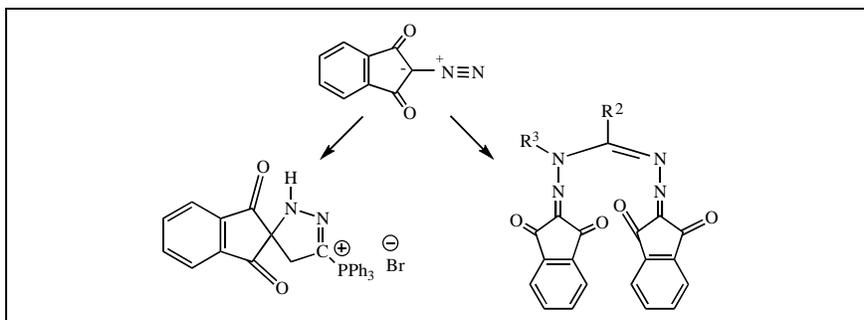


Diverse Reactivity of α -Carbanions Derived from Alkylidenephosphoranes toward 2-(1 λ^5 -Diazynylidene)-1*H*-indene-1,3-(2*H*)dione. General Approach to Conjugated Oxadiazines, Pyridazines and Spiro[3]pyrazoles

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Different types of phosphonium carbanions were applied to 2-diazonio-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (**1**) in order to synthesize a number of condensed and fused *N*-heterocycles. When **1** was treated with cyanomethyltriphenylphosphonium chloride oxadiazine-, and pyridazine derivatives were obtained whereas bis-indanylidene derivatives resulted from the reaction of **1** with methyl- and ethyltriphenylphosphonium bromides. On the other hand, a series of substituted and unsubstituted spiro[3]pyrazoles were obtained from the diazo substrate when reacted with vinyl- and allyltriphenylphosphonium bromides.

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INTRODUCTION

Relatively little work has been reported on the reactions of phosphorus ylides and the relevant phosphonium salts on diazo compounds. Our continuing interest in the reactions of alkylidenephosphoranes and phosphonyl carbanions with carbon-nitrogen systems such as oximes [1], hydrazones [2], nitriles [3], anils [3] and azides [4] for the production of synthetically new nitrogen-heterocycles led us to investigate the application of the phosphonium salts **2a-e** to 2-(1 λ^5 -diazynylidene)-1*H*-indene-1,3-(2*H*)-dione (**1**, also known as 2-diazonio-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide, and 2-diazo-1,3-indanedione) (Figure 1).

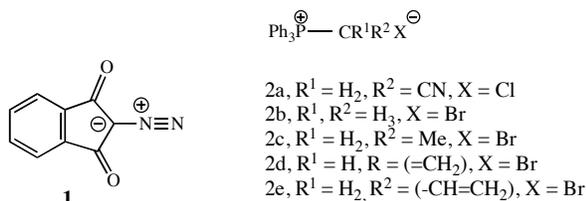
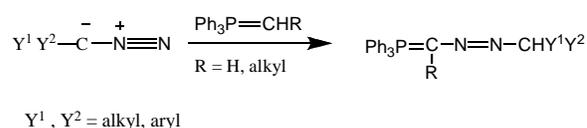


Figure 1

The diazo function is generally less reactive toward phosphorus ylides than the carbon-carbon double bond. In their early work [5], alkylidenephosphoranes were known

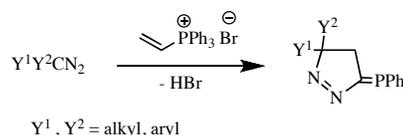
to form *N*-alkylated phosphorus ylides when treated with diazo compounds according to Scheme 1.

Scheme 1



Later on, Schweizer *et al* [6] elaborated a general scheme for pyrazoline synthesis from the reaction of diazo compounds with active ylides as outlined in Scheme 2.

Scheme 2



A few additional reports on reactions of this class of compounds with Wittig reagents have been added since 1980 [7,8]. In effect, reactions of phosphorus ylides with diazo compounds are not, however, as straightforward as implied by examples described in Schemes 1 and 2. For example, N₂ was lost when diazoacetophenone was

treated with benzoylmethylenetriphenylphosphorane, thereby 2,6-diphenyl-4-benzylidenepyran was the reported product [8a].

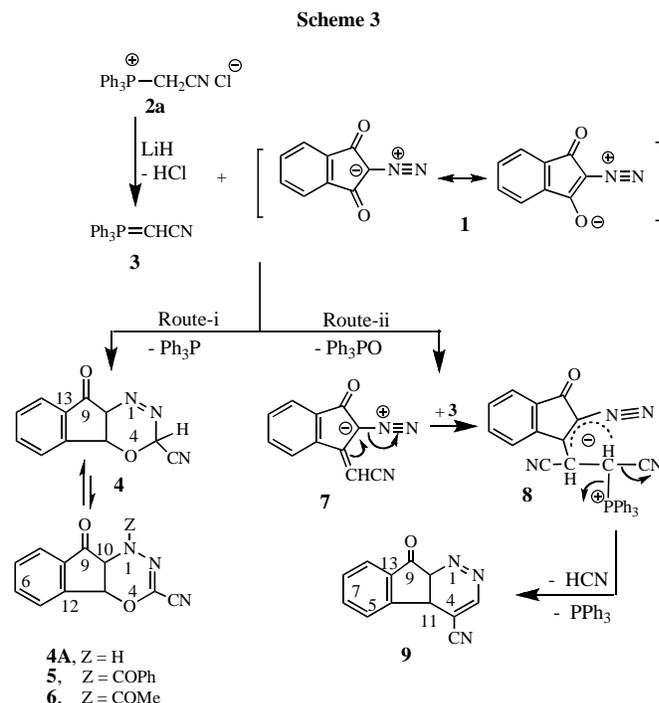
In this paper, we describe different routes leading to unexpected products that occurred in the reactions of α -diazoketones with phosphonium salts **2a-e**. In relation to this work, new condensed oxadiazines, pyridazines, and pyrazoles with substitution patterns required for a biological chemistry program could be synthesized in moderate to high yields.

RESULTS AND DISCUSSION

When a tetrahydrofuran (THF) solution of 2-diazo-1,3-indandione (**1**) was treated with two equivalents of resonance stabilized ylide, cyanomethylenetriphenylphosphorane (**3**), prepared *in situ* from the phosphonium chloride **2a** by addition of an excess of LiH, an immediate reaction occurred. The reaction mixture was further heated at the reflux temperature for 36 h to give, after separation by column chromatography, pyridazine **9** (46% yield) as the major product, along with oxadiazine **4** (21% yield) (Scheme 3). Compounds **4** and **9** were obtained in similar ratio, irrespective if one or two equivalents of **2a** were being used. Obviously, the oxadiazine **4** was formed *via* (11 + 1) cycloaddition between **1** and ylide **3**, under the elimination of triphenylphosphine (Scheme 3-route i). The (11 + 1) cycloaddition was previously reported by Ege and Gilbert for the formation of 3*H*-[1,2,4]triazolo-[4,3-*b*]indazoles from diazo-azoles with ylides [5d,7]. On the other hand, the formation of the pyridazine **9** can be explained through the initial Wittig olefination of **1** to give the intermediate **7**. The latter is longer-lived and Michael addition reaction of a second ylide species **3** to **7** is undertaken on the methide-carbon. Subsequent triphenylphosphine and HCN elimination **9** would happen (Scheme 3, route ii).

Structures **4** and **9** were assigned on the basis of their elemental analyses, ir, ^1H -, ^{13}C nmr, and mass spectral data [9,10]. The ir spectrum of **4** indicated that **4** is in equilibrium with **4A** since a sharp and strong band appeared at $\nu 1425$ assigned to $-\text{N}=\text{N}$ stretching band (**4**), and a frequency at 3362 cm^{-1} due to free NH group. The latter moiety (NH) was also recorded at $\delta_{\text{H}} = 13.62$ ppm in its ^1H nmr (CDCl_3) spectrum. The ^1H nmr deshielded the appearance of the oxadiazine-H(3) singlet (**4**) at 5.45 ppm, which was expected to give a chemical shift value not higher than 5 ppm. This deshielding could be attributed to the influence of the substitution on the methine-carbon atom in compound **4** at 3-position. Thus, the substituted electron withdrawing hetero-oxygen atom, and carbonitrile-group result in an increased acidity of the corresponding methine-proton ($\delta_{\text{H}} = 5.45$ ppm). Evidence for the two different tautomeric structures **4** and **4A** in

solution was however, proved by a series of nmr-experiments.



In the *J*-modulated spin-echo ^{13}C nmr spectrum of **4** in DMSO-d_6 one set of signals and a negative phase of the C3-signal at $\delta_{\text{C}} = 101.6$ ppm indicates that only tautomer **4** is present. In CDCl_3 -solution, however, two sets of signals are obtained, one for tautomer **4** with similar chemical shifts as in DMSO-d_6 and another one, in which the C3-signal has the character of a down field shifted quaternary carbon atom ($\delta_{\text{C}} = 123.4$ ppm). The structure of the second tautomer was proved to be **4A** by a series of heteronuclear $^{13}\text{C}\{^1\text{H}\}_n\text{Oe}$ experiments as follows: The irradiation of the H3-proton ($\delta_{\text{H}} = 5.45$ ppm) in DMSO-d_6 resulted only in the enhancement of the CN-carbon signal in the ^{13}C nmr spectra. In CDCl_3 solution irradiation of the most deshielded proton at $\delta_{\text{H}} = 13.62$ ppm, however, causes a strong signal enhancement of the C10-signal ($\delta_{\text{C}} = 121.3$ ppm) indicating the protonation of N1. Treatment of **4** with either benzoyl chloride or acetic anhydride in pyridine gave the expected *N*-benzoylated and *N*-acetylated products **5** and **6** in 76 and 71% yields, respectively.

On the other hand, in the ^1H NMR spectrum of compound **9** the (C3-*H*)-proton is shifted downfield at 8.48 ppm, which was expected to give a chemical shift value not higher than ~ 8.15 ppm. This deshielding could be due to the anisotropy of the heteroatomic system being effective in a nearly coplanar conformation [11].

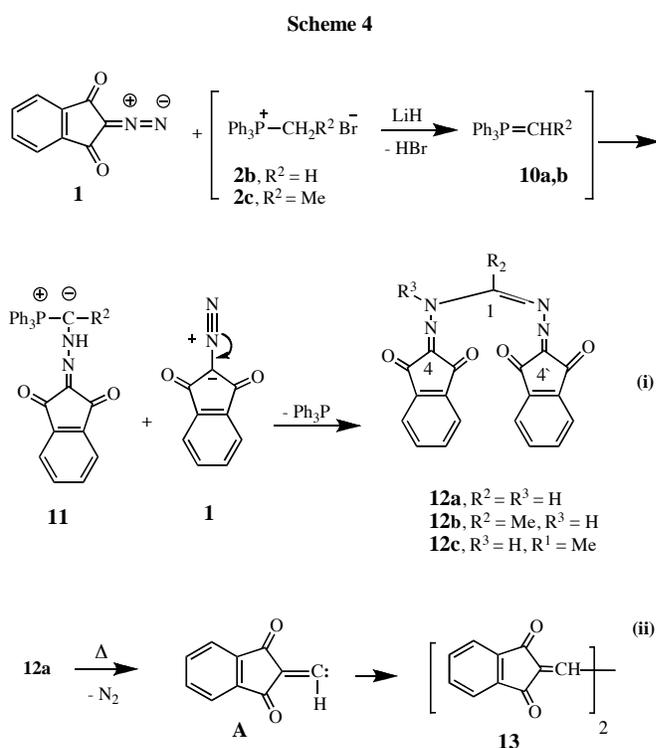
Next, we found that treatment of the lithiated methyl-triphenylphosphonium bromide **2b** with diazoketone **1**

proceeded smoothly, in THF solution at room temperature. The reddish-orange substance, mp 252-255°, which was isolated in 84% yield, had the formula $C_{19}H_{10}N_4O_4$, and was shown to be the dimeric product **12a**. A similar treatment of **1** with ethyltriphenylphosphonium bromide (**2c**) gave the parallel methyl analog **12b**. The ir spectra of **12a** and **12b** exhibited carbonyl stretching bands in the region 1785-1730 and a broad NH stretching band at $\nu \sim 3235\text{ cm}^{-1}$, while the C=N stretching frequencies concentrated in the region 1615-1558 cm^{-1} . The mass spectrum of **12a** indicated the presence of ion peaks at 186 (36) $[358-172\text{ (C}_9\text{H}_4\text{N}_2\text{O}_2)]^+$, 158 (77) $[186-28\text{ (N}_2)]^+$, and 172 (100) $[\text{C}_9\text{H}_4\text{N}_2\text{O}_2]^+$, which can originate *via* the cleavage of the molecular ion peak at m/z (%): 359 (8%) $[\text{M} + 1]^+$. Structure **12** was investigated by nuclear Overhauser effect (nOe) experiments, which were also useful for the assignment of the ^{13}C nmr signals.

The irradiation of the NH proton (**12a**, $\delta_{\text{H}} = 9.58\text{ ppm}$) in d_6 -DMSO solution resulted only in the enhancement of C(1)- ($\delta_{\text{C}} = 153.2\text{ ppm}$) and the C(4)- ($\delta_{\text{C}} = 134.7\text{ ppm}$) signals. On the other hand, irradiation of C(1)-proton (6.82 ppm) produced an equal nOe at the C(4) [$\delta_{\text{C}} = 134.7\text{ ppm}$], and the C(4') [$\delta_{\text{C}} = 156.4\text{ ppm}$] signals in the ^{13}C nmr spectra too. In compound **12b** nOes occurred at the C(1)- CH_3 -protons upon irradiation of NH-proton indicating the protonation of N(2). A possible mechanism for the formation of compounds **12** is given in Scheme 4. The diazo compound **1** couples with the alkylidene-phosphorane **10a** (or **10b**) to give the ylide intermediate **11**, which cannot be isolated since it reacts at once with a second equivalent of the diazo species **1** with extrusion of triphenylphosphine. Remarkably, similar observation has previously been reported [5a,12] for reactions of diazo compounds or diazonium salts with **2b** or **2c**.

Treatment of **12a** with MeI in the presence of EtONa in EtOH at room temperature afforded *N*-methylated derivative **12c** (from MeOH). Furthermore, compound **12a** decomposed thermally to give the known [13] dimeric product 2,2'-ethane-1,2-diylidene bis(1*H*-indene-1,3(2*H*)dione) (**13**, 67%). Compound **13** could be formed *via* reductive dimerization of carbene precursor **A** (Scheme 4). The carbene dimer **13** had a mass spectrum consistent with a parent $[\text{M}+1]^+$ ion at m/z 315, and a base fragment at m/z 157 (100). However, only one isomer of the dimer **13** was isolated.

Vinyltriphenylphosphonium bromide (**2d**), on reaction with **1** in THF solution at reflux temperature for 6 h yielded only the spiro-pyrazolophosphonium bromide **14a**, in excellent yield (87%) (Scheme 5-i). None of the corresponding 4-substituted salts was obtained. Undoubtedly, steric factors inhibit the formation of 4-substituted salt, which would require the phosphonium moiety of the vinyl salt **2d** to be adjacent to the

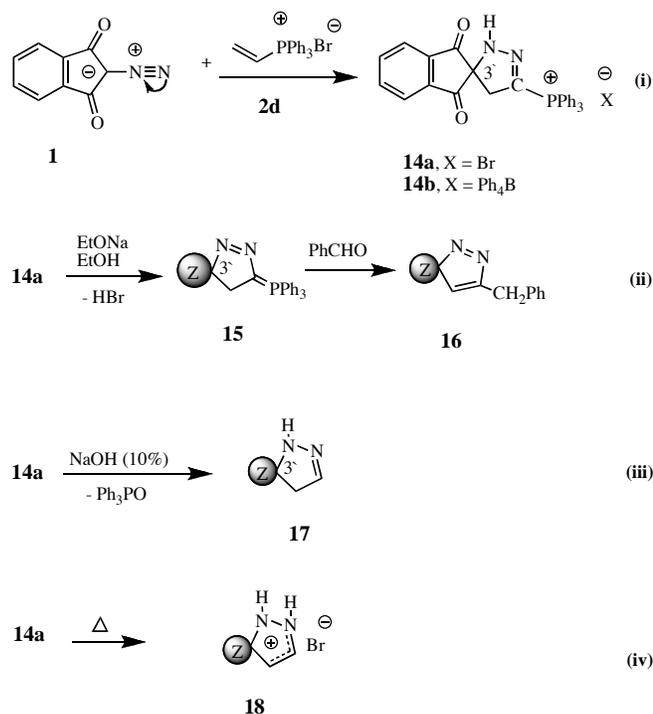


substituted (indanedione) moiety. The ir spectrum of **14a** showed a strong broad band at 3120 cm^{-1} indicating a strong intramolecular interaction between amine proton and bromine anion ($\text{N-H}\cdots\text{Br}^-$). This type of interaction is supported [15] by the observation that the N-H stretching vibration band shifted into higher frequencies (3255 cm^{-1}) when the bromine ion was replaced by tetraphenylborate anion in **14b**. The nmr data for **14b** is consistent with the assigned structure.

On heating **14a** with ethanolic sodium ethoxide solution for 1 h, the corresponding ylide **15** (84%) was obtained whereas the normal Wittig product **16** (78%) was isolated on treating **14a** with sodium ethoxide solution followed by benzaldehyde (Scheme 5-ii). On the other hand, when the reaction of **1** with **2d** was performed in the presence of a base (LiH), or treatment of the initial salt **14a** with 10% NaOH spiro-pyrazoledione (**17**) was isolated in 74% yield (Scheme 5-iii).

Even though it has been known [8b,14] that pyrazolines decompose thermally to give cyclopropanes and/or olefins with varying product distributions, when the phosphonium salt **14a** was heated to its melting point temperature for 30 min., spiro-pyrazole bromide (**18**) was isolated in a quantitative yield [6b] (Scheme 5-iv). However, the uniqueness of isolating **18** that retains the pyrazoline moiety over the expected products (hydrocarbons) previously reported [11], provides intermediates of great synthetic utility, which may undergo a number of interesting conversions.

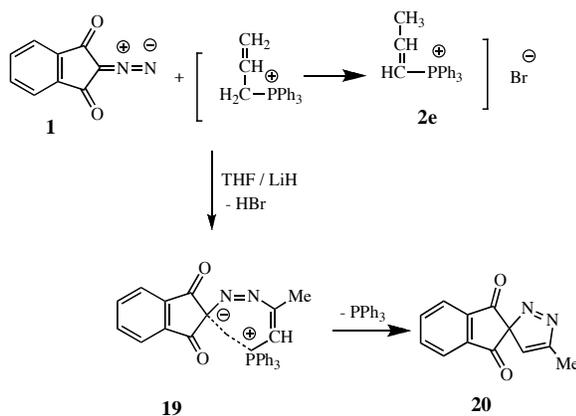
Scheme 5



15-18, Z = 2-(indane-1,3-dione)

No reaction was observed when a THF solution of equivalent amount of **1** and allyltriphenylphosphonium bromide (**2e**) was stirred at rt for three days, or heated under reflux for 20 h. Pyrazoline product **20** (78% yield) was, however obtained when **2e** was allowed to react with **1** in the presence of LiH. The mechanism for the formation of the spiro[2]pyrazole **20** can be rationalized through the attack of the azo group on the β -carbon of the salt **2e**, to generate the intermediate **19** with concomitant elimination of HBr. Extrusion of triphenylphosphine results in the formation of the final product **20** (Scheme 6). The electrophilic attack at the central atom of the allyl-

Scheme 6



group in **2e** is a known process [12]. Furthermore, the ready elimination of triphenylphosphine from **19** in the second step occurs through a carbanion mechanism, driven by the resulting gain of aromaticity.

In summary, the reactions described in the present paper are in line with those that have already been reported [5-14] on the chemistry of the diazo compounds with Wittig reagents. Thus, the results confirm, once again the concreteness of 1,3-dipolar cycloaddition reactions between unsaturated phosphorus carbanions and conjugated diazo-compounds (Schemes 5 and 6).

EXPERIMENTAL

All melting points are measured on an Electrothermal melting point apparatus. The IR spectra were recorded on a Perkin Elmer 317 Grating IR spectrophotometer, using KBr pellets. The ¹H and ¹³C NMR spectra were measured on a Jeol E.C.A-500 MHz instrument using SiMe₄ as an internal reference. The ³¹P NMR spectra were recorded with the same instrument, relative to external H₃PO₄ (85%). The mass spectra were performed on a Joel JMS-A X 500 spectrometer. Elemental analyses were carried out at the Microanalysis Laboratory, Cairo University, Cairo, Egypt. The appropriate precautions in handling moisture-sensitive compounds were observed. Solvents were dried by standard techniques. TLC: Merck 0.2 mm silica gel 60 F154 anal aluminum plates. Column chromatography (CC): silica gel (Kieselgel 60 mesh, particle size 0.2-0.5 mm; E. Merck, Darmstadt). The substrate 2-diazonio-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (**1**) was prepared according to the reported method [16].

Reaction of α -Diazoketone 1 with Cyanomethylenetriphenylphosphonium Chloride (2a). (A) **Preparation of Compounds 4 and 9: General Method.** A solution of 1.52 g of phosphonium chloride **2a** (4.5 mmol) in 15 mL dry tetrahydrofuran (THF), was added dropwise to 200 mg slurry of LiH dispersion (60% in paraffin oil) in 10 mL THF. The reaction mixture was stirred at rt until all hydrogen evolution had ceased, and 0.6 g diazoketone **1** (~ 3 mmol) was introduced all at once. The reaction mixture was heated under reflux for 36 h (TLC). The product mixture was concentrated to 10 mL, diluted with 30 mL dist H₂O, acidified with *conc.* HCl, and then extracted with two portions (100 mL) of ethyl acetate. The AcOEt extracts were combined, back-washed with 100 mL H₂O, dried, and the solvents were evaporated to dryness. The residue was chromatographed on silica gel with *n*-hexane/AcOEt as the eluents, whereupon compounds **4** and **9** were isolated.

9-Oxo-1,9-dihydroindeno[2,1-*e*][1,3,4]oxadiazine-3-carbonitrile (4) was obtained (1:1, v/v) as yellow leaflets (155 mg, 21%), mp 143-145° (CH₂Cl₂); ir: ν NH 3362 (**4A**), CN 2223, 9-C=O 1732; C=C, C=N 1598, 1610, -N=N- 1425 cm⁻¹; ¹H nmr (CDCl₃): δ 5.45 (s, 1H, 3-CH, **4**), 7.42, 7.73 (2d, 3H, *H*-Ar), 8.13 (dd, J = 2.5, 6.8 Hz, H, *peri*-H), 13.62 ppm (s, 1H, HN, **4A**); ¹H nmr (DMSO): 13.62 ppm (s, 1H, HN, **4A**) did not appear; ¹³C nmr (CDCl₃): δ 101.6 (3-C, **4**), 113.6, 114.4 (-CN, **4** & **4A**), 121.3, 126.8, 127.2, 129.6, 131.2, 135.1, 139.3 (C-Ar), 123.4 (3-C, **4A**), 146.3 (11-C), 185.3 ppm (9-C=O); ¹³C nmr (DMSO): among others, only one recorded data for (3-C) at δ 101.6 ppm; ms: m/z (EI) 211 (42) [M⁺], 220 (66), 194 (100),

166 (22), 77 (68). *Anal.* Calcd. for $C_{11}H_5N_3O_2$: C, 62.56; H, 2.39; N, 19.9. Found: C, 62.64; H, 2.34; N, 19.97.

9-Oxo-9H-indeno[2,1-c]pyridazine-4-carbonitrile (9) was obtained (2:8, v/v) as yellow crystals (460 mg, 46%), mp 123–125° (MeCN); ir: ν CN 2216, C=O 1728 cm^{-1} . 1H nmr: δ 7.36, 7.73 (2d, 3H, *H*-Ar), 8.17 (dd, $J = 2.5, 6.8$ Hz, 1H, *peri*-H), 8.48 ppm (s, 1H, 3-H); ^{13}C nmr: δ 112.6 (4-C), 127.4 (CN), 121.6, 124.6, 126.7, 129.3, 132.4, 137.6 (C-Ar), 135.4 (11-C), 136.7 (13-C), 156.4 (3-C), 190.3 ppm (9-C=O); ms: m/z (EI): 207 (37) $[M^+]$, 179 (100), 151 (23), 123 (57), 77 (42). *Anal.* Calcd. for $C_{12}H_5N_3O$: C, 69.56; H, 2.43, N, 20.28. Found: C, 69.66; H, 2.36, N 20.36.

Acylation of 4 with Benzoyl Chloride or Acetic Anhydride.

Preparation of 5 and 6. Benzoyl chloride (or acetic anhydride) (1.1 mmol) was added to a solution of 0.2 g of **4** (1.0 mmol) in 5 mL of dry pyridine. The reaction mixture was allowed to stand for 2 days at room temperature. The product mixture, with a small amount of pyridine hydrochloride present, was poured onto 40 g of crushed ice. Stirring and scratching afforded a white solid, which was collected by filtration and washed with 20 mL of ice water, air-dried, and recrystallized from a small amount of $CHCl_3$ to give a pure sample of **5** (or **6**).

1-Benzoyl-9-oxo-1,9-dihydroindeno[2,1-e][1,3,4]oxadiazine-3-carbonitrile (5) was obtained in 76% yield, mp 176–178° (CH_2Cl_2); ir: ν CN 2221, 9-C=O 1729, C=O- benzoyl 1682, C=N 1595 cm^{-1} . 1H nmr: δ 7.38–7.93 (m, 6H, *H*-Ar), 8.13, 8.16 (dd, $J = 2.3, 6.4$ Hz, 2H, *peri*-H); ^{13}C nmr: δ 110.5 (10-C), 111.6 (CN), 121.4, 124.3, 126.3, 126.9, 130.3, 131.3, 133.7, 136.5, 139.4 (C-Ar), 166.7 (C=O, benzoyl), 183.3 ppm (9-C=O); ms: m/z (EI) 315 (37) $[M^+]$, 194 (100). *Anal.* Calcd. for $C_{18}H_9N_3O_3$: C, 68.57; H, 2.88; N, 13.33. Found: C, 68.64; H, 2.93; N, 13.27.

1-Acetyl-9-oxo-1,9-dihydroindeno[2,1-e][1,3,4]oxadiazine-3-carbonitrile (6) was obtained in 71% yield, mp 164–166° (acetone/ether, 1:1 v/v); ir: ν CN 2218, 9-C=O 1723, C(O), acetyl, 1668, C=N 1598 cm^{-1} . 1H nmr: δ 2.35 (s, 3H, CH_3), 7.42, 7.81 (2d, 3H, *H*-Ar), 8.11 ppm (dd, $J = 2.5, 6.8$ Hz, 1H, *peri*-H); ^{13}C nmr: δ 21.6 (CH_3), 111.6 (CN), 121.4, 126.4, 128.9, 135.4, 139.6, 140.6 (C-Ar), 132.8 (3-C), 166.4 (C=O, acetyl), 182.3 ppm (9-C=O); ms: m/z (EI) 253 (28) $[M^+]$, 206 (39), 194 (100), 166 (21), 123 (57), 77 (48). *Anal.* Calcd. for $C_{13}H_7N_3O_3$: C, 61.66; H, 2.79; N, 16.6. Found: C, 61.61; H, 2.84; N, 16.54.

Reaction of 1 with Alkyltriphenylphosphonium Bromides 2b and 2c: A. Preparation of Compounds 12a and 12b. A THF solution of 4.06 mmol of the appropriate salt **2b** or **2c** and 0.7 g of the diazoketone **1** (4.06 mmol) was treated with LiH under the experimental conditions described in the general procedure for the reaction of **1** and **2a**. The reaction mixture was further stirred, at room temperature for 12 h (with **2b**) or 18 h (with **2c**), followed by the usual working up and chromatography to give **12a** or **12b**, respectively.

***N,N'*-Bis(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-hydrazonoformic hydrazide (12a)** was obtained (1:1, v/v) as reddish-orange crystals (610 mg, 84% yield), mp 252–255° (from $CHCl_3$); ir: ν NH 3433, 5-, 10, 5', 10'-C=O ~1784, ~1736, C=Ns 1588, 1608 cm^{-1} . 1H nmr: δ 6.82 (s, 1H, 1-CH), 7.45, 7.74 (2d (m), $J_{H-H} = 4.4$ Hz, 2 \times 4H, *H*-Ar), 9.58 ppm (s, 1H, NH, exchangeable with D_2O); ^{13}C nmr: δ 124.2, 124.4, 124.6, 124.9, 126.6 (m), 131.2–131.6 (m), 135.4, 136.2, 147.1, 147.8 (C-Ar, and C'-Ar'), 134.7 (4-C), 153.2 (1-C), 156.4 (4'-C), 178.6, 184.7 ppm (5-, 10, and 5', 10'-C=O); ms: m/z (EI) 359 (8) $[M + 1]^+$, 358 (11), 357 (10), 186 (36), 172 (100, $C_9H_4N_2O_2$), 158 (77).

Anal. Calcd. for $C_{19}H_{10}N_4O_4$: C, 63.69; H, 2.81; N, 15.64. Found: C, 63.77; H, 2.75; N, 15.59.

(1Z)-*N,N'*-Bis(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-ethanehydrazonohydrazide (12b) was obtained (1:1, v/v) as reddish-orange crystals (590 mg, 78% yield), mp 224–225° ($CHCl_3$); ir: ν NH 3341, 5-, 10, 5', 10'-C=O ~1785, ~1733, C=Ns ~1558, ~1610 cm^{-1} . 1H nmr: δ 1.22 (s, 3H, H_3C -C-1), 6.28 (s, 1H, HC-1), 7.45, 7.74 (2d (m), $J_{H-H} = 4.4$ Hz, 2 \times 4H, *H*-Ar), 9.47 ppm (s, 1H, NH, exchangeable with D_2O); ^{13}C nmr: δ 16.74 (CH_3 -C-1), 124.6 (m), 126.1, 126.4, 126.8, 131.6 (m), 133.2 (m), 135.4, 136.3, 143.7, 144.8 (C-Ar, and C'-Ar'), 134.7 (4-C), 152.3 (C-1), 155.6 (C-4'), 183.6, 187.5 ppm (5-, 10, and 5', 10'-C=O); ms: m/z (EI) 373 (< 8) $[M + 1]^+$, 372 (11), 371 (10), 357 (18), 200 (48), 172 (100, $C_9H_4N_2O_2$), 158 (77). *Anal.* Calcd. for $C_{20}H_{12}N_4O_4$: C, 64.51; H, 3.25; N, 15.05. Found: C, 64.57; H, 3.22; N, 15.17.

B. Alkylation of Bis-indenylidene 12a: Preparation of 12c.

To a solution of 0.13 g of sodium (0.006 g-atom) dissolved in 50 mL of EtOH was added 0.5 g of **12a** (1.34 mmol). The resulting yellow mixture was allowed to stir with 0.4 g of MeI (0.003 mol) at rt for 18 h. The solution was precipitated by adding to 300 mL of ether and the solid collected by filtration to give **12c**.

***N,N'*-Bis(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-*N*-methylhydrazonoformic hydrazide (12c)** was obtained (1:1, v/v) as yellow crystals (285 mg, 55% yield), mp 186–188° (MeCN); ir: $\tilde{\nu}$ 5-, 10, 5', 10'-C=O ~1784, ~1720, C=Ns ~1600, ~1618 cm^{-1} . 1H nmr: δ 3.04 (s, 3H, H_3CN), 7.28 (s, 1H, HC-1), 7.37, 7.78 ppm (2d (m), $J_{H-H} = 4.4$ Hz, 2 \times 4H, *H*-Ar); ^{13}C nmr: δ 37.3 (CH_3N), 124.1 (m), 126.6 (m), 131.3 (m), 133.5, 136.2, 139.7, 141.8 (C-Ar, and C'-Ar'), 131.5 (4-C), 148.3 (1-C), 156.4 (4'-C), 186, 188.9 ppm (5-, 10, and 5', 10'-C=O); ms: m/z (EI) 373 (8) $[M + 1]^+$, 372 (17), 371 (9), 357 (28), 200 (48), 172 (100, $C_9H_4N_2O_2$), 158 (77). *Anal.* Calcd. for $C_{20}H_{12}N_4O_4$: C, 64.51; H, 3.25; N, 15.05. Found: C, 64.44; H, 3.3; N, 15.09.

C. Thermal Decomposition of 12a: Preparation of Compound 13.

A sample of 0.2 g of **12a** was heated to its melting point temperature for 20–30 min in an oil bath (temperature maintained 10° over melting point). After cooling, the solidified decomposition product was washed with 10 mL of CH_2Cl_2 ; and further crystallized from MeOH to give (117 mg, 67% yield) of **2,2'-ethane-1,2-diylidenebis(1H-indene-1,3(2H)-dione) (13)**, mp 113–115° (from EtOH) (lit. [13]; mp 115°).

Reaction of 1 with Vinyltriphenylphosphonium Bromide (2d): A. Preparation of 14a, 14b. A stirred mixture of 1.5 g of the unsaturated salt **2d** (4.1 mmol) and 0.7 g of the diazoketone **1** (4.06 mmol) in 30 mL THF was heated under reflux for 6 h. After removal of the volatile materials under reduced pressure, the solid product, so obtained, was crystallized from ethanol to give yellow crystals of **14a**.

(1,3-Dioxo-1,2',3,4'-tetrahydrospiro-[indene-2,3'-pyrazol]-5'-yl)triphenylphosphonium bromide (14a) (1.9 g, 87% yield), mp 200–202°; ir: ν NH, hydrogen-bromine bonded 3120, 1-, 3-C=O 1782, 1724, N=C 1595, C-P 1115, phenyl 685 cm^{-1} . 1H nmr: δ 2.03 (d, $^3J_{P-H} = 4.4$ Hz, 2H, 4'- CH_2), 7.40–8.27 (m, 19H, *H*-Ph), 9.45 ppm (s, 1H, HN); ^{13}C nmr: δ 28.6 (d, $^2J_{P-C} = 33.5$ Hz, 4'- CH_2), 70.4 (d, $^3J_{P-C} = 8.2$ Hz, 3'-C), 26.3 (m), 127.4, 128.7 (m), 128.9, 130.6 (m), 132.5, 133.3, 135.8, 143.1 (C-Ar), 144.4 (d, $^1J_{P-C} = 196.4$ Hz, 5'-C-P), 178.4, 188.9 ppm (1-, 3-C=O); ^{31}P nmr: δ 16.3 ppm; ms: m/z (EI) 540 (14) $[M - 1]^+$, 460 (100), 198 (63), 164 (34), 262 (66). *Anal.* Calcd. for $C_{29}H_{22}BrN_2O_2P$: C, 64.34; H, 4.1; Br, 14.76; N, 5.17; P 5.72. Found: C, 64.41; H, 4.17; Br, 14.68; N, 5.11; P 5.61.

A sample of pyrazolin-5'-yl-triphenylphosphonium bromide **14a** was added to a solution of a molar amount of sodium tetraphenylborate in CH_2Cl_2 . The solution was boiled for 15 min and filtered. The filtrate was concentrated while adding AcOEt to precipitate the borate salt **14b**, mp 218-220°; ir: NH 3255, 1-, 3-C=O 1782, 1724, N=C 1590, C-P 1115, phenyl 675 cm^{-1} .

B. Reaction of **14a** with Ethanolic Sodium Ethoxide.

Preparation of 15. A sample of 0.5 g of the salt **14a** was added to a solution of 0.2 g sodium in 50 mL of ethanol. The mixture was allowed to reflux for 1 h. After cooling, the crude mixture was concentrated, poured into 100 mL of dist H_2O , acidified with *conc* HCl and extracted with CHCl_3 (2×100 mL). The combined organic extracts were washed with 50 mL of dist H_2O and dried. After evaporation of the solvent under reduced pressure, the residue was crystallized from MeCN to give **15**.

5'(Triphenyl-phosphoranylidene)-4,5'-dihydrospiro[indene-2,3'-pyrazole]-1,3-dione (15) (357 mg, 84% yield), mp 200-202°; ir: $\tilde{\nu}$ 1782, 1724 (1-, 3-C=O), 1429 (N=N), 1117 (C-P), 682 (phenyl) cm^{-1} ; ^1H nmr: δ 2.11 (d, $^3J_{\text{P-H}} = 6.4$ Hz, 2H, 4'- CH_2), 7.39-8.23 ppm (m, 9H, H-Ph); ^{13}C nmr: δ 28.6 (d, $^2J_{\text{P-C}} = 33.5$ Hz, 4'- CH_2), 103.7 (d, $^3J_{\text{P-C}} = 11.2$ Hz, 3'-C), 126.3 (m), 127.4, 128.7 (m), 128.9, 130.6 (m), 132.5, 133.3, 135.8, 143.1 (C-Ar), 168.4 (d, $^1J_{\text{P-C}} = 149$ Hz, 5'-C-P), 186.4, 189.4, (1-, 3-C=O); ^{31}P nmr: δ 19.6 ppm; ms: m/z (EI): 461 (90) [M + 1]⁺, 262 (66), 198 (100). *Anal.* Calcd. for $\text{C}_{29}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$: C, 75.64; H, 4.6; N, 6.08; P, 6.73. Found: C, 75.71; H, 4.67; N, 6.11; P 6.82.

C. Preparation of Compound 16. To a mixture of 0.5 g of the salt **14a** (1.08 mmol) and 0.12 g of benzaldehyde (1.1 mmol) in 15 mL of ethanol was slowly added 10 mL of an ethanolic sodium ethoxide solution. The mixture was allowed to reflux for 3 h (TLC). After the solvent was evaporated to dryness, the residue was extracted with boiling petroleum ether (br 60-80°) to separate triphenylphosphine oxide, on cooling. Crystallization of the insoluble portion from MeCN afforded **16**.

5'-Benzylspiro-[indene-2,3'-pyrazole]-1,3-dione (16) (210 mg, 78% yield), mp 172-174°; ir: ν 1-, 3-C=O 1782, 1724, N=N 1429 cm^{-1} ; ^1H nmr: δ 2.34 (s, 2H, - CH_2), 6.36 (s, 1H, 4'- CH), 7.45-8.15 ppm (m, 9H, H-Ph); ^{13}C nmr: δ 39.2 (- CH_2), 78.6 (3'-C, spiro), 110.7 (4'-C), 124.4, 126.3, 127.4, 128.7, 128.9, 130.6, 132.5, 133.3, 135.8, 143.1 (C-Ar), 152 (5'-C), 188.2, 190.4 ppm (1-, 3-C=O); ms: m/z (EI) 288 (100) [M]⁺, 260 (18), 232 (24), 204 (37), 197 (22). *Anal.* Calcd. for $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_2$: C, 74.99; H, 4.19; N, 9.72. Found: C, 74.93; H, 4.23; N, 9.81.

D. Aqueous Basic Hydrolysis of **14**. Preparation of

Compound 17. A sample (0.5 g) of the salt **14a** (or **15**) was allowed to stir with 20 mL of NaOH (*aqu.* 10%) by warming the mixture to ~ 80° for 3 h. The product mixture was diluted with an equal amount of water, and extracted with ethyl acetate, washed, dried, and the solvent was evaporated to dryness. The residue was extracted with boiling petroleum ether (br 60-80°) to give triphenylphosphine oxide, on cooling. Crystallization of the insoluble portion from CH_2Cl_2 afforded **17**.

2,4'-Dihydrospiro-[indene-2,3'-pyrazole]-1,3-dione (17): (136 mg, 74% yield, based on **14a**), mp 126-128°; ir: ν NH 3325, 1-, 3-C=O 1782, 1724, C=N 1600 cm^{-1} ; ^1H nmr: δ 2.77 (d, $J_{\text{H-H}} = 2.1$ Hz, 2H, 4'- CH_2), 6.68 (t, $J_{\text{H-H}} = 2.1$ Hz, 1 H, 5'- CH), 7.45, 7.78 (2d, $J_{\text{H-H}} = 6.6$ Hz, 4H, H-Ar), 9.55 ppm (s, 1H, NH exchangeable with D_2O); ^{13}C nmr: δ 34.2 (4'- CH_2), 74.6 (3'-C), 124.8, 126.9, 133.8, 142.4 (C-Ar), 141.6 (5'- CH), 194, 200.3 ppm (1-, 3-C=O); ms: m/z (EI) 198 (100) [M - 2]⁺, 170 (25), 1432 (48), 77 (38). *Anal.* Calcd. for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$: C, 65.99; H, 4.03; N, 13.99. Found: C, 66.04; H, 4.12; N, 13.92.

Compound **17** (78% yield, based on **1**) could be directly obtained from the reaction of **1** with **2d**, in the presence of LiH, using the same amounts, and the same procedure applied to the reaction of **1** with **2a**.

E. Thermal Decomposition of **14**: Preparation of **18**.

A sample of 0.5 g of **14a** was heated to its melting point temperature for 30 min in an oil bath (temperature maintained 10° over melting point). The residue was extracted with boiling petroleum ether (br 60-80°), which afforded triphenylphosphine and triphenylphosphine oxide, on cooling. Crystallization of the insoluble portion from benzene yielded straw yellow needles of **18**.

1,3-Dioxo-1,1',2',3'-tetrahydrospiro[indene-2,3'-pyrazol[5-yl]ium] bromide (18) (176 mg, 67% yield), mp 175-177°; ir: $\tilde{\nu}$ 1-, 3-C=O 1780, 1723 cm^{-1} ; ^1H nmr: δ 6.54 (d, $J_{\text{H-H}} = 2.4$ Hz, 1H, 4'- HC), 7.46, 7.78 (2d, $J_{\text{H-H}} = 4.8$ Hz, 4H, H-Ar), 9.98 ppm (br, 2H, NHs); ms: m/z (EI): 279 (77) [M - 1]⁺, 278 (28), 198 (100), 172, (40), 77 (55). *Anal.* Calcd. for $\text{C}_{11}\text{H}_7\text{BrN}_2\text{O}_2$: C, 47.34; H, 2.53; Br, 28.63; N, 10.04. Found: C, 47.24; H, 2.51; Br, 28.55; N, 10.12.

Reaction of **1** with Allyltriphenylphosphonium Bromide

(2e): Preparation of Compound 20. A THF solution of 1.57 of the phosphonium salt **2e** (4.1 mmol) and 0.7 g of the diazotone **1** (4.06 mmol) was treated with LiH under the experimental conditions described in the general procedure for the reaction of **1** and **2**. The reaction mixture was heated at the reflux temperature for 10 h, followed by the usual working up, and chromatography to give compound **20**.

5'-Methylspiro[indene-2,3'-pyrazole]-1,3-dione (20) (244 mg, 78% yield), mp 190-192° (benzene); ir: ν 1-, 3-C=O 1786, 1743, N=N 1436 cm^{-1} ; ^1H nmr: δ 2.15 (s, 3H, - CH_3), 6.71 (s, 1H, 4'- CH), 7.75, 7.88 ppm (2d, $J_{\text{H-H}} = 4.4$ Hz, 4H, H-Ph); ^{13}C nmr: δ 13.2 (- CH_3), 80.6 (3'-C, spiro), 118.7 (4'-C), 124.3, 123.6, 124.7, 128.7, 135.8, 143.1 (C-Ar), 168.4 (5'-C), 190.3, 196.4 ppm (1-, 3-C=O); ms: m/z (EI) 212 (100) [M]⁺, 197 (85), 169 (33), 141 (16), 77 (32). *Anal.* Calcd. for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$: C, 67.92; H, 3.8; N, 13.2. Found: C, 67.98; H, 3.75; N, 13.27.

No reaction was observed in a parallel experiment when the above reaction (**1** + **2e**) proceeded in absence of the base.

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