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# Synthesis of Spiro and Fused Five Membered *N*-Heterocycles from Alkylidenephosphoranes

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**Summary.** Triketoindan-2-oxime reacted readily with ethoxycarbonylmethylene triphenylphosphorane to give mainly the corresponding spiro-pyrrole (38%) along with the fused 1′-hydroxydihydropyrrole (14%), whereas the spiro-dimer (29%) was obtained from the reaction of the oxime with methoxycarbonylmethylenetriphenyl phosphorane in addition to the corresponding 1′-hydroxydihydropyrrole (31%). Conversely, *Wittig* products, mono-olefin (52%) and diolefin (<7%) along with the reduced substrate (10%), were observed when the oxime was treated with a cyano ylide. The reactions of the oxime with allyl- and vinyl phosphonium salts proceeded under phase-transfer catalysis to afford fused oxazole (46%) and spiro[2]oxazole (17%), while with the latter the fused 1′-hydroxypyrrole (55%) was produced.

**Keywords.** *Wittig* reaction; $\alpha$-Iminoketones; Spiro-compounds; Fused *N*-heterocycles.

## Introduction

Reactions of phosphorus ylides with $\alpha$-iminoketones have received attention within the past two decades [1, 2]. The methodology has led to the construction of versatile nitrogen containing heterocycles of potential pharmacological values. In the preceding communication we reported the synthesis of quinolines, indoles, and benzoxazoles by treating phenanthren-9,10-quinone monoxime with the appropriate phosphorus ylide [3]. Similarly, indoles, indazoles, 1,4-benzoxazin-2-ones, cinnolines, and benzoxazoles as well as a series of 1,4-benzoxazines were also synthesized [4].

The work described in this paper involves the reactions of 1,2,3-trioxo-2-indan monoxime (**1**) [5a] with alkoxycarbonylmethylene-**2a**, **2b** and cyanomethylenetriphenyl-phosphorane (**3**) as well as the relevant unsaturated phosphonium

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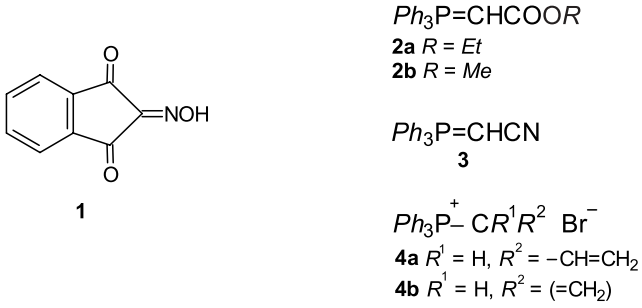
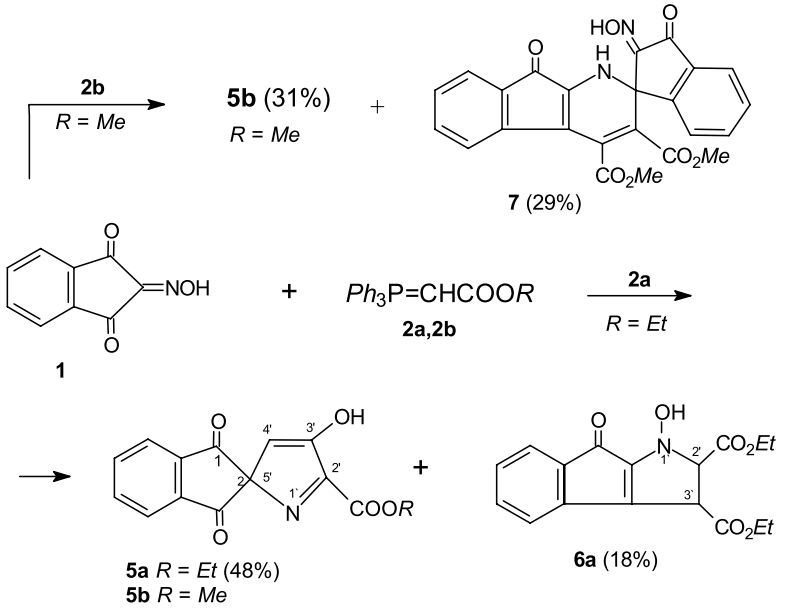



**Fig. 1.** Formulae of compounds **1**, **2a**, **2b**, **3**, **4a**, and **4b**

salts **4a** and **4b**, in order to synthesize spiro-*N*-heterocycle, oxazole, and pyrrole containing compounds.

## Results and Discussion

Treatment of **1** with the ylide **2a** (two molar amounts) in chloroform solution at room temperature afforded ethyl 3′-hydroxy-1,3-dioxospiro[indan-2,5′-pyrrole-2′-carboxylate] (**5a**, 48%) as the major product in addition to diethyl 2′,3′-dihydro-1′-hydroxy-1-oxoindan[2,3-*b*]pyrrole-2′,3′-dicarboxylate (**6a**, 18%). A similar treatment of **1** with **2b** gave unexpectedly spiro-dimer **7** together with **5b** in almost equal yields (∼30%) (Scheme 1). Repetition of the reactions between equimolar amounts of the substrates **1** and **2a**, or **2b**, again afforded **5a** (21%) and **6a** (8%) or **5b** and **7** in ∼18% yield. The starting material **1** (30%) was also isolated in each




**Scheme 1**

case from the latter reaction. The chemical structures **5a**, **5b**, **6a**, and **7** were in accord with the elemental analyses, molecular weight measurements (MS), and the spectroscopic data. The IR spectra of **5a** and **5b** exhibited the presence of carbonyl stretching vibration bands (1775–1700 $cm^{-1}$), thus excluding any cycloaddition reaction involving these moieties. Their $^{13}C$ NMR spectra displayed two signals at $\delta \sim 73$, 153 ppm assignable to spiro-C and 3′-C–OH.

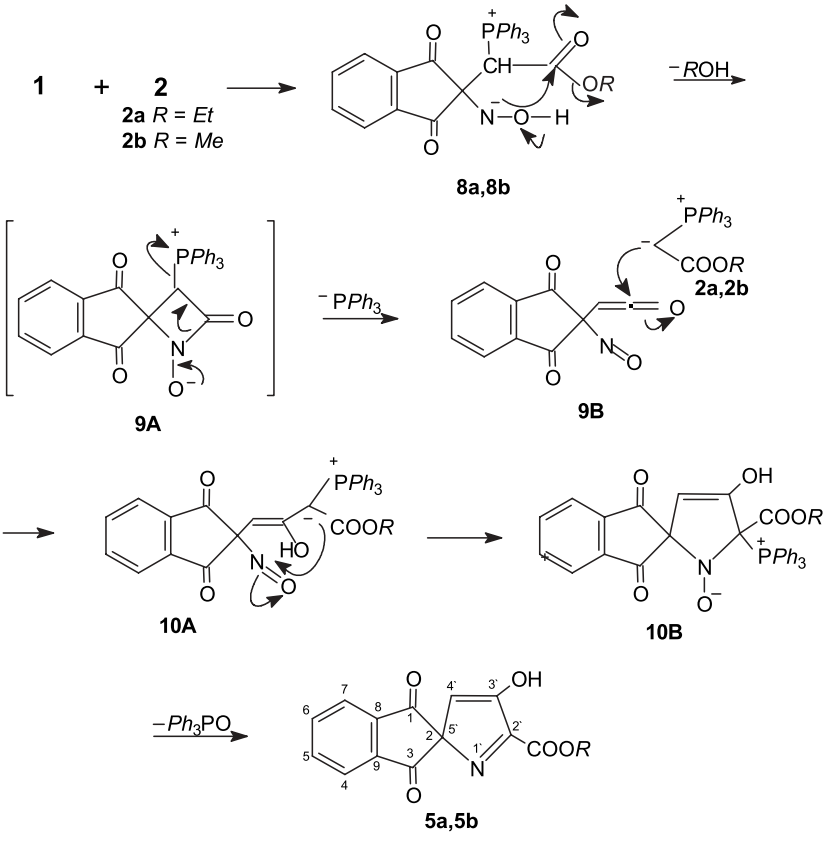
In contrast, the $^{1}H$ NMR spectrum of **6a** showed the presence of two doublets ($J = 9.8$ Hz) at $\delta = 4.82$ and 5.39 ppm assignable to the pyrroline 2′-H and 3′-H. The 2′-C and 3′-C atoms in the $^{13}C$ NMR spectrum of **6a** appeared at $\delta = 58.3$ and 61.1 ppm. On the other hand, the 1′-hydroxyl-proton resonance of **6a** was clearly seen as a broad band at $\delta = 12.41$ ppm, although it could not be detected in the $^{1}H$ NMR spectra in some cases of 1-hydroxyindoles [5b]. Treatment of **6a** with benzoyl chloride in pyridine gave the expected *O*-benzoylated derivative **6b** in 62% yield. The oxidation of **6a** with *N*-bromosuccinimide (*NBS*) in carbon tetrachloride containing a catalytic amount of benzoyl peroxide gave the dehydrogenated product **13** (67%). Meanwhile, the dehydration of **6a** with polyphosphoric acid (*PPA*) led to the indenepyrrolone **14** in a satisfactory yield (50%) (Scheme 3).

The spectroscopic results clearly demonstrated that in case of the spiro-dimer **7** no isomeric oximes arised. The oxime diastereomerism (*Z*/*E*) of **7** can not be, however, assigned with certainty. The mass spectrum of **7** indicated the presence of ion peaks at 412 [444–32 (*Me*OH)], 397 [412–15 (*Me*)], 338 [397–59 ($CO_2Me$)], 310 [338–28 ($CO_2$)], and 279 [338–59 ($CO_2Me$)], which can originate *via* cleavage of the molecular ion peak at *m*/*z* (%): 444 (100) [$M^+$].

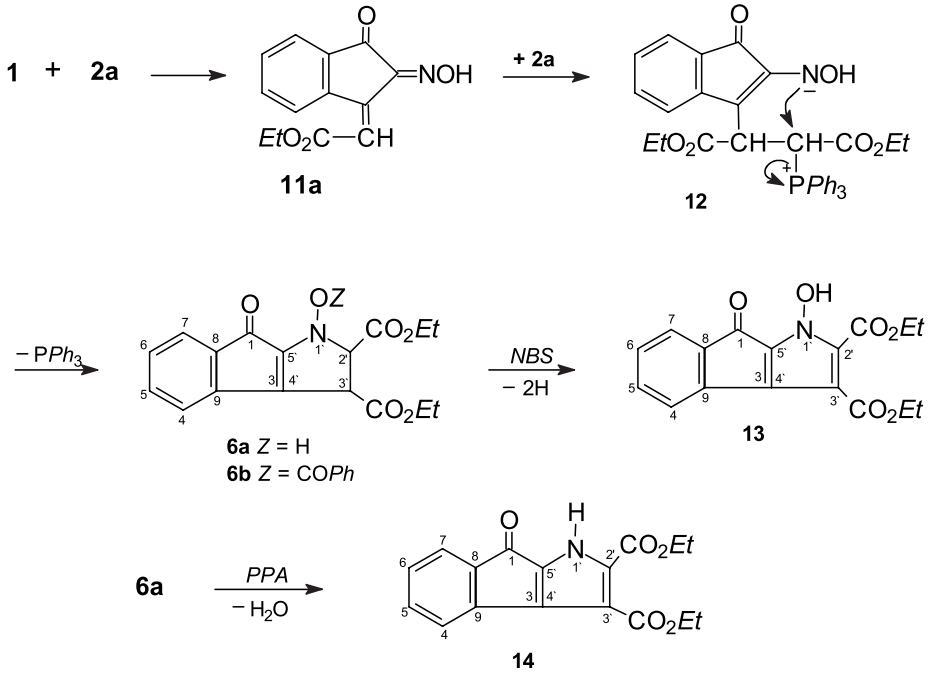
A reasonable mechanistic explanation for these transformations is outlined in Schemes 2–4. The formation of compounds **5a** and **5b** can be interpreted in terms of an initial nucleophilic attack of the ylidic carbon in **2a** and **2b** on the 2-hydroxyimino carbon (2-C=NOH) [6] with subsequent ring closure to afford **9A** *via* the intermediates **8a** and **8b**. Under elimination of an appropriate alcohol moiety the zwitterion **9A** is presumably formed. The cleavage of spiroazetidinone **9A** affords the reactive ketene species **9B** through the extrusion of triphenylphosphine. Further attack of a second ylide species **2** at an $sp^2$ carbon in **9B** would afford the betaine **10A**. An intramolecular attack of the betaine carbon on the nitroso group in **10A** would produce the final products **5a** and **5b** *via* **10B** with concomitant elimination of triphenylphosphine oxide (Scheme 2).

The formation of **6** can be rationalized by an initial *Wittig* olefination of **1** leading to the intermediate **11**. Further 1,4-addition of a second ylide **2a** to **11**, followed by an intramolecular cyclisation involving the ylide carbon and subsequent loss of triphenylphosphine would result in the product **6a** (Scheme 3 [4c, 7]). It is also noteworthy that the MS analysis of a crude sample of the mixture of **1** + **2a** indicated the formation of the ethyl derivative of the spiro-dimer **7** (*m*/*z* 472). However, the results of an $^{1}H$ NMR analysis performed on the crude reaction mixture were far from conclusive. Notwithstanding, perusal of the literature indicated the similar behavior of **2a** and **2b** as well as their phosphoryl carbanion counterparts toward electrophiles, but there are some instances known where they behave differently [8].

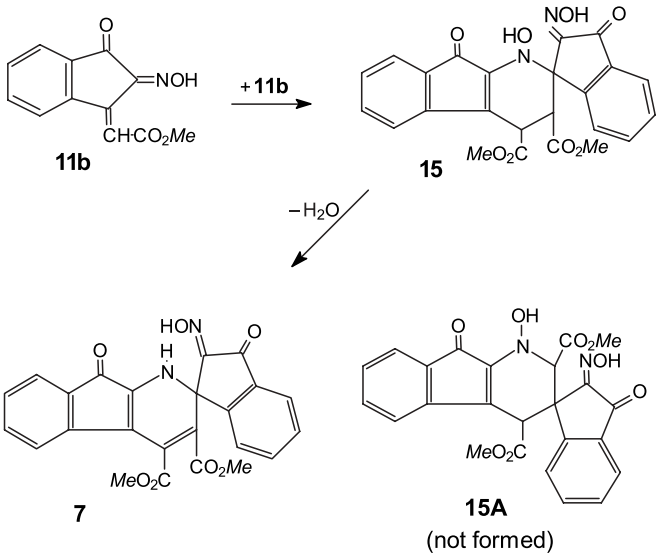
Most probably, the formation of **7** involves the transformation of the initially formed **11b** to **15** by a process of homodimerisation. Elimination of water from **15**




**Scheme 2**




**Scheme 3**




**Scheme 4**

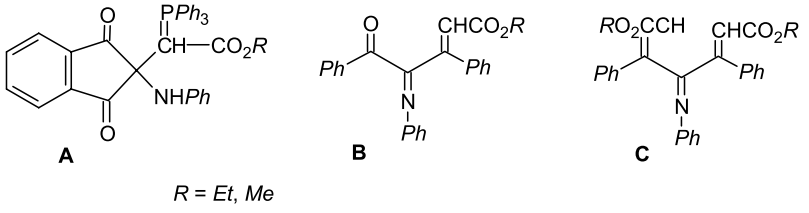
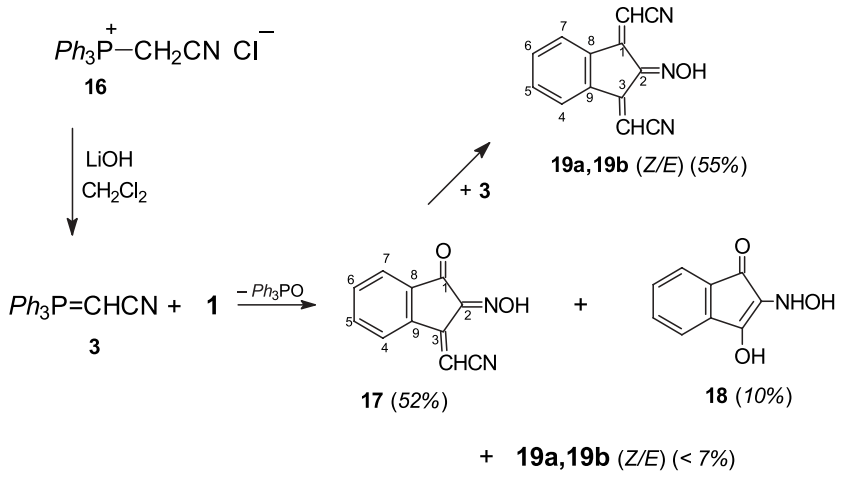



**Fig. 2.** Formulae of *Wittig* products **A**, **B**, and **C**

leads to the spiro-dimer **7** (Scheme 4). The formation of the other possible intermediate, the regio-dimer **15A** was excluded, as the intermediacy of **15A** could not explain the presence of the NH function in the final spiro-product **7**. Analogous dimerisations were also observed from some unstable *o*-quinone methide imines [9a] and by heating the *Wittig* product of 10-(methoxyimino)phenanthren-9-one [9b].

In contrast to the above results obtained from the reaction of **1** with **2a** and **2b**, it was reported that the ylides **A** were isolated by applying the *Wittig* reagents **2a** and **2b** on 2-phenylimino-1,2,3-indanetrione [10a], whereas the *Wittig* products **B** and/or **C** were obtained when using 1,3-diphenyl-2-(phenylimino)-1,3-propanedione [10b].

When **1** was treated with two equivalents of cyanomethylenetriphenylphosphorane **3**, prepared *in situ* from the phosphonium salt **16** by addition of an aqueous solution of LiOH (0.5 *N*) in dichloromethane, the olefin **17** (52%) and a mixture (<7%) of stereoisomers of the diolefin **19** were obtained along with 3-hydroxy-2-hydroxyamino-1H-inden-1-one **18** (10%). The products **17**–**19** were obtained in similar ratio, irrespective whether one or two mole equivalents of **16** were used. However, no reaction was observed when **1** was stirred in a mixture of



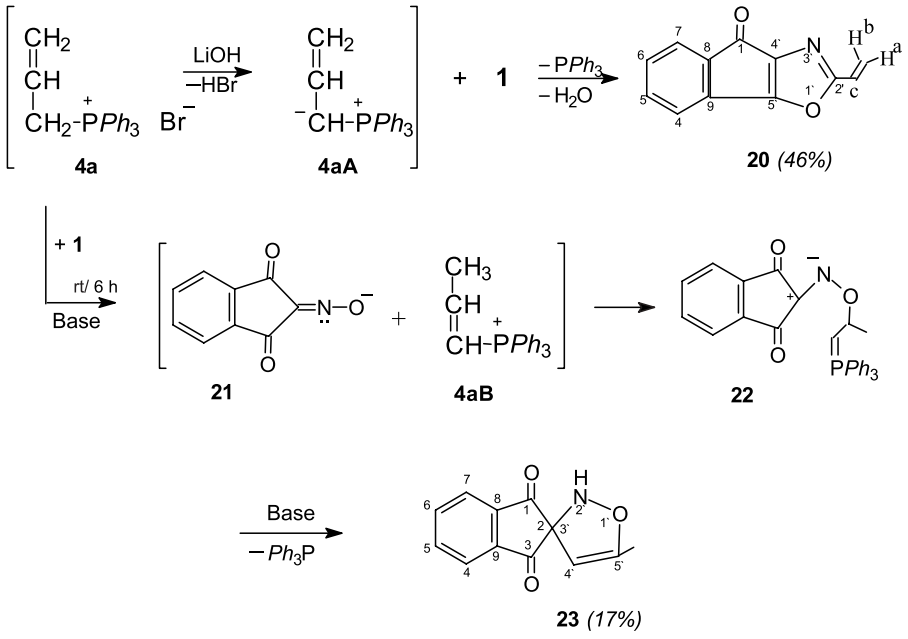

**Scheme 5**

dichloromethane containing an aqueous solution of LiOH (0.5 *N*) for 48 h. Compound **1** (>90%) was recovered unchanged and there was no indication of the formation of the reduced form **18** (TLC).

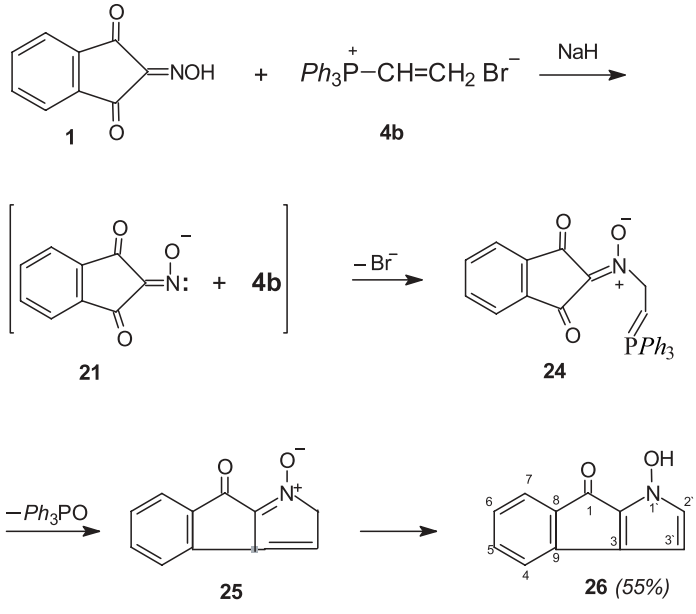
Otherwise, treating **17** with one equivalent of **3** in a mixture of $LiOH/H_2O/CH_2Cl_2$, in a way analogous to the one described above, **19a** (18%) and **19b** (37%) were obtained (Scheme 5). The mono-methanide **17** was obtained as a single diastereomer. Its configuration could not be assigned unequivocally. The *cis*-configuration for the dimethanides **19a** and **19b** (*Z*) was suggested according to $^1$H NMR chemical shifts and melting points. The down-field shift of the signals of the olefinic proton and the melting points observed for the isomers suggested a *cis*-configuration because they are higher than those of the corresponding *trans*-isomer, in agreement with Ref. [11].

Next, we studied the reactions of **1** with unsaturated phosphonium salts **4a** and **4b** as shown in Schemes 6 and 7. Treatment of **1** with allyltriphenylphosphonium bromide **4a** in a mixture of $LiOH/H_2O/CH_2Cl_2$ yielded 1-oxo-2′-vinylindan[2,3-*d*]-1,3-oxazole (**20**, 46%) and 5′-methylspiro[1,3-dioxoindan[2,3′]-(2′H)-1′,2′-oxazole] (**23**, 17%). Similar to **20**, oxazolo fused derivatives were obtained previously [4b, 4c, 12] from the reaction of $\alpha$-iminoketones with **4a**. Meanwhile, the mechanism for the formation of the spiro[2]oxazole **23** can be rationalized through the attack of the initially formed oxygen anion **21** on the $\beta$-carbon atom of the ylide **4aB**, to generate the intermediate **22**. Extrusion of triphenylphosphine and proton rearrangement affords the final product **23** (Scheme 6). The electrophilic attack at the central atom of the allyl group in **4aB** is a known process [13]. Furthermore, the ready elimination of triphenylphosphine from **22** in the second step occurs through a carbanion mechanism, driven by the resulting gain in aromaticity.

On the other hand, treating **1** with one equivalent of NaH in THF followed by one equivalent of **4b** yielded 1′-hydroxy-1-oxoindan[2,3-*d*]pyrrole (**26**, 55%) (Scheme 7). The structure elucidation of **26** was based on the elemental analysis, molecular weight determination (MS), and spectroscopic data. Its IR spectrum exhibited an intense band at $\bar{\nu} = 1728\,\mathrm{cm}^{-1}$ corresponding to the 1-C=O and a




**Scheme 6**




**Scheme 7**

broad OH stretching frequency at $\bar{\nu} = 3315\,\mathrm{cm}^{-1}$. The $^1$H NMR spectrum of **26** showed two doublets ($J = 2.8$ Hz) at $\delta = 6.34$ and 6.78 ppm that were assigned to the AB pattern of the pyrrole ring positions 2′ and 3′. *N*-hydroxypyrrole **26** may be regarded as a product of an intramolecular *Wittig* reaction. Such an addition-cyclization product apparently results from initial attack of the anion **21** to **4b** to form the phosphorane **24**, which is converted into **26** according to Scheme 7. An

analogous mechanism has been previously reported by *Schweizer* [14a] and recently by *Yavari* et al. [14b] for the reaction of vinyltriphenylphosphonium bromide **4b** with $\alpha$-iminocarbonyl compounds.

## Conclusion

In view of all the facts mentioned in the present and the previous [3, 4] studies, it can be concluded that $\alpha$-iminocarbonyl compounds undergo different courses of reactions in the presence of various alkylidenephosphoranes or the relevant salts, to yield spiro-, fused-, linear heterocycles, or that unexpected products. The divergent pathways in Scheme 1 are, in fact, consequences of different stoichiometeries rather than a result from the differences in ylide structure. The nature and the structure of the substrate, the $\alpha$-substituent of the ylide used, and the experimental conditions (solvent, catalyst, and temperature) most significantly, however, affect the course of the reactions in Schemes 5–7.

## Experimental

The melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer spectrophotometer model 297 MHz using KBr discs. The $^1$H and $^{13}$C NMR spectra were recorded on a JNM-GX-400 Joel spectrometer, using *TMS* as internal reference. The mass spectra were taken at 70 eV on an MS-50 Kratos (A.E.I.) spectrometer provided with a data system. Elemental analyses were found to be in good agreement with the calculated values. Appropriate precautions in handling moisture-sensitive compounds were observed. Materials and reagents were purchased from Aldrich.

### *Reaction of 1,2,3-Trioxo-2-indanmonoxime* **1** *with Ester Ylide* **2a**, *Preparation of Compounds* **5a**, **6a, 6b**, **13**, *and* **14**

To a stirred solution of 3.27 g of ethoxycarbonylmethylenetriphenylphosphorane (**2a**) (9.1 mmol) in 20 cm$^3$ of anhydrous $CHCl_3$ was added dropwise within 30 min a solution of 0.8 g of **1** [15] (4.57 mmol) in 15 cm$^3$ of the same solvent. The reaction mixture was further stirred at rt for 24 h (TLC). After removing the solvent, the residue was chromatographed on silica gel using *n*-hexane/*Ac*O*Et* as the eluent.

*Ethyl 3′-hydroxy-1,3-dioxospiro[indan-2,5′-pyrrole-2′-carboxylate]* (**5a**, $C_{15}H_{11}NO_5$)

Obtained (7:3, *V*/*V*) as straw yellow crystals (360 mg, 48%), mp 131–133°C ($CH_2Cl_2$); $^1$H NMR ($CDCl_3$): $\delta = 1.37$ (t, $J = 7.2$ Hz, $OCH_2CH_3$), 4.34 (q, $J = 7.2$ Hz, $OCH_2$), 6.32 (s, 4′-CH), 7.48–7.55 (m, 5-, 6-CH(Ar)), 7.72–7.86 (m, 4-, 7-CH–Ar), 12.3 (br s, C–OH) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 15.4$ ($CH_3$), 62.8 ($OCH_2$), 74.2 (spiro-C), 115.4 (4′-C), 123.2, 123.7 (5-C, 6-C), 124.0, 124.4 (8-C, 9-C), 125.6, 125.8 (4-C, 7-C), 144.2 (2′-C), 153.4 (3′-C), 161.4 (C(O), ester), 168.4, 180.6 (1- + 3-C(O)) ppm; MS: $m/z$ (%) = 285 (100) [M$^+$], 270 (7), 242 (25), 240 (33), 212 (16), 186 (28) 126 (55), 112 (37); IR (KBr): $\bar{\nu} = 3420$ (OH), 1771, 1735 (1- + 3-C(O)), 1719 (C(O), ester), 1585, 1548 (C=N, C=C) cm$^{-1}$.

*Diethyl 2′,3′-dihydro-1′-hydroxy-1-oxoindan[2,3-b]pyrrole-2′,3′-dicarboxylate* (**6a**, $C_{17}H_{17}NO_6$)

Obtained (1:1, *V*/*V*) as pale-yellow flakes (255 mg, 18%), mp 153–155°C (acetonitrile); $^1$H NMR ($CDCl_3$): $\delta = 1.21$–$1.33$ (m, $2CH_3$), 4.17–4.31 (m, $2OCH_2$), 4.82 (d, $J = 9.8$ Hz, 2′-C–H), 5.39

(d, $J = 9.8$ Hz, 3′-C–H), 7.55–7.86 (m, 3ArH), 8.19 (dd, $J = 2, 7$ Hz, *peri*H), 12.41 (br s, $D_2O$ exchangeable, –NOH) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta = 14.6, 15.1$ ($2CH_3$), 58.3, 61.1, 62.4, 62.7 (2′-, 3′-CH; $2OCH_2$), 113.5 (4′-C) 121.5 (9-C), 123.6, 124.2 (5-C, 6-C), 124.9 (8-C), 125.6 (7-C), 133.1 (4-C), 143.2 (5′-C), 159.6, 161.8, 168.8 (3C(O)) ppm; MS: $m/z$ (%) = 331 (14) [$M^+$], 329 (100), 313 (55), 298 (13), 283 (23), 255 (17), 227 (33), 214 (9), 126 (33), 112 (35); IR (KBr): $\bar{\nu} = 3260$ (NOH), 1728 [1-C(O)], 1722–1718 (2C(O), esters) $cm^{-1}$. $Ph_3P$ and $Ph_3PO$ were isolated and identified from the reaction.

*Benzoylation of* **6a**, *Preparation of* **6b**

Benzoyl chloride (0.15 g, 1.1 mmol) was added to a solution of 0.3 g of **6a** (0.9 mmol) in 5 $cm^3$ of dry pyridine. The reaction mixture was allowed to stand for 2 days at rt. The product mixture, with a small amount of pyridine hydrochloride present, was poured onto 40 g of crushed ice. Stirring and scratching afforded a pale-yellow solid, which was filtered and washed with 15 $cm^3$ of ice-$H_2O$, air-dried, and recrystallized from a small amount of $CH_2Cl_2$ to give a pure sample of 0.24 g (62%) of **6b** ($C_{24}H_{21}NO_7$), mp 174–176°C; $^1H$ NMR ($CDCl_3$): $\delta = 1.21–1.33$ (m, $2CH_3$), 4.15–4.28 (m, $2OCH_2$), 4.78 (d, $J = 9.8$ Hz, 2′-CH), 5.36 (d, $J = 9.8$ Hz, 3′-CH), 7.57–8.07 (m, 3ArH, 5-PhH), 8.34 (dd, $J = 2$ Hz and 7 Hz, *peri*H) ppm; MS: $m/z$ (%) = 435 (28) [$M^+$], 433 (100), 405 (48), 377 (27), 279 (55), 255 (17), 227 (33), 214 (9), 126 (33), 112 (35); IR (KBr): $\bar{\nu} = 1728$ [1-C(O)], 1724, 1718 (2C(O), esters), 1682 (C(O), benzoyl) $cm^{-1}$.

*Conversion of Compound* **6** *to* **13**

*N*-Bromosuccinimide (*NBS*) (20 mg, 0.1 mmol) and 37 mg of benzoyl peroxide (0.15 mmol) were added to a solution of 0.13 mg of **6a** (0.39 mmol) in 15 $cm^3$ of dry $CCl_4$. The mixture was heated at reflux temperature for 2 h and filtered while hot. Evaporation of the solvent left a residue, which was triturated with diethyl ether, and crystallized from cyclohexane to give 37 mg (67%) of **13** ($C_{17}H_{15}NO_6$), mp 138–140°C; $^1H$ NMR ($CDCl_3$): $\delta = 1.25–1.36$ (m, $2CH_3$), 4.18–4.36 (m, $2OCH_2$), 7.54–8.02 (m, 3ArH), 8.28 (dd, $J = 2, 7$ Hz, *peri*H), 12.44 (br s, $D_2O$ exchangeable, –NOH) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta = 15.1$ ($2CH_3$), 62.2, 64.5 ($2OCH_2$), 113.5 (4′-C) 121.5 (9-C), 123.7, 124.5 (5-C, 6-C), 124.3 (8-C), 125.7 (7-C), 131.3 (4-C), 141.6 (5′-C), 142.5, 143.9 (2′-, 3′-C), 160.3, 161.6, 167.7 (3C(O)) ppm;. MS*:* $m/z$ (%) = 329 (100) [$M^+$], 313 (53), 298 (11), 283 (22), 255 (20), 227 (44), 214 (9), 126 (33), 112 (36); IR (KBr): $\bar{\nu} = 3362$ (NOH), 1728, 1720, 1718 (3C(O)) $cm^{-1}$.

*Conversion of Compound* **6a** *to* **14**

Compound **6a** (0.13 g) in 5 g of polyphosphoric acid (*PPA*) was heated at 120–130°C for 1 h. The cooled reaction product was poured onto 20 $cm^3$ of ice-$H_2O$ and then extracted with $CHCl_3$. After evaporation of the dried $CHCl_3$ solution, the residue was crystallized from $CH_2Cl_2$ to give 55 mg (50%) of **14** ($C_{17}H_{15}NO_5$) as pale-yellow crystals, mp 146–148°C; $^1H$ NMR ($CDCl_3$): $\delta = 1.36–1.42$ (m, $2CH_3$), 4.29–4.35 (m, $2OCH_2$), 7.55–7.88 (m, 3ArH), 8.06 (dd, $J = 2, 7$ Hz, *peri*H), 8.81 (m, Ar–H); 9.33 (br s, $D_2O$ exchangeable, –NH) ppm; MS: $m/z$ (%) = 313 (100) [$M^+$], 298 (13), 272 (28), 270 (23), 242 (21), 239 (33), 212 (28), 186 (13), 126 (50); IR (KBr): $\bar{\nu} = 3230$ (NH), 1731, 1720, 1717 (3C(O)) $cm^{-1}$.

*Reaction of Oxime* **1** *with Ester Ylide* **2b**, *Preparation of Compounds* **5b** *and* **7**

The reaction mixture of 0.8 g of **1** (4.57 mmol) and 3.1 g of methoxycarbonylmethylene-triphenylphosphorane (9.4 mmol) in 25 $cm^3$ of dry $CHCl_3$ was stirred at rt for 24 h. The pale-yellow material that precipitated was taken up and recrystallized from $C_2H_5OH$ to give 300 mg (29%) of **7** ($C_{24}H_{16}N_2O_7$ ), mp 212–213°C; $^1H$ NMR (*DMSO*-$d_6$): $\delta = 3.87, 3.92$ (2s, $2OCH_3$), 5.76 (br s, $D_2O$ exchangeable,

NH), 7.36–7.94 (m, Ar–H), 8.08–8.16 (m, Ar–H), 12.85 (br s, $D_2O$ exchangeable, =NOH) ppm; MS: $m/z$ (%) = 444(100) [$M^+$], 442 (78), 414 (5), 412 (13), 397 (28), 338 (22), 310 (31), 279 (55), 126 (18), 112 (28); IR (KBr): $\bar{\nu}$ = 3260, 3252, (NOH, NH), 1735, 1728, 1722, 1718, [4C(O)], 1623 (C=NOH) $cm^{-1}$. The filtrate was evaporated and the remainder was chromatographed on silica gel, gradient eluting from 2% to 10% *Ac*O*Et* in hexane, yielding (7:3, $V/V$) 370 mg (31%) of **5b**.

*Methyl 3′-hydroxy-1,3-dioxospiro[indan-2,5′-pyrrole-2′-carboxylate]* (**5b**, $C_{14}H_9NO_5$)

Obtained as colorless crystals, mp 168–171°C (*Et*OH); $^1H$ NMR ($CDCl_3$): $\delta$ = 3.89 (s, $OCH_3$), 6.35 (s, 4-C–H), 7.51–7.58 (m, 5-, 6-CH(Ar)), 7.78–7.99 [m, 4-, 7-CH(Ar)], 9.33 (s, OH)) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta$ = 55.4 ($OCH_3$), 72.5 (2-C), 117.9 (4′-C), 122.7, 123.2 (5-C, 6-C), 124.4, 124.7 (8-C, 9-C), 125.6, 125.72 (4-C, 7-C), 142.6 (2′-C), 153.1 (3′-C), 159.6 (C(O), ester), 179.8, 182.6 [1-, 3-C(O)] ppm; MS: $m/z$ (%) = 271 (100) [$M^+$], 256 (6), 241 (15), 212 (28), 186 (23), 126 (55); IR (KBr): $\bar{\nu}$ = 3420 (OH), 1772, 1735, 1722 (3C(O), 1588, 1548 (C=N,C=C) $cm^{-1}$.

The reaction between equimolar amounts of **1** and **2a** or **2b** in $CHCl_3$ was also carried out and the mixture was worked up according to the above-described procedures for **2a** and **2b**, respectively. The product mixture gave (with **2a**) **5a** (21%) and **6a** (8%) and (with **2b**) **7** (16%) and **5b** (18%). Unreacted **1** (~30%) was isolated in each case.

*Reaction of* **1** *with Cyanomethylenetriphenylphosphorane* **3**, *Preparation of Compounds* **17**–**19**

A solution of 1.55 g of **16** (4.6 mmol) and 0.8 g of **1** (4.57 mmol) in 30 $cm^3$ of $CH_2Cl_2$ was stirred by means of an efficient magnetic stirrer. Freshly prepared 25 $cm^3$ of an aqueous LiOH solution (0.5 *N*) were added in one portion to the mixture and the two-phase system was stirred at rt for 30 h (TLC). The product mixture was poured into 100 $cm^3$ of $H_2O$, acidified with conc. HCl, and then extracted with 3×100 $cm^3$ of $CHCl_3$. The combined organic extracts were washed with 50 $cm^3$ of $H_2O$, dried, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane:*Ac*O*Et* as eluent to give compounds **17** (9:1, $V/V$), **19a**, **19b** (8:2 to 6:4, $V/V$) and **18** (1:1, $V/V$), respectively.

*3-(Cyanomethylene)-2-(hydroxyimino)indan-1-one* (**17**, $C_{11}H_6N_2O_2$)

Obtained (470 mg, 52%) as straw yellow crystals, mp 115–117°C (cyclohexane); $^1H$ NMR ($CDCl_3$): $\delta$ = 6.08 (s, =CH), 7.56–7.68 (m, 5-, 6-CH(Ar)), 7.87–8.02 (m, 4-, 7-CH(Ar)), 12.58 (br s, $D_2O$ exchangeable, =NOH) ppm, $^{13}C$ NMR ($CDCl_3$): $\delta$ = 110.5 (*C*H–CN), 118.3 (CH–*C*N), 119.8 (2-C=NOH), 123.0, 123.6 (5-C, 6-C), 122.6, 124.8 (8-C, 9-C), 125.5, 125.8 (4-C, 7-C), 134.7 (3-*C*=CH), 180.5 (1-C=O) ppm; MS: $m/z$ (%) = 198 (100) [$M^+$], 181 (60), 172 (25), 155 (11), 127 (33); IR (KBr): $\bar{\nu}$ = 3249 (OH), 2208 (CN), 1735 [C(O)], 1700 (C=CH), 1589 (C=NOH) $cm^{-1}$. Next fraction (up to 6:4, $V/V$) afforded compounds **19a** and **19b** (<7%). Physical and spectroscopic data of **19a** and **19b** are given below.

*3-Hydroxy-2-(hydroxyamino)-1H-indan-1-one* (**18**, $C_9H_7NO_3$)

Obtained as colorless crystals (80 mg, 10%), mp 220–222°C (acetone); $^1H$ NMR ($CDCl_3$): $\delta$ = 7.67 (m, 5-, 6-CH(Ar)), 7.99 (m, 4-, 6-CH (Ar)), 9.85, 12.66 (2 br s, NH, 2OH) ppm; MS: $m/z$ (%) = 177 (11), 175 (63), 158 (100); IR (KBr): $\bar{\nu}$ = 3422 (OH), 3250 (NHOH), 1700 (C=O) $cm^{-1}$.

No reaction was observed when 0.2 g of **1** were stirred in a mixture of 10 $cm^3$ of $CH_2Cl_2$ and 5 $cm^3$ of an aqueous LiOH solution (0.5 *N*) for 48 h. The resulting solid material (yield 93%) was crystallized from $C_2H_5OH$ to give pale-yellow crystals identified as compound **1**, mp 200–202°C (Ref. [15] 200–202°C), and comparative IR spectra.

When compound **1** was allowed to react with two molar amounts of the salt **16** under the previous experimental conditions, the same products **17** (50%), **18** (11%), and **19** (9%) were isolated.

*Reaction of* **17** *with* **3**

A solution of 0.4 g of **17** (2.02 mmol) and 0.69 g of **16** (2.04 mmol) in 30 $cm^3$ of $CH_2Cl_2$ was treated with 12 $cm^3$ of an aqueous LiOH solution (0.5 *N*) for 24 h. The reaction mixture was worked up as described for the reaction of **1** with **16** and separated by column chromatography using *n*-hexane/*AcOEt* as eluent to give compounds **19b** and **19a**.

*E-1,3-(dicyanomethylene)indan-2-oxime* (**19b**, $C_{13}H_7N_3O$)

Obtained (7:3, *V*/*V*) as straw yellow crystals (165 mg, 37%), mp 108–110°C (pentane); $^1$H NMR ($CDCl_3$): $\delta = 6.06$, 6.32 (2CHCN), 7.57 (m, 5-, 6-CH(Ar)), 8.09 (m, 4-, 7-CH(Ar)), 12.33 (br s, $D_2O$ exchangeable, =NOH) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 108.7$, 110.2 (2*C*H–CN), 117.4, 118.9 (2CH–*C*N), 121.2 (C=NOH), 123.1, 123 (5-C, 6-C), 122.4, 122.7 (8-C, 9-C), 125.4, 125.6 (4-C, 7-C), (2 *C*=CH), 131.5, 133.6 (1-, 3-*C*=CH) ppm; MS: $m/z$ (%) = 221(100) [$M^+$], 194 (18), 167 (26), 136 (38); IR (KBr): $\bar{\nu} = 3255$ (OH), 2198, 2208 (2 CN), 1614, 1610 (2 =CH), 1588 (C=N) $cm^{-1}$.

*Z-1,3-(dicyanomethylene)indan-2-oxime* (**19a**, $C_{13}H_7N_3O$)

Obtained (6:4, *V*/*V*) as straw yellow crystals (80 mg, 18%), mp 122–124°C ($CH_2Cl_2$); $^1$H NMR ($CDCl_3$): $\delta = 6.12$, 6.34 (2CHCN), 7.57–8.05 (m, 4ArH), 12.03 (br s, $D_2O$ exchangeable, =NOH) ppm; MS: $m/z$ (%) = 221(100) [$M^+$], 194 (18), 167 (26), 136 (38); IR (KBr): $\bar{\nu} = 3255$ (OH), 2000, 2210 (2 × CN), 1614, 1610 (2 =CH), 1588 (C=N) $cm^{-1}$.

*Reaction of* **1** *with Allyltriphenylphosphonium Bromide* (**4a**), *Preparation of Compound* **20** *and* **23**

A solution of 1.8 g of **4a** (4.8 mmol) and 0.8 g of **1** (4.57 mmol) in 40 $cm^3$ of $CH_2Cl_2$ was treated with 5 $cm^3$ of an aqueous LiOH solution (0.5 *N*) for 6 h. The product mixture was then extracted with 2 × 50 $cm^3$ of $CHCl_3$. The combined extracts were washed with 40 $cm^3$ of $H_2O$, dried, and the solvent was removed under reduced pressure. The residue was chromatographed using *n*-hexane/*AcOEt* as eluent.

*1-Oxo-2′-vinylindan[2,3-d]-1′,3′-oxazole* (**20**, $C_{12}H_7NO_2$)

Obtained (6.5:3.5, *V*/*V*) as colorless crystals (414 mg, 46%), mp 103–105°C (diethyl ether); $^1$H NMR ($CDCl_3$): $\delta = 5.65$, 5.74 (2d, $J = 11.4$, 2.5 Hz, $H^b$), 5.97, 6.11 (2d, $J = 11.4$, 2.5 Hz, $H^a$), 6.52–6.68 (dd(m), $J = 11.4$, 8.4 Hz, $H^c$), 7.37–7.78 (m, 3ArH), 7.99 (dd, $J = 2$, 7 Hz, *peri*H) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 113.8$ (CH=*C*$H_2$), 121.1 (9-C), 123.2, 123.7 (5-C, 6-C), 124.5 (4′-C), 125.1 (8-C), 125.6 (7-C), 130.8 (4-C), 134.7 (*C*H=$CH_2$), 138.6 (2′-C), 143.2 (5′-C), 168.6 (1-C=O) ppm; MS: $m/z$ (%) = 197 (45) [$M^+$], 169 (33), 141 (11), 116 (55), and 114 (100); IR (KBr): $\bar{\nu} = 1730$ (C=O), 1618 (C=C, exocyclic), 1595 (C=N) $cm^{-1}$.

*5′-Methylspiro[1,3-dioxoindan[2,3′]-(2′H)-1′,2′-oxazole]* (**23**, $C_{12}H_9NO_3$)

Obtained (6:4, *V*/*V*) as yellow crystals (156 mg, 17%), mp 96–98°C (pentane); $^1$H NMR ($CDCl_3$): $\delta = 1.98$ (s, 5′-C–$CH_3$), 6.62 (s, 4′-C–H), 7.42–7.56 (m, 5-, 6-CH(Ar)), 7.67–7.82 (m, 4-,7-CH(Ar)),

9.03 (br s, NH) ppm; $^{13}$C NMR ($CDCl_3$): $\delta =$ 21.4 (5′-C–*C*H$_3$), 73.3 (3′-C), 116.2 (4′-C), 123.3, 123.88 (5-C, 6-C), 124.3, 125.6 (8-C, 9-C), 125.66, 125.98 (4-C, 7-C), 130.6 (5′-C), 169.3, 183.6 (1- + 3-C=O) ppm; MS: $m/z$ (%) = 215 (68) [M$^+$], 201 (23), 173 (100), 145 (16), 115 (55); IR (KBr): $\bar{\nu} = 3220$ (NH), 1757, 1731 (2C(O)) cm$^{-1}$.

*Reaction of Oxime* **1** *with Vinyltriphenylphosphonium Bromide* (**4b**), *Preparation of 1′-Hydroxypyrrole* **26**

To a slurry of 160 mg of a NaH dispersion (57% of mineral oil) in 15 cm$^3$ of dry THF were added dropwise 0.5 g of **1** (2.86 mmol) in 15 cm$^3$ of THF. The deeply red colored reaction mixture was stirred at rt until all hydrogen evolution had ceased, and 1.1 g of **4b** (3.0 mmol) were introduced all at once. The reaction mixture turned almost colorless. After stirring for 6 h the product mixture was poured into 300 ml of $H_2O$ and extracted with $2 \times 120$ cm$^3$ of $CHCl_3$. The combined organic extracts were washed with 50 cm$^3$ of $H_2O$, dried, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane/*Ac*O*Et* (9:1, *V*/*V*) as eluent to give **26**.

*1′-Hydroxy-1-oxoindan[2,3-d]pyrrole* (**26**, $C_{11}H_7NO_2$)

Obtained as colorless crystals (0.29 g, 55%), mp 151–152°C (benzene); $^1$H NMR ($CDCl_3$): $\delta = 6.18$ (d, $J = 2.8$ Hz, 2′-CH), 6.35 (d, $J = 2.8$ Hz, 3′-CH) [5b], 7.33–7.76 (m, 3ArH), 7.99 (dd, $J = 2$, 7 Hz, *peri*H), 11.85 ($s_w$, –OH) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 114.1$ (4′-C), 122.6, 124.8 (2′-C 3′-C),122.5 (9-C), 122.7, 123.4 (5-C, 6-C), 124.8 (8-C), 125.6 (7-C), 131.4 (4-C), 140.3 (5′-C), 172.5 (1-C=O) ppm; MS: $m/z$ (%) = 185 (100) [M$^+$], 168 (36), 140 (17); IR (KBr): $\bar{\nu} = 3315$ (OH), 1728 (C=O) cm$^{-1}$.

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