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REACTION OF QUINONEIMINES WITH KETENES

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Abstract

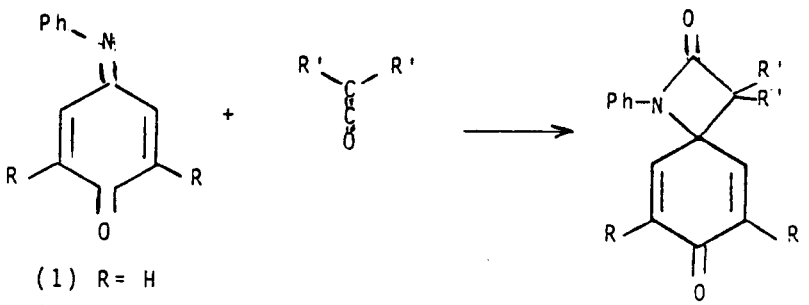
The reactivity of quinoneimines towards ketene and diphenylketene was examined. N-Phenylbenzoquinoneimines (1), (2) and also N-phenylnaphthoquinoneimine react with ketene to give the spiro-adducts (5), (7) and (11) respectively. These adducts were stable even after prolonged heating in high boiling solvent. Reaction of the above imines with diphenylketene also afforded ß-lactam spiro-adducts (6), (8) and (12), but they rearranged to oxindole derivatives (9), (10) and (13) by heating in boiling ethanol. N-Phenyl-9, 10-anthraquinoneimine, however, was inert towards ketene or diphenylketene under the same reaction conditions.

Introduction

Among the addition reaction of carbon-nitrogen double bond, the imine-ketene cycloaddition reaction is a well established and versatile route to racemic ß-lactams [1-9]. In the course of the synthesis of quinoneimine N-oxides, we found an unusual reactivity of imines-nitrogen towards N-oxidation by peracids [10]. This observation stimulated our interest to examine the reactivity of the above-mentioned imines with ketenes, since the same prerequisites, i.e. the availability of lone pair electrons of imine-nitrogen, hold in both reactions. Herein, we report our results from the reaction of benzo, naphtho and anthraquinoneimine with ketene and diphenylketene.

Results and Discussion

Addition of ketene gas, which was produced from the pyrolysis of acetone, into the chloroform solution of benzoquinoneimines (1) and (2) at room temperature, decolorized the red colour of the solution and gave spiro-adducts (5) and (7) respectively. Diphenylketene also reacts with imines (1) and (2) in dry benzene at room temperature to give adducts (6) and (8). In all cases, the reaction required less than five minutes to complete. The recovered spiro-adducts yield were quantitative.



(1) R= H
(2) R= Me

Keywords: Quinoneimines; Ketenes

Products were fully characterized through spectral data. The main feature of the resulting adducts was their IR spectra and the high frequency of carbonyl stretching, which is typical for all ß-lactams carbonyl moiety (Table 1).

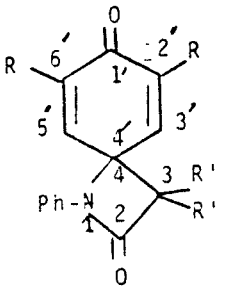


Table 1. Spectral data of adducts 5-8

Compound	R	R'	$\nu_{(C=O)_2}$	$\nu_{(C=O)_1}$	δ_{H_3}	$\delta_{H_{3',5'}}$	$\delta_{H_{2',6'}}$	δ_{H_R}
			Nujol	(cm^{-1})	($CDCl_3$ from TMS)			
5	H	H	1750	1670	3.3 s	6.5 m	6.3 m	–
6	H	Ph	1760	1680	–	6.7 m	6.5 m	–
7	CH_3	H	1770	1680	3.25	6.8 s	–	1.95 s
8	CH_3	Ph	1750	1650	–	6.2 s	–	2.0 s

N-Phenyl-1,4-naphthoquinoneimine (3) reacted with ketene and diphenylketene in a similar fashion to give adducts (11) and (12) respectively. The spectral data of spiro-adducts are given in Table 2.

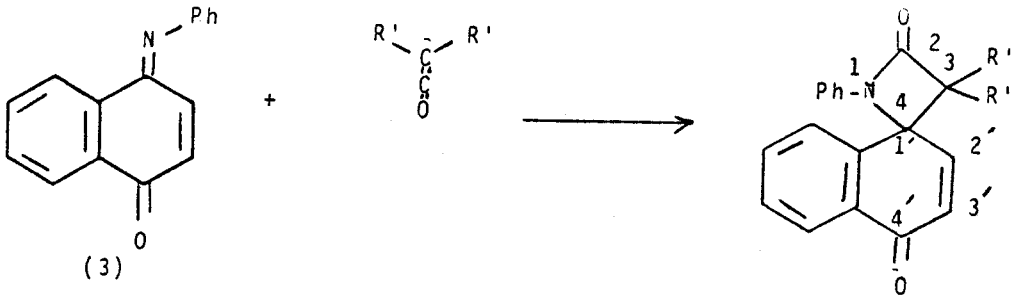
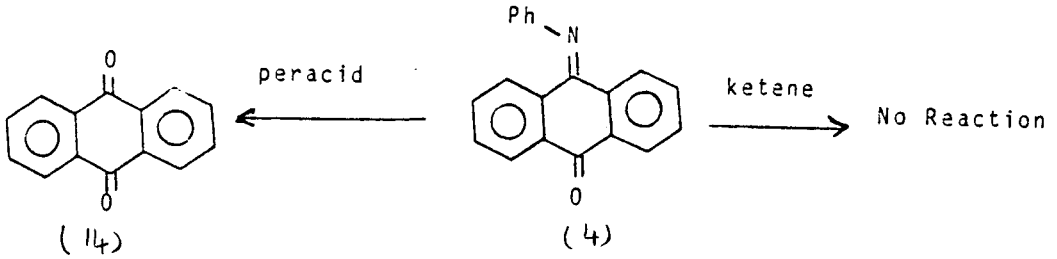


Table 2. Spectral data of adducts 11 and 12

Compound	R'	$\nu_{(C=O)_1}$	$\nu_{(C=O)_2}$	$\delta_{H_{3'}}$	$\delta_{H_{3'}}$	$\delta_{H_{2'}}$
		Nujol (cm^{-1})		($CDCl_3$ from TMS)		
11	H	1660	1760	3.55*	7.1 m	6.8 m
12	Ph	1675	1755	–	6.7 m	(2H)
* as AB quartet signal						

The analogous imine, i. e. N-phenyl-9, 10-anthraquinoneimine (4), however, was totally inert toward ketene or diphenylketene. Exposing the chloroform solution of imine (4) to ketene gas for several hours led to the recovery of the starting material [18].

Interestingly, a similar trend was seen for N-oxidation



(14) (4)

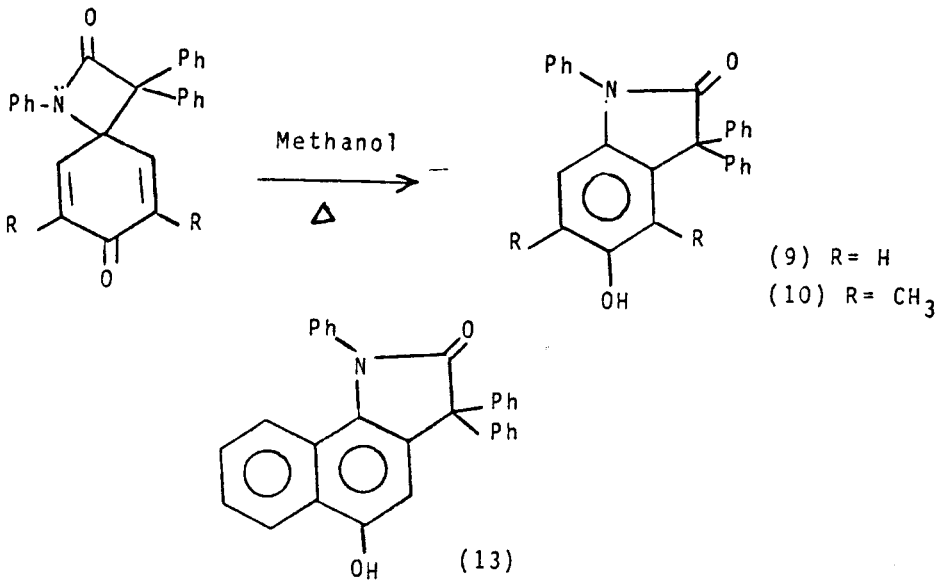
reactions in quinoneimine series. Whereas benzo and naphthoquinoneimines (1), (2) and (3) react readily with perbenzoic acid to give the corresponding N-oxide [10], 9,10-anthraquinoneimine (4) failed to react with peracid in a similar manner. A short treatment of imine (4) with perbenzoic acid gave unreacted starting materials. Long treatment, however, transformed all quinoneimine (4) to 9,10-anthraquinone (14) [11]. The highly attenuated reactivity of imine (4) towards ketenes or N-oxidation is attributed to severe steric congestion.

All spiro azetidinones obtained from the reaction of ketene with quinoneimines i. e. (5), (7) and (11) were crystalline compounds and stable even after prolonged heating in toluene or ethanol. Adducts (6), (8) and (12), which were products of the addition of diphenylketene, however, were not stable in boiling ethyl alcohol. They rearranged to oxindole derivatives (9), (10) and (13) respectively. The structural assignment of oxindoles was based upon their ^{1}H NMR and IR spectral data. All rearranged products showed a strong band at 3250 cm^{-1} which is due to -OH stretching and a low frequency carbonyl band around 1700 cm^{-1} which is due to oxindole carbonyl stretching. The ^{1}H NMR spectra of products indicated a lack of olefinic protons and the presence of aromatic hydrogens only.

These features together with molecular weight extracted from mass spectrum data were consistent with the structure of oxindoles.

Experimental Section

Melting points are taken in open glass capillaries and are uncorrected. IR spectra were recorded in Nujol on a Beckmann Acculab 3 spectrophotometer. ^{1}H NMR (60 MHz) spectra were obtained with Perkin Elmer 248 spectrometer (except where mentioned otherwise), and the shifts are given in scale with Me_4Si as the internal standard. Mass spectra were run by Varian MAT 311 mass spectrometer. Benzene was dried over sodium wire before use. Diphenylketene was prepared by the Hoehn-Smith method [12] and distilled at reduced pressure (3-5 mmHg) before use. Ketene was produced by pyrolysis of acetone at 700-750°C as described by Hurd [13]. N-Phenyl-1,4-benzoquinoneimine (1) was synthesised by Fremy salt oxidation of diphenylamine [14]. 2,6-Dimethyl-N-phenyl-1,4-benzoquinoneimine (2) and N-phenyl 1,4-naphthoquinoneimine (3) were prepared by condensation of corresponding phenols with nitrosobenzene [15, 16]. N-Phenyl-9,10-anthraquinoneimine was synthesised by condensation of nitrosobenzene with anthrone [17].



General Procedure for the Reaction of Quinoneimine with Ketene

A stream of ketene gas was bubbled slowly into the chloroform solution (20 ml) of imine (1 mmol) until the colour of the solution changed from red to yellow. The solvent was removed under reduced pressure and the remaining precipitate was crystallised from ethanol to give the spiro-adduct.

1-Phenylspiro(2',5'-cyclohexadiene-1'-one)-4,4'-azetidine-2-one (5)

215 mg, (95% yield), m. p. 148-9°C, IR ν_{max} (Nujol) 1750, 1670, 1625 and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.5(s, 2H), 6.3 (m, 2H), 6.5 (m, 2H), 7.15 (m, 5H); MS m/z 225, 193, 119, 91, 77.

2', 6'-Dimethyl-1-phenylspiro (2', 5'-cyclohexadiene-1'-one)-4,4'-azetidine-2-one (7)

240 mg (98% yield); m. p. 178-9°C, IR ν_{max} (Nujol) 1770, 1680, 1650 and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (s, 6H), 3.2 (s, 2H), 6.8 (s, 2H), 7.2 (m, 5H); MS m/z 253, 167, 134, 119, 106, 91, 77.

1-Phenylspiro(1',4'-dihydronaphthalene-1'-one)-4,4'-azetidine-2-one (11)

260 mg, (94% yield), m. p. 151-3°C; IR ν_{max} (Nujol) 1760, 1660, 1605 cm^{-1}; ^1HNMR (250 MHz, $CDCl_3$) δ 3.55 (AB quartet, 2H), 6.8 (m, 1H), 7.1 (m, 1H), 7.3 (m, 5H), 7.7 (m, 3H), 8.4 (d, 1H); MS m/z 275, 170, 156, 128.

General Procedure for the Reaction of Quinoneimine with Diphenylketene

A solution of quinoneimine (1 mmol) in dry benzene (20 ml) was treated dropwise with freshly distilled diphenylketene until only the product spot was evident by TLC ($CHCl_3$) and the spot of original imine disappeared. The reaction could also be monitored by the change in the colour of the solution. The dark red turned to a light yellow when the reaction was complete. The solvent was removed by rotary evaporation and the residue was either crystallised from ethanol or purified by flash chromatography on silica gel (elution with chloroform).

1,3,3-Triphenylspiro (2', 5'-cyclohexadiene-1'-one)-4, 4'-azetidine-2-one (6)

360 mg (95% yield), m. p. 231-3°C; IR ν_{max} (Nujol) 1760, 1680, 1640 and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.6 (s, 2H), 6.7 (s, 2H), 7.2-7.8 (br. m, 15H); MS m/z 377, 348, 272, 270.

2', 6'-Dimethyl-1, 33-triphenylspiro (2', 5'-cyclohexadiene-1'-one)-4, 4'-azetidine-2-one (8)

390 mg (98% yield), m. p. 238-9°C; IR ν_{max} (Nujol) 1750, 1650 and 1600 cm^{-1}; ^1HNMR ($CDCl_3$) δ 2.0 (s, 6H), 6.3 (s, 2H), 7-7.8 (br.m, 15H); MS m/z 405, 390, 376, 328, 300, 77.

1,3,3-Triphenylspiro (1',4'-dihydronaphthalene-1'-one)-4,4'-azetidine-2-one (12)

360 mg (85% yield), m. p. 178-9°C; IR ν_{max} (Nujol) 1755, 1675, 1610 cm^{-1}; ^1HNMR (CCl_4) δ 6.7 (m, 2H), 6.9-7.8 (br.m, 19H); MS m/z 427, 233, 195, 194, 166, 165.

General Procedure for Rearrangement of Spiro ß-Lactams to Oxindole Derivatives

Spiro ß-lactam (100 mg) was dissolved in ethanol (10 ml) and the mixture was heated under reflux for three hours. The solvent was removed under reduced pressure and the residue was crystallised either in benzene or ethanol to give the oxindole derivatives.

5-Hydroxy-4,6-dimethyl-1,3,3-triphenyl-2-indolinone (10)

95 mg (95% yield); m. p. 248-250°C; ν_{max} (Nujol) 3480, 1700, 1625 and 1600 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.8 (s, 3H), 2.2 (s, 3H), 6.5 (s, 1H), 7.3 (m, 15H); MS m/z 405, 376, 328, 301.

5-Hydroxy-1,3,3-triphenyl-2-indolinone (9)

85 mg (85% yield); m. p. 234-5°C; IR ν_{max} (Nujol) 3250, 1685 and 1600 cm^{-1}.

5-Hydroxy-1,3,3-triphenyl-6,7-benzoxindole (13)

92 mg (92% yield), m. p. 229-232°C; IR ν_{max} (Nujol) 3250, 1700 and 1600 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7(s, 1H), 7.2-7.6 (m, 19H); MS m/z 427, 397, 350, 322.

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