were acetone and benzophenone. Benzophenone formed in quantitative yield. The yield of acetone could not be determined as it is evaporated together with the chloroform.

Reaction of Mixed Azine (**13**)[21] with BPC in Chloroform in the Presence of Benzoic Acid - Mixed azine **13** and benzoic acid were dissolved in $CHCl_3$ in a 1:2 molar ratio. Solid BPC was added in portions to the solution until all the azine was consumed. During the reaction, the solution turned red and gases were given off. The solution was extracted with aqueous $NaHCO_3$ until all the benzoic acid was removed and then it was dried with Na_2SO_4. The solvent was taken off in vacuo, the residue was taken up in CCl_4, and the benzamide was separated by filtration. Then the CCl_4 was taken off in vacuo and the residue was recrystallized from ethanol to yield white needles with a sharp melting point of 88°. This compound was indentified as diphenylmethyl benzoate (lit.[22] mp

88-89°): ^{1}H NMR (60 MHz) δ 8.2 (2H, m), 7.4 (13H, m), 6.6 (1H, br s).

The only product present in the final residue after evaporation of CCl_4 was diphenylmethyl benzoate which formed in quantitative yield. When this reaction was carried out in $CDCl_3$ in an NMR tube, it was also observed that as the methyl hydrogen signals of **13** disappeared, the methyl hydrogen signals of acetone appeared. However in this case no benzophenone was detected at all.

Reaction of N-Benzylidene-N'-diphenylmethyleneazine (**14**) in Chloroform with BPC - Mixed azine **14**[23] was dissolved in $CHCl_3$ and BPC was added in small portions to the solution. Reaction was immediate with the liberation of gases. Sufficient BPC was added to consume all of the azine and then the solvent was taken off in vacuo. The residue was taken up in CCl_4 and the benzamide was removed by filtration. Analysis of the filtrate showed that it was made up of benzophenone, benzaldehyde, and azine monoxide **15**[17] as solutes. The yields were 76% for benzophenone, 74% for benzaldehyde, and 23% for **15**. For **15**: ^{1}H NMR (60MHz) δ 9.6 (1H, s), 8.0 (2H, m), 7.3 (13H, m).

Reaction of Mixed Azine (**14**)[23] with BPC in Chloroform in the Presence of Benzoic Acid - Mixed azine **14** and benzoic acid were dissolved in $CHCl_3$ in a 1:2 molar ratio. Solid BPC was added to the solution in portions until all the azine was consumed. During the reaction, the solution turned reddish and gases were given off. The solution was extracted with aqueous $NaHCO_3$ until all the benzoic acid was removed and then it was dried with Na_2SO_4. The solvent was taken off in vacuo, the residue was taken up in CCl_4, and the benzamide was separated by filtration. Analysis of the filtrate showed that the solutes present were azine monoxide **15**,[17] benzophenone, benzaldehyde, diphenylmethyl benzoate (**16**),[22] and benzyl benzoate **17**. The yields were 21% for **15**, 10% for benzophenone, 70% for benzaldehyde, 66% for **16**, and 10% for **17**. For **17**: IR 3050w, 3020w, 2930w, 1720s, 1600w, 1490w, 1440m, 1370m, 1310m, 1260s, 1170m, 1105s, 1060m, 1020m, 710s cm^{-1}; ^{1}H NMR (60 MHz) δ 8.0 (2H, m), 7.4 (8H, m), 5.25 (2H, s).

Reaction of 4,4-Dimethyl-3,5-diphenyl-4H-pyrazole (**20**) with BPC in THF - The azine **20**,[2] dissolved in THF at room temperature, was treated, while stirring, with an equivalent of solid BPC added in small portions. After addition was complete, the reaction mixture was stirred for an additional hour. The reaction mixture was diluted with pentane and the precipitated benzamide was separated by filtration. TLC on the filtrate revealed the presence of four compounds including unreacted azine. The mixture was separated by column chromatography. The main product was 2,2-dibenzoylpropane[20] obtained in 60% yield, but the azine monoxide also formed in about 7% yield. About 30% yield of rearranged product **22** formed in the reaction. During the course of the reaction, a red color appeared. For 4,4-dimethyl-3,5-diphenyl-4[H]-pyrazole-1-oxide:[2] IR (CCl_4) 3050w, 2970w, 1660w, 1585w, 1555m, 1520s, 1440m, 1140m, 760m, 695s cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.4 (2H, m) 8.1 (2H, m), 7.5 (6H, m), 1.8 (6H, m).

Benzophenone Azine (**1a**) Reaction with MCPBA - Into a 100-mL round-bottom flask equipped with magnetic stirrer and cork stopper were added 721 mg (2.00 mmol) **1a**,[16] 100 mg (0.44 mmol) benzyltriethylammonium chloride, 4.0 mL $CHCl_3$, and 30.0 mL saturated aqueous sodium bicarbonate. To the mixture was added a solution of 2.070 g (9.60 mmol) 80-85% m-chloroperoxybenzoic acid dissolved in 30.0 mL $CHCl_3$. After four hours rapidly stirring at ambient temperature, the organic layer was separated and concentrated by rotary evaporation at reduced pressure to give a yellow solid. Purification by flash chromatography using silica gel and eluting with 20% ethyl acetate/80% hexane gave 54.5 mg (7%) pale yellow solid benzophenone azine oxide (R_f=0.25).[17] This material was found to decompose to benzophenone upon standing several hours at ambient temperature. All spectra were identical to authentic benzophenonone azine oxide.

There were also obtained 1.0314 g pale yellow solid (R_f=0.54-0.65) which was further purified by flash chromatography on silica gel eluting with 30% $CHCl_3$/70% hexane to give 316.9 mg (44%) benzophenone azine (R_f=0.09), 299.9 mg (41%) benzophenone (R_f=0.20), and 327.5 mg white solid which was m-chlorobenzoylperoxide mp 121.0-121.8° (hexane) (lit.[24] mp 125.0°): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (1H, t, J=1.8 Hz), 7.95 (1H, d of t, J_d=7.8 Hz and J_t=1.3 Hz), 7.64 (1H, ddd, J=8.1, 2.1 and 1.1 Hz), 7.47 (1H, t, J=7.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (C=O), 135.1 (quat), 134.5 (CH), 130.3 (CH), 129.8 (CH), 127.9 (CH), 127.1 (quat); MS (m/e) 312 (M^++2, 3), 310 (M^+, 4), 266(10), 249(7), 186(4), 156(9), 139(100), 111(41), 75(36), 50(15).

Benzaldehyde Azine (**1b**) Reaction with MCPBA - A 10-mL round-bottom flask was equipped with magnetic stirrer and pressure-equalizing addition funnel. To the flask were added 59.5 mg (0.286 mmol) **1b**,[18] 7.1 mg (0.031 mmol) benzyltriethylammonium chloride, 0.50 mL $CDCl_3$ and 2.00 mL saturated aqueous sodium bicarbonate. A solution of 148 mg (0.686 mmol) 80-85% m-chloroperoxybenzoic acid (MCPBA) in 2.0 mL $CDCl_3$ was added over a period of four minutes. After stirring for two hours at ambient temperature, the organic layer was separated and dried over anhydrous sodium sulfate. To the solution were added 43.6 mg (0.3025 mmol) dimethylmaleate as internal standard and the ^{1}H NMR (300 MHz) was taken. The absolute yields were determined by integration of the benzaldehyde resonance at 10.01 ppm, the benzaldehyde azine oxide resonance at 9.41 ppm and the benzaldehyde azine resonance at 8.66 ppm relative to the dimethylmaleate resonance at 6.22 ppm. There were obtained 0.9755 mmol (17.1%) benzaldehyde, 0.02465 mmol (8.6%) benzaldehyde azine oxide,[17] and 0.09577 mmol (33.5%) benzaldehyde azine remained unreacted.

Benzaldehyde Azine (**1b**) Reaction with Dimethyldioxirane - Into a small vial were weighed 5.0 mg (0.0240 mmol) **1b**. To the vial were added 1.00 mL (0.055 mmol) of a 0.055 M acetone-d_6 solution of dimethyldioxirane-d_6 prepared according to the literature.[7] The clear, colorless solution was added to a small vial containing 6.2 mg (0.0430 mmol) dimethylmaleate as internal standard and the ^{1}H NMR (300 MHz) was taken. Integration of the benzaldehyde resonance at 10.06 ppm, the benzaldehyde azine oxide resonance at 9.42 ppm and the benzaldehyde azine resonance at 8.70 ppm relative to the dimethylmaleate internal standard at 6.41 ppm gave the absolute yields. There were obtained 0.0161 mmol (33%) benzaldehyde, 0.00243 mmol (10%) benzaldehyde azine oxide, and there remained 0.0113 mmol (47%) benzaldehyde azine.

Benzophenone Azine (**1a**) Reaction with BPC in the Presence of Trifluoroacetic Acid - Into a 25-mL round-bottom flask equipped with magnetic stirrer and nitrogen inlet stopcock, were added 800 mg (2.22 mmol) **1a**, 10 mL $CHCl_3$, 506 mg (4.44 mmol) trifluoroacetic acid, and 1.206 g (6.66 mmol) BPC. The yellow mxture was allowed to stir at ambient temperature for 17 hours. The insoluble white solid was removed by suction filtration and washed with 1 mL $CHCl_3$. The $CHCl_3$ solution was concentrated by rotary evaporation at reduced pressure to give a mixture of liquid containing a

pale yellow solid. The mixture was purified by flash chromatography using silica gel and eluting with 20% ethyl acetate/80% hexane. A total of 74.2 mg (9%) pale yellow solid benzophenone azine oxide (**2a**)[17] (R_f=0.46) were obtained. There were also obtained 810 mg pale yellow liquid (R_f=0.73) which was a mixture of benzophenone and benzhydryl trifluoroacetate, which could not be further separated by chromatography. Analysis by ^1H NMR (300 MHz, $CDCl_3$) was performed. The amount of benzophenone was determined by integration of the aromatic resonance at 7.76 ppm, while the benzhydryl trifluoroacetate was determined by integration of the benzhydryl methine resonance at 6.96 ppm. In the mixture there were 426 mg (53%) benzophenone and 384 mg (62%) benzhydryl trifluoroacetate.

Benzophenone Azine Oxide (2a) Reaction with Trifluoroperoxyacetic Acid - A 25-mL, single-necked, round-bottom flask was equipped with magnetic stirrer and rubber septum with a needle attached to a source of N_2. To the flask were added 22.7 mg (0.601 mmol) 90% H_2O_2 and 0.100 mL CH_2Cl_2. The flask was cooled in an ice water bath and then 151.2 mg (0.720 mmol) trifluoroacetic anhydride were added by syringe over a period of two minutes. The ice bath was removed and a solution of 112.9 mg (0.300 mmol) **2a** in 1.00 mL CH_2Cl_2 was added, followed by 223 mg (2.08 mmol) anhydrous sodium carbonate. The pale yellow mixture was allowed to stir at ambient temperature for two hours. To the mixture were added 5 mL water and 5 mL CH_2Cl_2. The organic layer was separated, washed with 2.0 mL 15% sodium carbonate, dried over anhyd sodium sulfate and concentrated by rotary evaporation at reduced pressure to give a pale yellow oil. The ^1H NMR (300 MHz, $CDCl_3$) was taken. Integration of the benzophenone aromatic resonance at 7.80 ppm, the benzophenone azine oxide aromatic resonance at 7.08 ppm, and the benzhydryl trifluoroaceate benzhydryl resonance at 6.98 ppm gave the relative amounts of each compound. There were obtained 29% benzophenone, 21% benzhydryl trifluoroacetate and there remained 49% benzophenone azine oxide.

Benzophenone Azine Oxide (2a) Reaction with Trifluoroacetic Acid - Into a 10-mL screw-cap vial were added 68.4 mg (0.600 mmol) trifluoroacetic acid, 1.0 mL CH_2Cl_2, and 112.9 mg (0.300 mmol) **2a**. After 15 hours at ambient temperature, the solvent was removed by rotary evaporation at reduced pressure to give 159.2 mg pale yellow oil which was redissolved in 10.0 mL $CHCl_3$, washed three times with 5.0 mL portions 15% aq sodium carbonate, dried over anhyd sodium sulfate and concentrated by rotary evaporation at reduced pressure to give 110.0 mg pale yellow oil containing some solid. The ^1H NMR (300 MHz) was taken. Integration of the benzophenone aromatic resonance at 7.80 ppm, the benzophenone azine oxide aromatic resonance at 7.07 ppm, and the benzhydryl trifluoroacetate benzhydryl resonance at 6.98 ppm gave the relative amounts of each compound. There were obtained 23% benzophenone, 11% benzhydryl trifluoroacetate, and there remained 66% benzophenone azine oxide.

Reaction of Cyclohexanone Azine with BPC in Chloroform in the Presence of Excess Benzoic Acid - Cyclohexanone azine (0.0100 mol, 1.92 g) and benzoic acid (0.0200 mol, 2.44 g) were dissolved in about 50 ml of $CHCl_3$. To this solution at room temperature while stirring was added in portions 3.39 g of BPC of 80% purity (0.015 mol). The $CHCl_3$ reaction mixture was extracted with a saturated aq $NaHCO_3$ solution until all the unreacted benzoic acid was taken out. The $CHCl_3$ solution was then dried with anhyd $MgSO_4$ and the $CHCl_3$ taken off in vacuo. The residue was taken up in hexane and the solid benzamide filtered out. The hexane was then evaporated. The reddish liquid residue weighed 2.12 g. An NMR spectrum and a thin layer chromatograph showed that the residue was a mixture of unreacted azine, cyclohexanone and cyclohexyl benzoate. Column chromatography of the residue on silica gel allowed the separation of the ester as the first fraction (1.38 g, 0.0067 mol) and the unreacted azine (0.44 g, 0.0023 mol). The yield of ester based on reacted azine was 87%.

Acetone Methylphenylhydrazone (9) Reaction with Peroxyacetic Acid - Into a 10-mL round-bottom flask equipped with rubber septum and magnetic stirrer were added 187.1 mg (4.95 mmol) 90% hydrogen peroxide and 0.50 mL of a CH_2Cl_2 solution prepared by adding one drop of concentrated H_2SO_4 to 50 mL CH_2Cl_2. The flask was cooled in an ice bath for 10 minutes, then 673.8 mg (6.60 mmol) acetic anhydride were added by syringe over a period of five minutes. After 15 minutes at ambient temperature, the clear, colorless peracetic acid solution was added to an ice-cooled solution of 811.2 mg (5.00 mmol) acetone methylphenylhydrazone[26] in 10.0 mL CH_2Cl_2 which was in a 25-mL round-bottom flask equipped with rubber septum and magnetic stirrer. Addition was completed in five minutes. The ice bath was removed and the amber reaction mixture, which contained some insoluble globules of liquid, was allowed to stir for 12 hours at ambient temperature. Concentration by rotary evaporation at reduced pressure gave a dark amber oil which was purified by flash chromatography using silica gel and eluting with 50% ethyl acetate/50% hexane. There were obtained 153.0 mg (22%) amber liquid (R_f=0.71) which was N-methyl-N-nitrosoaniline;[27] IR (film) 3060w, 2930w, 2410w, 1660w, 1600m, 1500m, 1470m, 1440s, 1400w, 1315w, 1295w, 1205s, 1090s, 1030w, 950m, 820w, 755s, 690m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.42 (m, 4H), 7.33 (t of t, J=14.4 and 1.4 Hz), 3.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3 (quat), 129.4 (CH), 127.3 (CH), 119.1 (CH), 31.4 (CH_3).

There were also obtained 291.3 mg (39%) pale yellow solid (R_f=0.40) which was N-methyl-N-phenyl-acetamide.[28] Further purification by flash chromatography using silica gel and eluting with 5% ethyl acetate/95% hexane gave 166.4 mg pale amber solid (R_f=0.39) mp 95.8-97.2° (lit.[29] mp 102-104°): IR (KBr) 3040m, 2930m, 1910w, 1655vs, 1590m, 1490s, 1415s, 1375s, 1290m, 1135m, 1080m, 1020m, 960w, 770m, 700s, 585w, 550m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.37-7.30 (m, 1H), 7.20 (m, 2H), 3.27 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 (C=O), 144.6 (quat), 129.7 (CH), 127.7 (CH), 127.1 (CH), 37.1 (NCH_3), 22.4 (CH_3CO); MS m/e 149 (M^+, 62), 134(1), 106(100) 77(43), 65(8), 56(17), 51(26), 43(63), 39(19).

From the original chromatography using 50% ethyl acetate/50% hexane were also obtained 154.0 mg (19%) amber solid (R_f=0.20) which was 2-methyl-2-phenylacetic acid hydrazide[30] mp 87-92° (lit.[31] mp 92-93°): IR (KBr) 3260s, 3030m, 2960w, 2890w, 2810w, 1665s, 1600m, 1525m, 1500s, 1445w, 1370m, 1325w, 1280m, 1210m, 1185w, 1120m, 1110m, 1035m, 1020w, 990w, 975m, 875m, 745s, 690s, 600m, 510m, 490w, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 and 7.33 (1H, two broad s, NH), 7.27 and 7.19 (2H, two m), 6.94-6.72 (3H, m), 3.09 and 3.05 (3H, two s, NCH_3), 2.01 and 1.92 (3H, two s, CH_3CO); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1 (C=O), 169.4 (C=O), 149.4 (quat), 149.3 (quat), 129.4 (CH), 129.0 (CH), 120.6 (CH), 119.5 (CH), 113.3 (CH), 113.0 (CH), 42.0 (NCH_3), 40.6 (NCH_3), 20.9 (CH_3CO), 19.1

(CH_3CO); MS (m/e) 164 (M^+, 68), 121(100), 105(76), 92(57), 77(77), 65(19), 51(42), 43(51), 39(15).

Acetone Methylphenylhydrazone (9) Reaction with BPC - A 50-mL round-bottom flask was equipped with magnetic stirrer. To the flask were added 811.2 mg (5.00 mmol) acetone methylphenylhydrazone[26] and 10.0 mL $CHCl_3$. To the clear, colorless solution were slowly added 996.3 mg (5.50 mmol) BPC, a little bit at a time, over a period of seven minutes. The reaction was immediate and exothermic with the vigorous evolution of gas. After 30 minutes at ambient temperature, concentration by rotary evaporation at reduced pressure gave an amber solid which was purified by flash chromatography using silica gel and eluting with 10% ethyl acetate/90% hexane. There were obtained 224.5 mg (37%) pale amber solid (R_f=0.62) which was 1,4-dimethyl-1,4-diphenyl-2-tetrazine mp 138.3-140.0° (lit.[32] mp 141-142°): IR (KBr) 3050w, 2930w, 1590s, 1490s, 1450m, 1430m, 1195m, 1175m, 1150w, 1090s, 1020m, 995m, 880m, 750m, 740s, 685s, 615m, 605w, 520w cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.21 (m, 4H), 6.92 (t of t, 1H, J=7.0 and 1.4 Hz), 3.45 (s, 3H, NCH_3); MS (m/e) 240 (M^+, 36), 212(1), 197(3), 120(6), 106(100), 77(65), 51(12).

There were also obtained 107.9 mg (16%) amber liquid (R_f=0.39) which was N-methyl-N-nitrosoaniline[27] and 159.8 mg (20%) amber liquid (R_f=0.2) which was recovered acetone methylphenylhydrazone.

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