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Reactivity of Indanedioneketene Dimer with Amines

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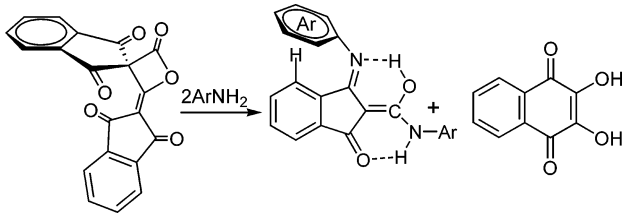


The highly reactive indanedioneketene **5**, resulting from the thermal decomposition of phenyliodonium ylide of 2-hydroxy-1,4-naphthoquinone (lawsone, **4**), in the absence of nucleophiles dimerizes to the corresponding tetraoxo spiro oxetanone **6** in quantitative yield. This oxetanone exhibits an interesting reactivity toward amines.

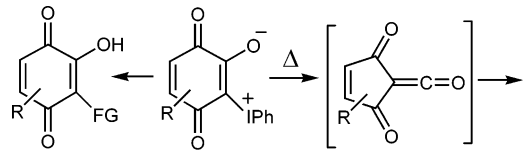
Introduction

Zwitterionic iodonium compounds (ZIC) play an important role in the chemistry of hypervalent iodine. These compounds exhibit a diverse reactivity depending mainly on the nature of the anionic counterpart of the aryliodonio moiety. Among ZIC phenyliodonium ylides of 2-hydroxyquinones **1** have attracted our attention mainly for two reasons: Their interesting reactivity and the fact that a great number of 2-hydroxyquinones are found in nature and their majority exhibit some kind of biological activity.[1]

Two distinguished modes of reactivity of the above-mentioned ylides exist: The replacement of the labile phenyliodonio moiety by another functional group to afford **2** and the thermal degradation of ylides to the very reactive α,α′-dioxoketenes **3** (Scheme 1).

In the first reaction mode, the hydroxyquinone frame is retained leading to a variety of substituted hydroxyquinones. Especially noteworthy are the C−C bond forming reactions taking place either under photochemical conditions[2] or under metal catalysis. Sonogashira,[3a] Stille,[3b,c] and Suzuki[3d] coupling reactions take place under palladium catalysis, whereas substitution of the phenyliodonio group by functionalized indoles is effected by catalytic amounts of copper triflate.[4]

SCHEME 1



Regarding the second reaction mode, the interesting issue from a synthetic point of view is the formation of cyclopentenediones. In refluxing acetonitrile, dioxoketenes **3** afford substituted cyclopentenediones through reaction with water present in the solvent and spontaneous decarboxylation of the intermediary acid.[5] This thermal degradation of ylides **1** offers an effective access to these interesting dienophiles, which can be used further for the construction of more complicated structures.[6]

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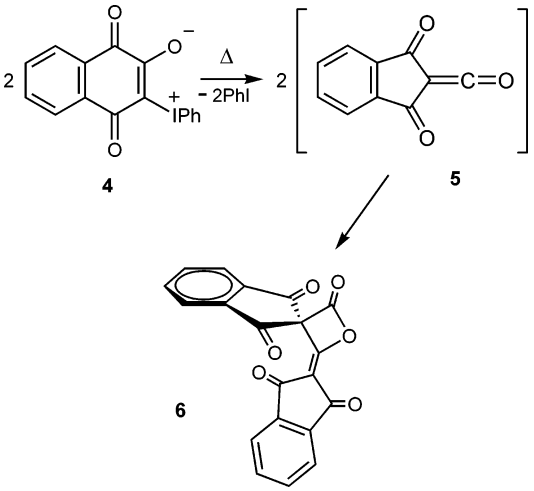
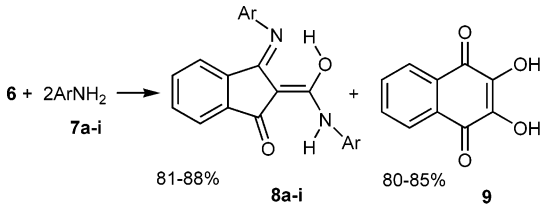
SCHEME 2



SCHEME 3



7, **8a**, Ar = 4-Me-C_6H_4-
7, **8b**, Ar = 2-Me-C_6H_4-
7, **8c**, Ar = 4-MeO-C_6H_4-
7, **8d**, Ar = 2,5-di-Me-C_6H_3-
7, **8e**, Ar = 2,6-di-Me-C_6H_3-
7, **8f**, Ar = 2,4,6-tri-Me-C_6H_2-
7, **8g**, Ar = 4-Cl-C_6H_4-
7, **8h**, Ar = 2-Cl-C_6H_4-
7, **8i**, Ar = 1-naphthyl

Dioxoketenes analogous to **3** are very reactive and only a few are reported in the literature.[7] Dioxoketene **5**, resulting from the phenyliodonium ylide of lawsone (**4**) in refluxing dichloromethane, reacts smoothly with aromatic amines to afford amides existing in solution in a most unusual enol form.[8] The same type of reactivity was observed with other amino compounds such as amino acids and their esters, aminophenols, amino-alcohols, and ureas,[9] as well as with *C*-nucleophiles such as indoles and enamines.[4] In the absence of nucleophiles, dioxoketene **5** dimerizes to oxetanone **6** (Scheme 2).[4] The latter proved to be a reactive and interesting molecule and we wish to report the results of its reaction with amines.

Results and Discussion

Oxetanone **6** was prepared by refluxing dispersions of ylide **4** in dichloromethane and isolated as yellow crystals by crystallization from the resulting clear solution, as described in a previous publication.[4] By careful and thorough treatment of the reaction solution, yield can reach 95−98%, if ylide **4** is used in a scale of 3−4 mmol. Oxetanone **6** is fairly stable and can be stored in the refrigerator, with exclusion of moisture,

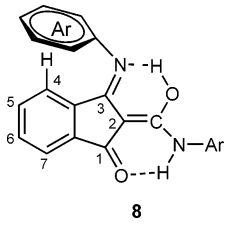
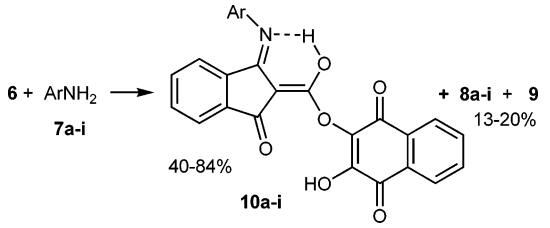
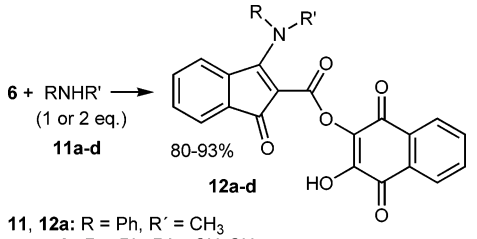


FIGURE 1. Shielding of 4-H by the aryl group.

SCHEME 4



SCHEME 5



11, **12a:** R = Ph, R′ = CH_3
b: R = Ph, R′ = CH_2CH_3
c: R = Ph, R′ = CH_2Ph
d: R = CH_2Ph, R′ = CH_3

for prolonged periods without apparent decomposition. Exposed in air it turns reddish as it is transformed to red-colored dihydroxyquinone **9**, obviously by humidity. It must be noted that this type of [2+2] dimerization to oxetanone **6** is rather unusual, as other α-oxoketenes also dimerize but mainly in [4+2] cycloaddition mode.[7]

Oxetanone **6** reacts easily with primary aromatic amines **7**. Upon addition of 2 equiv of amine to stirred suspensions of compound **6** in dichloromethane two products were obtained from the reaction mixture in high yields: The yellow imino-amides **8**, isolated by column chromatography, and the red 2,3-dihydroxy-1,4-naphthoquinone (**9**), crystallized from the reaction solution, as illustrated in Scheme 3.

It is interesting to note that in the ^{1}H NMR spectra of iminoamides **8** a strong shielding effect is observed for the aromatic proton of the fused benzene ring next to the imino group (4-H). Indeed this proton, normally resonating at δ ∼7.80, appears as a doublet at δ 6.55−6.12. This upfield shift can be explained by a Z to the fused benzene ring configuration of the imino group, caused by the formation of a hydrogen bond between the nitrogen of the imino group and the enolic hydrogen of the amide moiety, and by the restricted rotation of the aryl ring, as shown in Figure 1.

The shielding is gradually increasing from para-substituted (δ 6.45−6.55) to ortho-substituted (δ 6.29) and to ortho,ortho-disubstituted aryl compounds (δ 6.18−6.12), due possibly to the increasing hindrance of rotation of the aryl ring.

Upon addition of 1 equiv of primary aromatic amine **7** to a dispersion of oxetanone **6** in CH_2Cl_2 the iminoesters **10a**−**i** were isolated in good yields by crystallization from the reaction solution, usually accompanied by small amounts (13−20%) of

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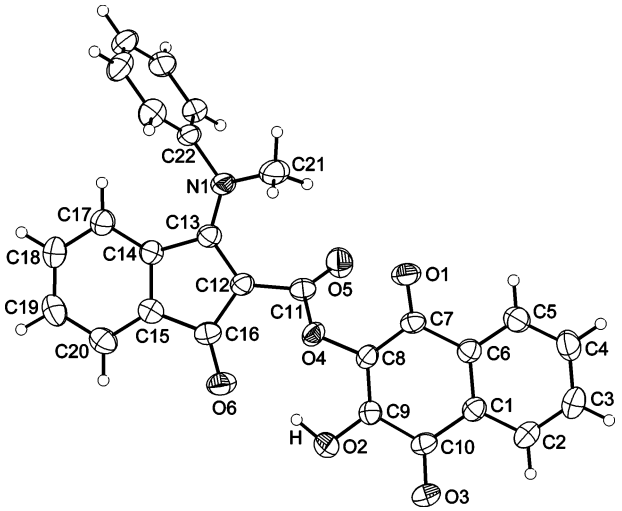


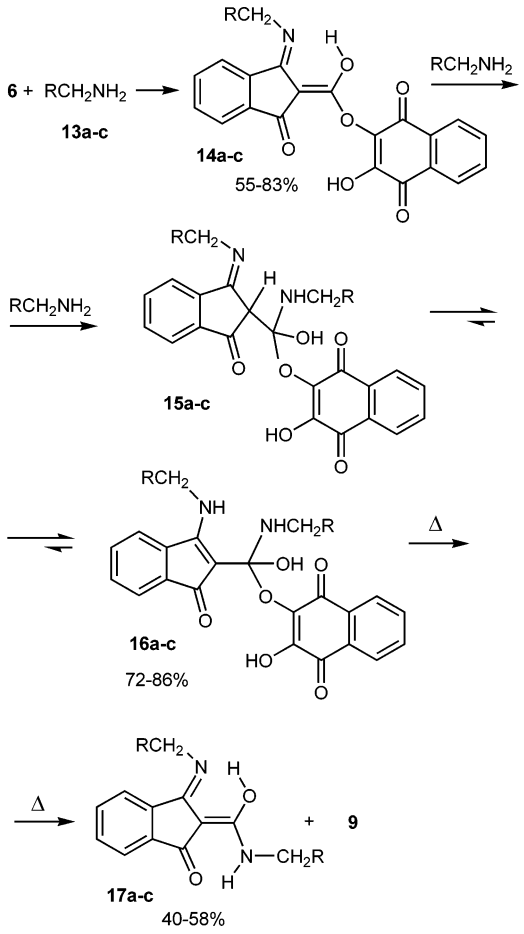
FIGURE 2. Ellipsoid drawing (50% probability) of **12a**.

iminoamides **8** and dihydroxyquinone **9** (Scheme 4). If a second equivalent of amine **7a** was added to a suspension of isolated **10a** the reaction proceeded further to afford **8a** and **9**, proving thus that the reaction proceeds indeed in two steps. Again an upfield shift (δ 6.48−5.95) of the 4-H of the fused benzene ring is observed in iminoesters **10**, analogous to the Z configuration of the aryl ring of compounds **8**, due to internal hydrogen bond formation. Compounds **10** represent the first step of the reaction of oxetanone **6** with primary aromatic amines. Interestingly enough, the nucleophilic attack of the amine takes place on one of the carbonyls of the spiro-cyclopentenedione ring, and not on the oxetanone ring, with a simultaneous expansion of the second cyclopentenedione ring to the hydroxynaphthoquinone moiety.

To clarify the reactivity pattern of oxetanone **6**, its reaction with secondary amines, three aromatic **11a**−**c** and one nonaromatic **11d**, was then investigated. In this case the reaction proceeded smoothly under the previously described conditions but the only isolable products were the enaminoesters **12a**−**d**, either with 1 or 2 equiv of amine (Scheme 5). Compounds **12** resisted attack of a second amine molecule even if this attack was attempted on dispersions of **12** in refluxing dimethoxyethane. This difference in reactivity between imino- and enaminoesters **10** and **12** verifies the proposed structures, as will be discussed in detail.

The shielding effect of the phenyl group on the 4-H of the fused benzene ring is greater in compounds **12a**−**c** than that in the corresponding compounds **10**. This proton appears as a doublet at δ 5.60−5.70, a resonance value most unusual for aromatic protons, analogous to the conformation of the aryl ring of compounds **10**. X-ray structure determination of derivative **12a** verified this observation as is illustrated in Figure 2. The phenyl ring is almost perpendicular (84.5° tilt) to the ring system of C-12 to C-20 and hence the strong shielding effect of the hydrogen connected to C-17. This favorable less hindered conformation can be attributed to restricted rotation of the C−N(R′)Ph bond. As regards the greater shielding effect of the certain hydrogen, compared to the corresponding hydrogen in the iminoesters **10**, it can be explained in terms of the greater bulkiness of the R′ group in **12a**−**c** compared to that of the hydrogen in **10**. This bulkiness, combined with the lack of hydrogen bond developed between NH and CO in **10**, brings

SCHEME 6



13-17a: R = phenyl, **13-17b:** R = α-furyl, **13-17c:** R = benzyl

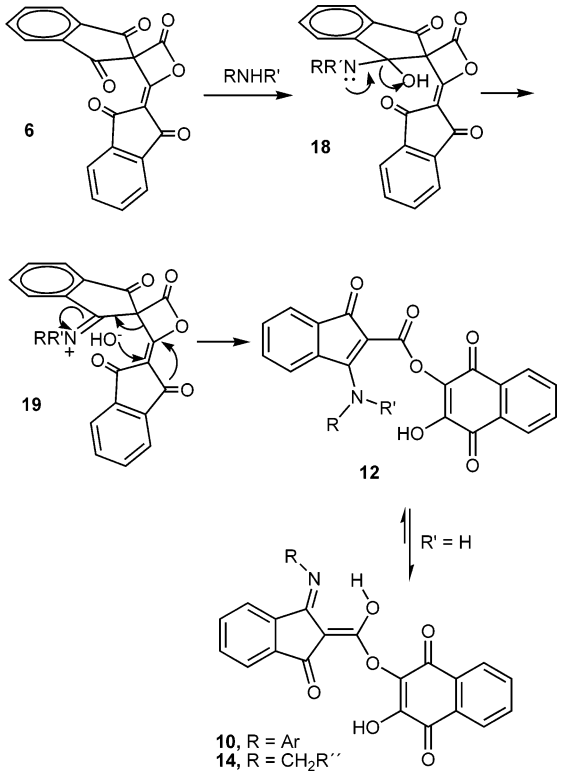
the phenyl group closer to the proton of C-17 and hence the upfield shift of the latter. It must be noted that this shielding effect is not observed in derivative **12d**, since in this compound the phenyl group is not directly attached to nitrogen and lies a greater distance from the proton that would be shielded.

This structure elucidation verifies the assumption that this ring expansion, from benzocyclopentenedione to naphthoquinone, takes place immediately after the first attack of the amine to the carbonyl of the spiro-cyclopentenedione ring of oxetanone **6**.

Finally, the reaction of the primary nonaromatic amines **13a**−**c** with oxetanone **6** was investigated and the results are shown in Scheme 6.

The reaction of oxetanone **6** with 1 equiv of amine **13** afforded the iminoesters **14a**−**c**, as in the case of primary aromatic amines. These compounds were isolated in high yields by crystallization from the reaction solution and exhibit no shielding of the 4-H of the fused benzene ring. Either by addition of 2 equiv of amine **13** in the initial reaction mixture or of 1 equiv in dispersions of pure isolated **14a**−**c** in dichloromethane, addition compounds **16a**−**c** were isolated in high yields. These compounds presumably arise from the Michael addition of amine to the enone system of **14a**−**c** to afford initially **15a**−**c**, which tautomerize to **16a**−**c**. Spectroscopic data strongly indicate that indeed these compounds exist in solution in the tautomeric form **16a**−**c**. Addition compounds **16a**−**c** are fairly stable even in refluxing dichloromethane. They are converted

SCHEME 7



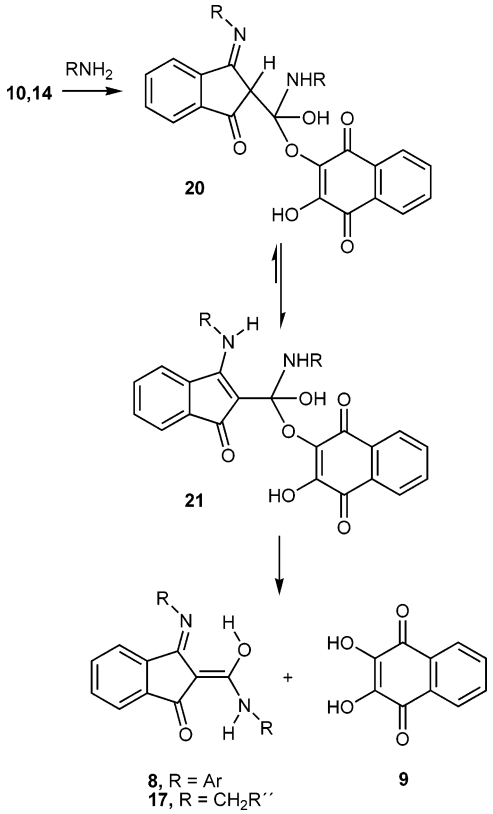
to the final iminoamides **17a**−**c** and 2,3-dihydroxy-1,4-naphthoquinone (**9**) only after heating in refluxing dimethoxyethane. These iminoamides exist also in an enol-amide form, analogous to that of compounds **8**, but no shielding effect for the corresponding 4-H is observed in ^{1}H NMR spectra. It is obvious that in this case there is no restriction in the rotation of the phenyl (or furyl) group due to its greater distance from the fused benzene ring.

It is most likely that compounds analogous to **16a**−**c** (or to their tautomers **15a**−**c**) are intermediates in the reaction of **6** with primary aromatic amines, although they have never been isolated or detected. In that case, the reaction proceeds spontaneously to afford the final iminoamides **8**.

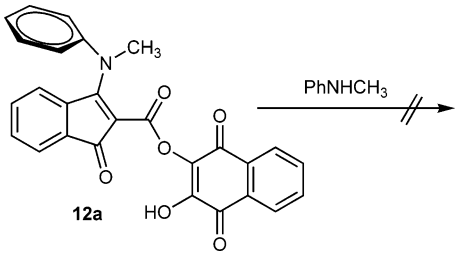
On the basis of all these findings the pathway for the reaction of oxetanone **6** with amines can be outlined. The reaction starts with nucleophilic attack of the amine to one of the carbonyls of the spiro-cyclopentenedione moiety to form **18**, which gives the iminium intermediate **19**. The latter initiates a skeletal rearrangement, which through ring expansion and attack of the hydroxy anion to the ethylenic carbon of the indanedione moiety leads to the enamino ester **12**, as shown in Scheme 7. In the case of secondary amines (R′ ≠ H) these compounds cannot react further with excess amine, as was already mentioned, and these compounds are isolated in the enaminoester form **12**. In the case of primary amines (R′ = H), a tautomerization takes place and these compounds are isolated in the form of iminoesters **10** and **14**, for aromatic and nonaromatic amines, respectively.

Whereas enaminoesters **12** do not react further with amine, the presence of the enone moiety in iminoesters **10** and **14** facilitates a Michael-type addition of the second equivalent of amine to afford **20**, which can tautomerize to **21** (Scheme 8). In the case of primary nonaromatic amines (R = CH_2R''), the intermediate **20** ⇄ **21** is stable and can be isolated (**15** ⇄ **16**).

SCHEME 8



SCHEME 9

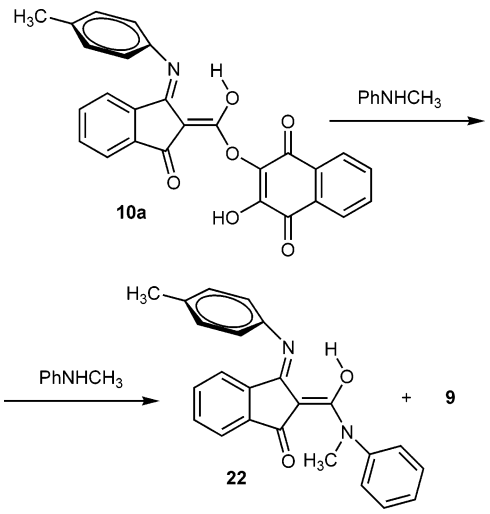


Finally, upon refluxing of the isolated intermediates **15** ⇄ **16** in dimethoxyethane, the iminoamides **17** and hydroxyquinone **9** are formed, whereas the corresponding iminoamides **8** (R = Ar) and compound **9** are obtained spontaneously without isolation of intermediates analogous to **15** or **16**. This difference in stability can be attributed to the different basicity of aromatic and nonaromatic primary amines.

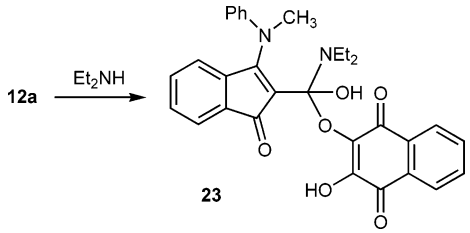
To verify that the difference in reactivity between enamino- and iminoesters **12** and **10** toward amines is the result of the enolic structure of the latter, the reaction of a representative derivative of both classes with a secondary amine was investigated. Whereas the reaction of enaminoester **12a** with *N*-methylaniline (**11a**) does not proceed at all, even in refluxing dimethoxyethane as was already mentioned (Scheme 9), the corresponding reaction of iminoester **10a** afforded the mixed iminoamide **22** and dihydroxyquinone **9** at room temperature (Scheme 10). This is a strong indication that indeed esters **10** exist in the enolic imino form and that the Michael-type addition of amine takes place at their enone moiety.

The observation that enaminoesters **12** cannot react further with secondary amines has an exception: From the reaction of **12a** with diethylamine at room temperature the addition product

SCHEME 10



SCHEME 11



23, analogous to **16**, was isolated. In this case it is most likely that diethylamine, being a stronger nucleophile, is able to attack the carbonyl of an enaminoester leading to the isolation of **23** (Scheme 11).

Moreover, the reaction of oxetanone **6** with 1 or 2 equiv of diethylamine afforded the enaminoester **24** and the addition product **25**, respectively. The latter is most stable and only after prolonged heating in dimethoxyethane afforded the enamine of indanedione **28** in moderate yield (Scheme 12). This compound presumably arises from the decarboxylation of the intermediate acid **27**, a hydrolysis product of the corresponding diethylamide **26**.

Spectroscopic data also support the suggested structures. In the IR spectrum, enaminoesters **12** exhibit carbonyl absorption at 1720−1740 cm^{-1}, indicating the presence of an ester group. This absorption is missing in the cases of compounds **10** and **14**, where the highest absorptions in the carbonyl region appear at 1660−1675 cm^{-1}, suggesting that these compounds exist in the enol form **A** and not in the ester form **B** in Figure 3 (X = O, R = Ar for **10**; X = O, R = CH_2R'' for **14**).

This enolic proton in ^1H NMR resonates at δ 10.60−10.90 (in $CDCl_3$ + DMSO-d_6) for **10** and **14**, whereas the hydrogen of the hydroxy group in the quinone ring is usually not observable. The corresponding enol proton in iminoamides **8** (**A**, X = NH, R = Ar) and **17** (**A**, X = NH, R = CH_2R'') appears as a broad singlet at δ 11.30−12.30 (in $CDCl_3$) and a second broad singlet at δ 9.50−10.90 is assigned to N−H.

In ^{13}C NMR a very characteristic and indicative peak for all compounds having the imino-enol structure **A** is that of a tertiary carbon at δ 97−99, which is assigned to C-2 (**A** in Figure 3). In the case of iminoesters **10** this peak, as well as other peaks for tertiary carbons, is hardly seen and the reason is the prolonged time needed to obtain a ^{13}C NMR spectrum, as these

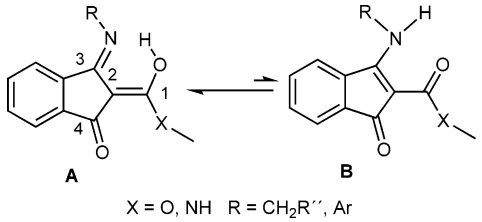
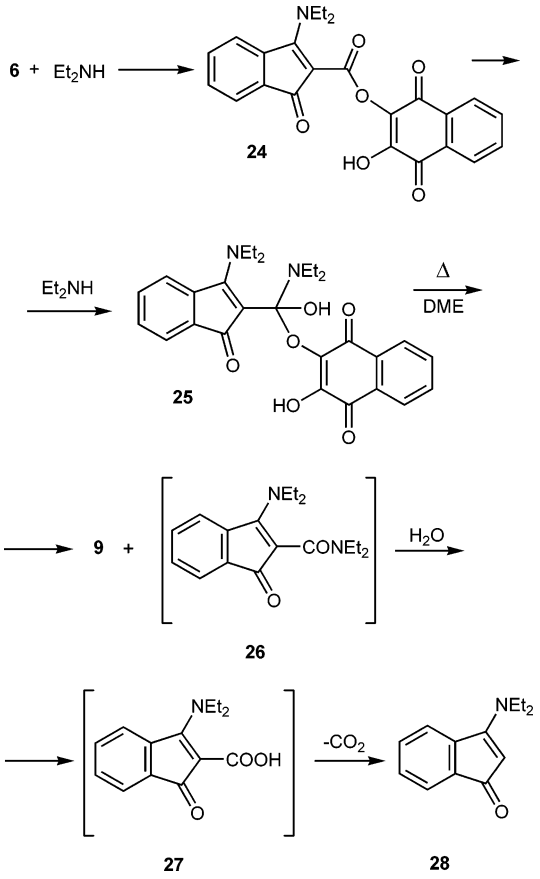


FIGURE 3. General structure of compounds **8**, **10**, and **14**.

SCHEME 12



compounds are highly insoluble. Iminoesters **10**, although stable in the solid state, start to decompose after some time in the NMR solvent ($CDCl_3$ + DMSO-d_6) and therefore clear spectra, at least for the tertiary carbons, cannot always be obtained. Other characteristic peaks in their ^{13}C NMR spectra are those at δ 189−190 for C-4, δ 169−170 for C-1, and δ 165−166 for C-3 (Figure 3).

Although spectroscopic data indicate that the imino form is the predominant one for compounds **8a**−**i** and **10a**−**i** in solution, X-ray crystal structure determination of **8b** revealed that it is crystallized in the enamino form presented in Figure 4.

Again two internal hydrogen bonds account for the stability of the molecule but the tilt (48.8°) of the *o*-tolyl ring does not justify well the shielding of the proton connected to C-5 (δ 6.29) as is clearly shown from a different view of the same structure. This is another indication that indeed in solution the predominant structure is the imino one accounting better for the observed upfield shift of the corresponding proton.

In conclusion, oxetanone **6**, obtained most conveniently from the thermal transformation of phenyliodonium ylide **4** and possessing an unusual tetraoxo spiro structure, exhibits an

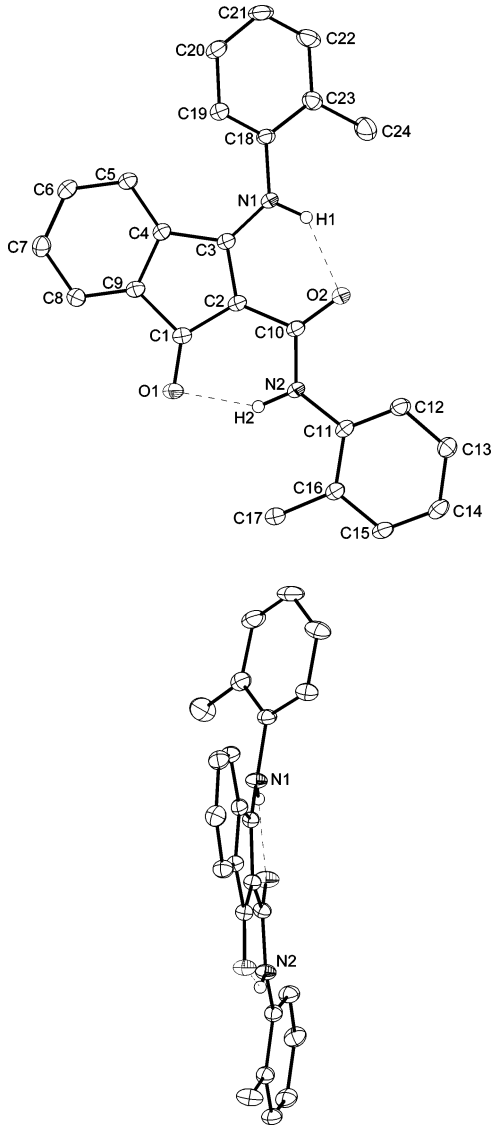


FIGURE 4. Two views of the ellipsoid drawing (35% probability) of **8b**.

interesting reactivity toward amines. Although the reaction path, involving as a first step the attack of amine to the carbonyl of the spiro-cyclopentenedione moiety, is the same for all amines, stability and isolation of intermediary products depends mainly on the nature of the amine. This study has shown that oxetanone **6** (as well as analogous oxetanones possibly accessible in the same way from other aryliodonium ylides) has the potential to be an interesting building block in organic synthesis. For this reason the investigation of its reactivity with other types of nucleophiles is now in progress.

Experimental Section

Indanedioneketene dimer, **4′-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)spiro[indene-2,3′-oxetane]-1,2′,3-trione** (**6**), was prepared as described in a previous publication.[4] Yields up to 95−98% can be obtained if a scale of 3−4 mmol of ylide **4** in 30−40 mL of dry CH_2Cl_2 is used.

General Procedure for the Reaction of Oxetanone 6 with Primary Aromatic Amines 7a−i. A. Reaction with 2 equiv of Amine. A solution of the aromatic amine **7a−i** (0.6 mmol) in CH_2Cl_2 (3 mL) was added to a stirred suspension of oxetanone **6** (0.3 mmol) in CH_2Cl_2 (4 mL) and stirring was continued overnight. The red crystals of dihydroxynaphthoquinone **9** (yields 80−85%) were filtered off and the filtrate was concentrated and chromatographed on column (silica gel, hexanes−ethyl acetate 3:1) to afford the iminoamides **8a−i**. The isolated derivatives **8a−i** were pure enough but analytical samples were obtained by recrystallization from CH_2Cl_2−hexanes. For simplicity reasons compounds **8a−i** are named according to their amide tautomeric form (e.g., compound **8a** in its enol-amide form should be named (2*E*, 3*E*)-2-{hydroxy[(4-methylphenyl)amino]methylene}-3-[(4-methylphenyl)imino]indan-1-one).

Quinone **9** was also prepared following a reported method[10] and its spectra were in all respects identical with the ones reported in the literature.[11]

B. Reaction with 1 equiv of Amine. A solution of the aromatic amine **7a−i** (0.3 mmol) in CH_2Cl_2 (3 mL) was added to a stirring suspension of oxetanone **6** (0.3 mmol) in CH_2Cl_2 (4 mL) and stirring was continued until a clear orange-colored solution resulted (30−60 min), except in the cases of the para-substituted anilines **7a**, **7c**, and **7g** where the reactions were completed almost immediately. By addition of hexanes (∼10 mL) to the reaction mixture iminoesters **10a−i** were precipitated and isolated by filtration. The yellow solids were washed repeatedly with a mixture of hexanes−dichloromethane (3:1) and were pure enough. No further purification was possible due to their tendency to decompose upon attempted recrystallization. The fitrate was concentrated and subjected to column chromatography (silica gel, hexanes−ethyl acetate 3:1) to afford the iminoamides **8a−i** in yields ranging from 13% to 20%. The other product of the reaction, dihydroxyquinone **9,** was detected by TLC but it could not be isolated by either crystallization or column chromatography.

The reaction of **6** with 2 equiv of primary amine **7a** was also repeated in two steps: The iminoester **10a** (0.1 mmol), isolated with the addition of the corresponding amine **7a** as described above, was dispersed in CH_2Cl_2 (4 mL) and 0.1 mmol of the same amine was added under stirring. The procedure was continued as in the case of reaction of **6** with 2 equiv of amine to afford iminoamide **8a** and hydroxyquinone **9** in 80% yield.

General Procedure for the Reaction of Oxetanone 6 with Secondary Amines 11a−d. A solution of the secondary amine **11a−d** (0.3 mmol) in CH_2Cl_2 (3 mL) was added to a stirring suspension of oxetanone **6** (0.3 mmol) in CH_2Cl_2 (4 mL) and stirring was continued until a clear orange-colored solution resulted (15−60 min). By gradual addition of hexanes (∼10 mL) to the reaction mixture enaminoesters **12a−d** were precipitated and isolated by filtration. The orange-yellow solids were washed repeatedly with a mixture of hexanes−dichloromethane (3:1) and recrystallized from dichloromethane−hexanes.

General Procedure for the Reaction of Oxetanone 6 with Primary Nonaromatic Amines 13a−c. The same procedure described above for secondary amines was followed.

Reaction of Compounds 14a−c with Amines 13a−c. A solution of the amine **13a−c** (0.1 mmol) in CH_2Cl_2 (2 mL) was added to a stirring suspension of compound **14a−c** (0.1 mmol) in CH_2Cl_2 (2 mL) and stirring was continued until a clear red-orange solution resulted (15−60 min). By addition of hexanes (3−4 mL) to the reaction mixture the addition compounds **16a−c** were precipitated and isolated by filtration. The red-orange solids were washed repeatedly with a mixture of hexanes−dichloromethane (3:1).

Thermal Transformation of Addition Compounds 16a−c to Iminoamides 17a−c. Dispersions of addition compounds **16a−c** (0.2 mmol) in DME (3 mL) were refluxed for 2 h. The resulting red solution was concentrated to dryness, CH_2Cl_2 (3 mL) was added, and the red crystals of dihydroxyquinone **9** were filtered off. The

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(11) Khandagale, P.; Chikate, R.; Joshi, S. B.; Kulkarni, B. A. *J. Alloys Compds.* **2005**, *392*, 112.

filtrate was concentrated and chromatographed on column (silica gel, hexanes−ethyl acetate 3:1) to afford the iminoamides **17a**−**c**. The isolated derivatives **17a**−**c** were pure enough but analytical samples were obtained by recrystallization from CH_2Cl_2−hexanes.

Compounds **16a**−**c** and **17a**−**c** were also obtained from the reaction of oxetanone **6** with excess amounts (2.5−3.0 mmol) of the corresponding amines **13a**−**c** in 62−65% and 16−18% yields, respectively.

Reaction of 10a with *N*-Methylaniline (11a). A solution of *N*-methylaniline (**11a**) (0.3 mmol) in CH_2Cl_2 (3 mL) was added to a stirring suspension of iminoester **10a** (0.3 mmol) in CH_2Cl_2 (4 mL) and stirring was continued overnight. The precipitated dihydroxyquinone **9** was filtered off and the concentrated filtrate was subjected to column chromatography to afford ***N*-methyl-3-[(4-methylphenyl)amino]-1-oxo-*N*-phenyl-1*H*-indene-2-carboxamide** (**22**). Yield 80%: mp 142−145 °C; IR (KBr) 1617, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 11.30 (br s, 1H), 7.38−7.25 (m, 10H), 7.18 (t, J = 6.9 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.46 (d, J = 7.8 Hz, 1H), 3.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 185.5, 169.2, 168.3, 145.7, 138.2, 136.0, 135.0, 134.7, 132.0, 130.8, 130.1, 128.8, 126.3, 125.9, 125.8, 123.2, 121.6, 100.4, 38.7, 21.2; EI-MS *m*/*z* (%) 368 (M^+, 7), 261 (100), 107 (78). Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 77.89; H, 5.81; N, 7.90.

Reaction of 12a with Diethylamine. The reaction under the previously described conditions was completed in a few minutes. Addition of hexanes to the reaction mixture afforded **2-[(diethylamino)(hydroxy){3-[methyl(phenyl)amino]-1-oxo-1*H*-inden-2-yl}methoxy]-3-hydroxynaphthoquinone** (**23**). Yield 88%: mp 146−147 °C; IR (KBr) 1698, 1677, 1628 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.07−7.99 (m, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.56−7.47 (m, 5H), 7.45−7.37 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.00 (t, J = 7.7 Hz, 1H), 5.55 (d, J = 7.9 Hz, 1H), 3.96 (s, 3H), 3.09 (q, J = 7.0 Hz, 4H), 1.35 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 190.2, 187.2, 176.3, 170.4, 162.4, 162.2, 145.2, 137.2, 135.8, 133.6, 133.4, 131.8, 131.5, 131.3, 131.0, 130.2, 129.3, 126.8, 126.0, 125.8, 124.3, 121.6, 101.3, 49.2, 42.3, 11.6; ESI-HRMS *m*/*z* calcd for $C_{31}H_{28}N_2O_6$ + H (MH^+) 525.20201, found 525.20164.

Reaction of Oxetanone 6 with 1 and 2 equiv of Diethylamine. The reactions were conducted under the same conditions described previously for nonaromatic primary amines and compounds **24** and **25** were isolated, respectively.

3-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl 3-(diethylamino)-1-oxo-1*H*-indene-2-carboxylate (24): Yield 57%; mp 186−188 °C; IR (KBr) 1727, 1682, 1663, 1639 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 300 MHz) δ 8.11−8.01 (m, 2H), 7.82−7.68 (m, 3H), 7.67−7.58 (m, 3H), 4.12−3.97 (m, 4H), 1.48 [t (broad), $J \approx$ 6.8 Hz, 6H]; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 75 MHz) δ 186.7, 180.0, 167.1, 161.3, 159.9, 148.5, 135.1, 133.1, 132.0, 131.2, 130.8, 129.8, 129.6, 125.8, 124.9, 124.4, 123.6, 120.7, 48.2, 12.0; ESI positive 440 $(M + Na)^+$, 418 $(M + H)^+$. Anal. Calcd for $C_{24}H_{19}NO_6$: C, 69.06; H, 4.59; N, 3.36. Found: C, 68.77; H, 4.59; N, 3.05.

2-{(Diethylamino)[3-(diethylamino)-1-oxo-1*H*-inden-2-yl]hydroxymethoxy}-3-hydroxynaphthoquinone (25): Yield 95%; mp 107−108 °C; IR (KBr) 1670, 1629 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.04 (d, J = 7.5 Hz, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.64−7.56 (m, 3H), 7.54−7.46 (m, 3H), 4.07 (q, J = 6.9 Hz, 4H), 3.06 (q, J = 7.2 Hz, 4H), 1.47 (t, J = 6.9 Hz, 6H), 1.31 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 188.9, 187.1, 176.3, 171.1, 162.8, 162.2, 137.1, 136.3, 133.7, 133.4, 132.1, 131.9, 131.5, 130.9, 125.9, 125.7, 124.1, 122.0, 99.5, 53.4, 42.1, 13.5, 11.5; ESI-HRMS *m*/*z* calcd for $C_{28}H_{30}N_2O_6$ + H (MH^+) 491.21766, found 491.21755.

Thermal Decomposition of Compound 25. Prolonged heating (20 h) of a suspension of **25** in dimethoxyethane afforded after column chromatography (silica gel, ethyl acetate) **3-(diethylamino)-1*H*-inden-1-one** (**28**). Yield 54%; oil; IR (KBr) 1690, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.47 (d, J = 6.4 Hz, 1H), 7.33−7.29 (m, 3H), 4.89 (s, 1H), 3.62 (broad, 4H), 1.37 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.6, 166.9, 137.3, 130.5, 130.1, 121.6, 120.7, 94.4, 47.2 (br), 13.5 (br); EI-MS *m*/*z* (%) 201 (M^+, 69), 172 (51), 158 (100). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.32; H, 7.39; N, 7.07.

X-ray Crystal Structure Determination. Single crystals suitable for X-ray structure determinations were obtained by adding diethyl ether to a solution of **8b** or **12a** in methylene chloride. All C, N, and O atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located and their positions refined for the amine and hydroxy hydrogen atoms; all other hydrogen positions were calculated for idealized positions.

Supporting Information Available: Spectral and analytical data for compounds **8a**−**i**, **10a**−**i**, **12a**−**d**, **14a**−**c**, **16a**−**c,** and **17a**−**c** and X-ray crystallographic files (CIF) for **8b** and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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