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The Behavior of 3,3-Diphenylindan-1,2-dione Towards Phosphonium Ylides

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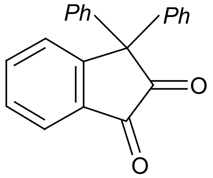
Summary. The reaction of alkoxycarbonyl- and cyanomethylene(triphenyl)phosphoranes with 3,3-diphenylindan-1,2-dione in dry benzene at room temperature for about 5 h led to the formation of a mixture of (*E*)- and (*Z*)-diastereomers. On the other hand, treatment of the dione with acetylmethylene (triphenyl)phosphorane afforded a mixture of (*E*)-3,3-diphenyl-1-(2-oxo-2-methylethylidene)indan-2-one and unexpected product (*E*)-3-(3,3-diphenyl-2-oxoindan-1-ylidene)-4-(triphenyl-λ^5-phosphanylidene)hexane-2,5-dione, whereas with benzoylmethylene(triphenyl)phosphorane gave a mixture of (*E*)-3,3-diphenyl-1-(2-oxo-2-phenylethylidene)indan-2-one, [(2*R**,3*S**)-3-benzoyl-8,8-diphenyl-3,8-dihydro-2*H*-indeno{2,1-*b*}furan-2-yl]phenylmethanone and 1,4-diphenyl-2-(3,3-diphenyl-2-hydroxy-3*H*-inden-1-yl)but-2-ene-1,4-dione. The reaction mechanisms are considered and structural assignments of the new compounds are based on spectroscopic evidence. The molecular structures of the two diastereomers and the unexpected product were elucidated by X-ray crystallography.

Keywords. 3,3-Diphenylindan-1,2-dione; Phosphonium ylides; X-Ray crystallography.

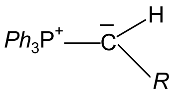
Introduction

The reaction of *o*-quinones and α-diketones with stabilized phosphonium ylides have been extensively studied in considerable details by several investigators [1–25]. Generally, these reactions initially undergo a *Wittig* mono-olefination to yield the (*Z*)- and (*E*)-diastereomers. In some cases, the reactive conjugated systems undergo a *Michael* addition with another ylide molecule, although a second *Wittig* reaction might also be observed [26–28]. Sometimes, the mono-olefination adducts react with another molecule of the same ylide to form a bis-alkylidene [24, 27, 29], fused to cyclobutene [27]. The products of these reactions depend on the nature of the α-dicarbonyls, type of ylides, or reaction conditions [30].

Previously, we have reported the reaction of 4-triphenylmethyl-1,2-benzoquinone and isatin with phosphonium ylides [2–6]. In the present communication, we examine the behavior of 3,3-diphenylindan-1,2-dione (**1**) as an asymmetrical α-diketone towards phosphonium ylides **2** and **3**.



1



2a, *R* = COO*Me*
2b, *R* = COO*Et*
2c, *R* = CN
3a, *R* = CO*Me*
3b, *R* = CO*Ph*

Results and Discussion

The reaction of equimolar amounts of **1** with stabilized phosphonium ylides **2a**–**2c** in dry benzene at room temperature for 3 h led to the formation of a mixture containing (*E*)-**6** and (*Z*)-**7** (examined by TLC) and triphenylphosphine oxide (Scheme 1). These two diastereomers were separated by silica gel column chromatography as pale yellow crystalline products and their structures were established by IR, ^{1}H NMR, and MS as well as elemental analyses. The IR spectra of both isomers **6** and **7** show a strong

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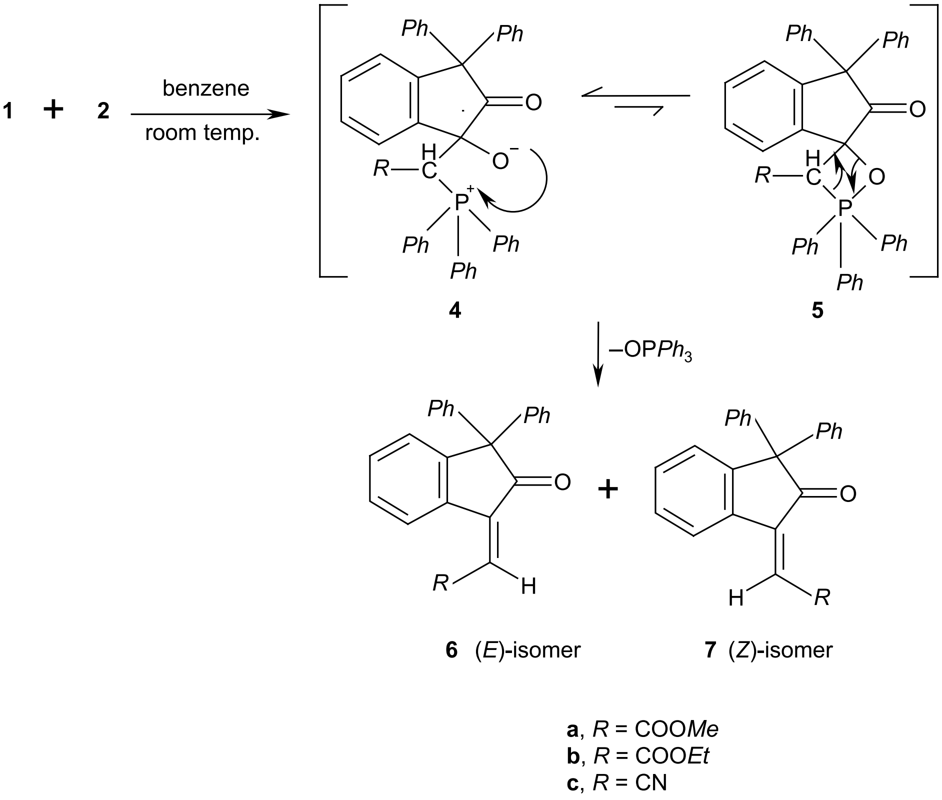


Scheme 1

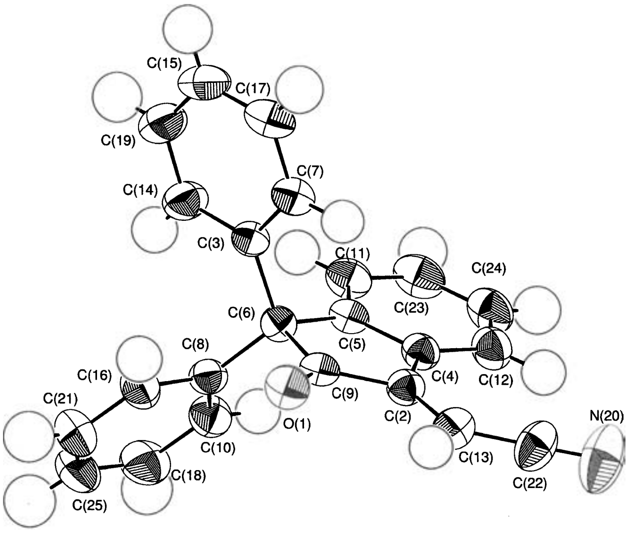


Fig. 1. X-Ray structure of isomer **6c** in the ORTEP presentation. Selected bond distances (Å) and bond angles (°): O(1)–C(9) = 1.211(2), C(2)–C(4) = 1.458(3), C(2)–C(9) = 1.489(3), C(2)–C(13) = 1.343(3), C(5)–C(6) = 1.519(3), C(13)–C(22) = 1.414(3), N(20)–C(22) = 1.141(3), C(13)–H(13) = 0.950(2), C(4)–C(2)–C(9) = 107.1(2), C(4)–C(2)–C(13) = 132.5(2), C(9)–C(2)–C(13) = 120.3(2), O(1)–C(9)–C(2) = 125.0(2), C(2)–C(13)–C(22) = 123.8(2), C(13)–C(22)–N(20) = 179.3(3), C(2)–C(13)–H(13) = 119.3(13), C(22)–C(13)–H(13) = 117.0(12)

absorption band around 1735 cm^{-1} due to the carbonyl group and their ^1H NMR spectra reveal the presence of the olefinic proton. Comparing (*E*)-**6** and (*Z*)-**7** with respect to their ^1H NMR spectra (*cf.* Experimental), it is obvious that the chemical shift of both the "diagnostic" protons at C-7 and the olefinic ones are always less deshielded in the (*Z*)-isomers **7** than those of the corresponding (*E*)-isomers **6** [31]. This is due to the anisotropic effect of either the carbonyl group of the ester or the nitrile residue [32]. Moreover, single crystal X-ray diffraction analysis of (*E*)-**6c** (Fig. 1) and (*Z*)-**7c** (Fig. 2), taken as examples, confirm the configurations.

The formation of (*E*)-**6** and (*Z*)-**7** may proceed through a *Wittig* reaction affording initially the phosphorus betaine **4**, which is followed by irreversible decomposition to give the alkenes **6** and **7** along with triphenylphosphine oxide. The 1,2-oxaphosphetane **5** was considered to be a transition state between the betaine **4** and the final products **6** and **7** (Scheme 1) [33].

On the other hand, if the dione **1** reacts with two equivalents of acetylmethylene(triphenyl)phosphorane (**3a**) in dry benzene at room temperature for about 30 h, a mixture of products was obtained

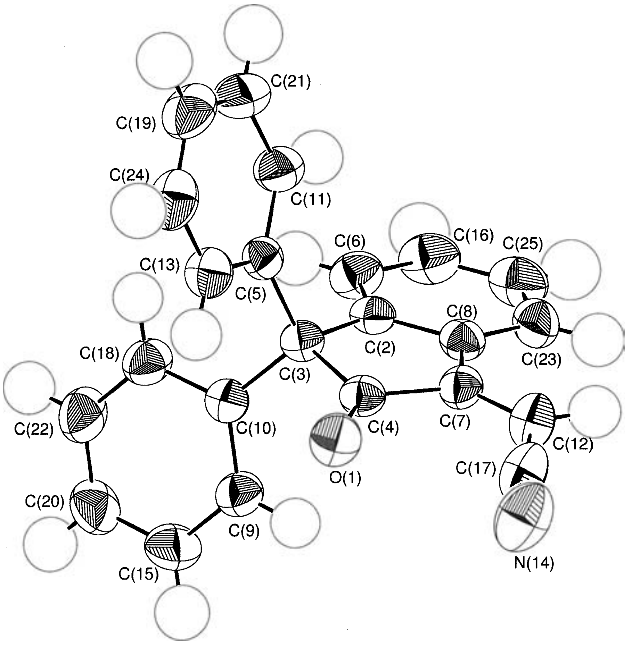


Fig. 2. X-Ray structure of isomer **7c** in the ORTEP presentation. Selected bond distances (Å) and bond angles (°): O(1)–C(4) = 1.210(2), C(2)–C(8) = 1.401(2), C(4)–C(7) = 1.495(2), C(7)–C(8) = 1.453(2), C(7)–C(12) = 1.339(2), C(12)–C(17) = 1.423(3), N(14)–C(17) = 1.150(2), C(12)–H(12) = 0.960(2), O(1)–C(4)–C(7) = 125.2(13), C(4)–C(7)–C(8) = 107.0(12), C(4)–C(7)–C(12) = 124.6(14), C(8)–C(7)–C(12) = 128.4(13), C(7)–C(12)–C(17) = 124.4(14), C(12)–C(17)–N(14) = 175.0(2), C(7)–C(12)–H(12) = 119.7(2), C(17)–C(12)–H(12) = 115.8(2)

consisting of (*E*)-3,3-diphenyl-1-(2-methyl-2-oxoethylidene)indan-2-one (**9a**) and the unexpected (*E*)-3-(3,3-diphenyl-2-oxoindan-1-ylidene)-4-(triphenyl-λ^5-phosphanylidene)hexane-2,5-dione (**12**) together with another compound which easily decomposed and could not be isolated in pure form. These compounds were separated by column chromatography on silica gel. Triphenylphosphine and triphenylphosphine oxide were also isolated and identified. The structures were assigned using elemental analyses and spectral properties, which were consistent with expectation. The IR spectrum of the yellow crystalline product **9a** revealed the presence of absorption bands around 1731, 1681 cm^{-1} corresponding to the carbonyl groups. Its ^{1}H NMR spectrum showed a signal at $\delta = 6.95$ ppm for the exocyclic vinyl proton. The phenyl proton at C-7 appeared as a doublet at $\delta = 8.84$ ppm with a coupling constant $J = 7.8$ Hz, whereas the other two phenyl protons at C-5 and C-6 appeared as two *di-ortho*/*meta* triplets of doublets [34] at $\delta = 7.42$ and 7.50 ppm with $J = 7.5$, 1.2 Hz.

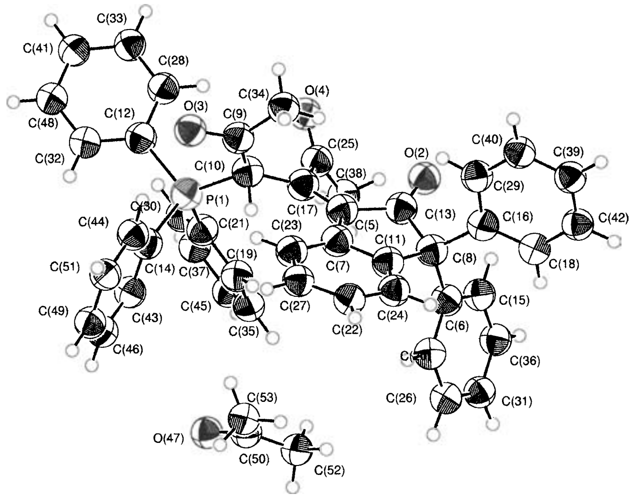
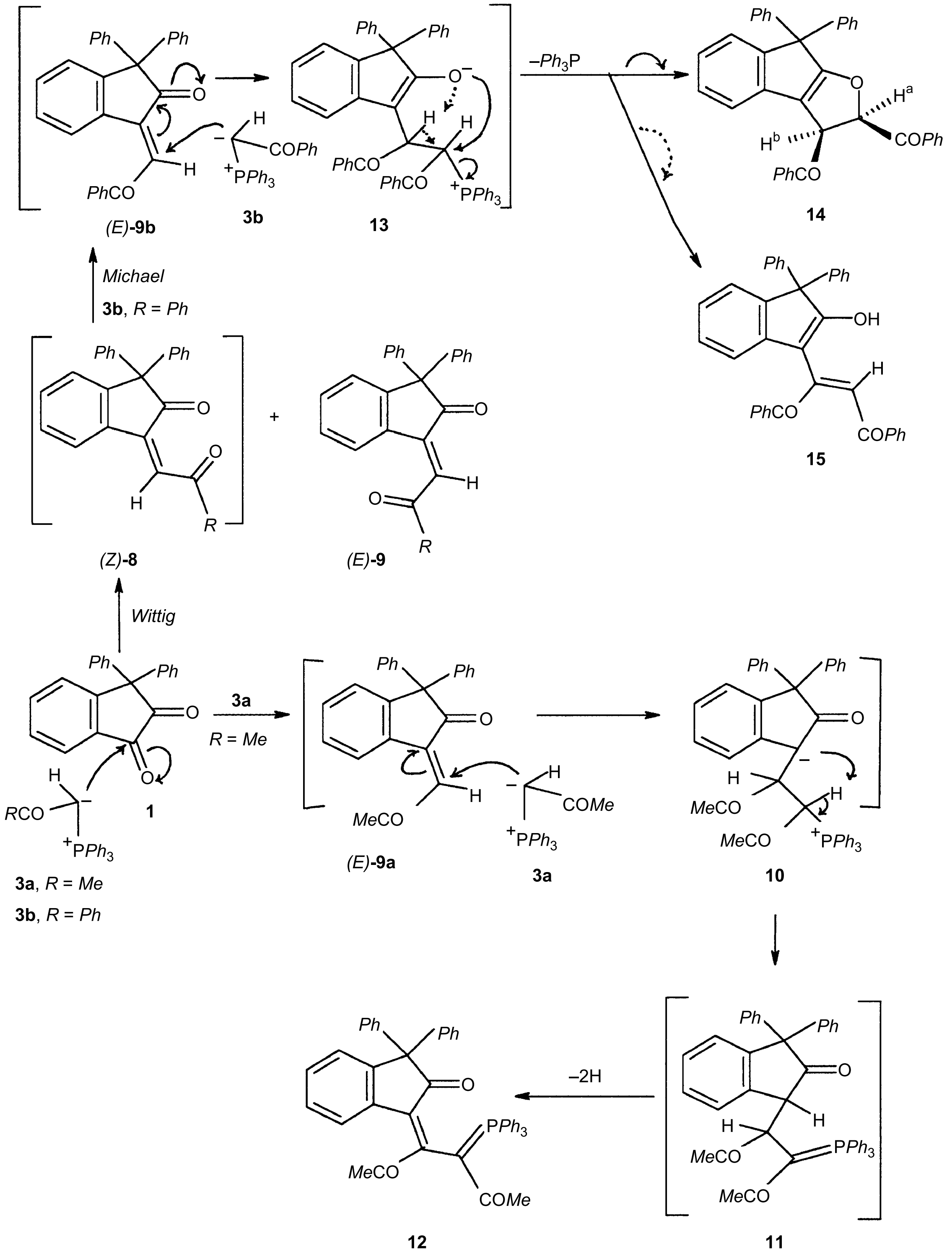


Fig. 3. X-Ray structure of compound **12** in the ORTEP presentation. Selected bond distances (Å) and bond angles (°): P(1)–C(10) = 1.736(3), O(2)–C(13) = 1.218(3), O(3)–C(9) 1.263(3), O(4)–C(25) = 1.211(4), C(5)–C(17) = 1.361(4), C(9)–C(10) = 1.407(4), C(9)–C(34) = 1.508(4), C(10)–C(17) = 1.466(4), C(17)–C(25) = 1.525(4), C(25)–C(38) = 1.505(5), C(13)–C(5)–C(17) = 124.0(3), O(3)–C(9)–C(10) = 120.1(3), C(10)–C(9)–C(34) = 123.0(3), P(1)–C(10)–C(17) = 126.6(2), O(2)–C(13)–C(5) = 125.9(3), C(10)–C(17)–C(25) = 116.4(3), O(4)–C(25)–C(17) = 117.2(3), O(4)–C(25)–C(38) = 120.9(3)

The unexpected product **12** was isolated as deep red crystals. Its IR and ^{1}H NMR spectra are consistent with the proposed structure (*cf.* Experimental). Moreover, a single crystal X-ray diffraction analysis of **12** (crystallized from acetone) (Fig. 3) confirmed the configuration. The bond lengths 1.361(4), 1.736(3) Å of the corresponding exocyclic C=C and C=P are in agreement with the established structure. A possible explanation for the formation of the adduct **12** as shown in Scheme 2 is suggested to involve initial *Wittig* mono-olefination from the reaction of dione **1** with ylide **3a** yielding the alkene (*E*)-**9a**, which in turn reacts with another molecule of **3a** to form the intermediate **10**. The phosphonium species **10** afforded eventually the novel type of phosphonium ylide **12** through dehydrogenation of **11**.

When dione **1** was treated with two mole equivalents of benzoylmethylene(triphenyl)phosphorane (**3b**) in boiling benzene for 35 h, (*E*)-3,3-diphenyl-1-(2-oxo-2-phenylethylidene)indan-2-one (**9b**), [(2*R**,3*S**)-3-benzoyl-8,8-diphenyl-3,8-dihydro-2*H*-indeno-[2,1-*b*]furan-2-yl]phenylmethanone (**14**), and 1,4-diphenyl-2-(3,3-diphenyl-2-hydroxy-3*H*-inden-1-yl)but-2-ene-1,4-dione (**15**) were obtained. These



Scheme 2

compounds were separated by column chromatography on silica gel. Triphenylphosphine and triphenylphosphine oxide were also isolated and identified. The assigned structures of the products **9b**, **14**, and **15** were established from the elemental analyses, IR, ^{1}H NMR, and MS.

Compound **9b** was isolated as yellow crystals. Its IR spectrum exhibited strong bands at 1736, 1658 cm^{-1} due to the carbonyl groups. The ^{1}H NMR spectrum showed a singlet signal at $\delta = 7.62$ ppm corresponding to the exocyclic vinyl proton and a doublet at $\delta = 8.57$ ppm, with a coupling constant value $J = 8.1$ Hz, due to the aromatic proton at C-7. The colorless crystals **14** showed characteristic bands in the IR spectrum at 1745, 1685, and 1674 cm^{-1} for the carbonyl groups and its ^{1}H NMR disclosed the presence of two doublets at $\delta = 4.10$, 4.18 ppm with coupling constant $J = 7.8$ Hz, ascribed to the two vicinal protons H^a and H^b, which are in a *cis*-configuration. This value is supported by the recorded coupling constants bearing a considerable likeness to those values reported for other similar *cis*-derivatives of dihydrofuran [15, 16]. The red product **15** revealed the presence of the hydroxyl group from an absorption band at 3421 cm^{-1} in the IR spectrum and in the ^{1}H NMR spectrum a singlet at $\delta =$ 4.85 ppm exchangeable with D_2O. The proposed mechanism for the formation of **14** and **15** is shown in Scheme 2. Compounds **1** and **3b** initially undergo a *Wittig* mono-olefination to form **8b** and **9b**, which by further *Michael* addition of a second ylide **3b** afford the indenoxy anion intermediate **13**. Intramolecular hydrogen abstraction of the β-hydrogen, or nucleophilic attack at the α-carbon of the phosphonium group by the indenoxy anion in **13** accompanied by triphenylphosphine elimination results in the formation of **14** and **15**.

Conclusion

From the results of the present investigation it was derived that the reaction of **1** with alkoxycarbonylmethylene(triphenyl)phosphoranes (**2a**, **2b**) and cyanomethylene(triphenyl)phosphorane (**2c**) proceeds in a mono-olefination at only one carbonyl group to yield the corresponding diastereomeric (*E*)-**6** and (*Z*)-**7**. If **1** reacts with acetylmethylene(triphenyl)phosphorane (**3a**) it affords **9a** and **12**, and with benzoylmethylene(triphenyl)phosphorane (**9b**), **14** and **15**. This means that the reactivity of the stabilized phosphoranes towards α-diketones is influenced to a great extent by the substituents at the ylide carbon atom and also depends on the type of the α-dicarbonyl compounds.

Experimental

Melting points were determined on an electrical digital-melting-point apparatus. The IR spectra were recorded in KBr disks, on a Jasco Fourier Transform Infra-red spectrophotometer Model FT/IR-3000E. The NMR spectra were recorded on a Varian MERCURY 300 spectrometer for ^{1}H operating at 300 MHz. Chemical shifts are given in positive values downfield from internal *TMS*. The mass spectra (MS) were determined at 70 eV on a Finnigan MAT SSQ 7000 spectrometer.

X-Ray Structure Determination

The crystal data were measured at $T = 298$ K on a Kappa CCD Enraf Nonius FR 590 diffractometer. The crystal structure was solved and refined using maXus (Nonius, Delft and MacScience, Japan). Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator were used for data collection. Further details of the structure determination (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) were deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom. Any request should be accompanied by the full literature citation and the CCDC reference numbers 626563 (**6c**), 626564 (**7c**), and 626565 (**12**).

*Reaction of Dione **1** with Methoxycarbonylmethylene(triphenyl)phosphorane (**2a**)*

A mixture of 0.6 g **1** [35] (2 mmol) and 0.73 g **2a** [36] (2.2 mmol) in 20 cm^3 dry benzene was stirred at room temperature for about 5 h. Then, the solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel using *n*-hexane and acetone as eluent to afford **6a**, **7a**, and triphenylphosphine oxide.

(E)-(3,3-Diphenyl-2-oxoindan-1-ylidene)acetic acid methyl ester (**6a**, $C_{24}H_{18}O_3$)

Yield 70%; pale yellow crystals; mp 159–160°C (benzene/*n*-hexane); IR: $\bar{\nu} = 1736$, 1714 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 3.85$ (s, O*Me*), 6.69 (s, =CH), 7.09–7.32 (m, 11 ArH), 7.45, 7.50 (2dt, $J = 7.5$, 1.5 Hz, 2 ArH at C-5, C-6), 8.92 (d, $J = 7.2$ Hz, ArH at C-7) ppm; MS: m/z (%) = 354 (M$^+$, 3).

(Z)-(3,3-Diphenyl-2-oxoindan-1-ylidene)acetic acid methyl ester (**7a**, $C_{24}H_{18}O_3$)

Yield 11%; pale yellow crystals; mp 164–165°C (CHCl$_3$/*n*-hexane); IR: $\bar{\nu} = 1732$, 1707 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 3.87$ (s, O*Me*), 6.11 (s, =CH), 7.18–7.33 (m, 10 ArH), 7.40–7.48 (m, 2 ArH at C-4, C-5), 7.63 (dt, $J = 7.5$, 1.5 Hz, ArH at C-6), 7.85 (d, $J = 7.2$ Hz, ArH at C-7) ppm; MS: m/z (%) = 354 (M$^+$, 32).

Triphenylphosphine Oxide

Yield quantitative; colorless crystals; identified by mp and mixed mp with an authentic sample.

*Reaction of Dione **1** with Ethoxycarbonylmethylene(triphenyl)phosphorane (**2b**)*

Carrying out the same experimental procedure as described above using 0.6 g **1** (2 mmol), 0.77 g **2b** [36] (2.2 mmol), and 20 cm^3 dry benzene. The chromatographic separation by *n*-hexane and acetone as eluent gave the two isomers **6b**, **7b**, and triphenylphosphine oxide.

(E)-3,3-Diphenyl-2-oxoindan-1-ylidene)acetic acid ethyl ester (**6b**, $C_{25}H_{20}O_3$)

Yield 65%; pale yellow crystals; mp 111–112°C [benzene/petroleum ether (bp 60–80°C)]; IR: $\bar{\nu} = 1738$, 1709 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (t, $J = 7.2$ Hz, OCH_2CH_3), 4.32 (q, $J = 7.2$ Hz, OCH_2), 6.68 (s, =CH), 7.08–7.32 (m, 11 ArH), 7.44, 7.49 (2dt, $J = 7.5$, 1.5 Hz, 2 ArH at C-5, C-6), 8.91 (d, $J = 7.2$ Hz, ArH at C-7) ppm; MS: m/z (%) = 368 (M$^+$, 5).

(Z)-(3,3-Diphenyl-2-oxoindan-1-ylidene)acetic acid ethyl ester (**7b**, $C_{25}H_{20}O_3$)

Yield 14%; pale yellow crystals; mp 143–144°C ($CHCl_3$/*n*-hexane); IR: $\bar{\nu} = 1728$, 1709 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (t, $J = 7.2$ Hz, OCH_2CH_3), 4.36 (q, $J = 7.2$ Hz, OCH_2), 6.11 (s, =CH), 7.18–7.33 (m, 10 ArH), 7.40–7.47 (m, 2 ArH at C-4 and C-5), 7.62 (dt, $J = 7.5$, 1.5 Hz, ArH at C-6), 7.35 (d, $J = 7.2$ Hz, ArH at C-7) ppm; MS: m/z (%) = 368 (M$^+$, 16).

Triphenylphosphine Oxide

Yield quantitative; colorless crystals; identified by mp and mixed mp with an authentic sample.

*Reaction of Dione **1** with Cyanomethylene(triphenyl)-phosphorane (**2c**)*

The reaction of 0.6 g **1** (2 mmol) with 0.66 g **2c** [37] (2.2 mmol) in 20 cm^3 dry benzene was carried out for 7 h and the reaction mixture was worked up according to the above described procedure for ylide **2a**. The chromatographic separation gave two isomers **6c**, **7c**, and triphenylphosphine oxide.

(E)-(3,3-Diphenyl-2-oxoindan-1-ylidene)acetonitrile (**6c**, $C_{23}H_{15}NO$)

Yield 63%; pale yellow crystals; mp 149–150°C (ethyl acetate/*n*-hexane); IR: $\bar{\nu} = 2216$ (C≡N), 1734 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 6.11$ (s, =CH), 7.04–7.36 (m, 11 ArH), 7.52, 7.57 (2dt, $J = 7.5$, 1.5 Hz, 2 ArH at C-5, C-6), 8.45 (dd, $J = 7.0$, 1.2 Hz, ArH at C-7) ppm; MS: m/z (%) = 321 (M$^+$, 61).

*Crystallographic Data of **6c***

$C_{23}H_{15}NO$, $M_r = 321.379$, triclinic, crystallizes in space group *P*-1, $a = 8.4354(2)$, $b = 10.0223(3)$, $c = 10.7948(5)$ Å, $V = 863.70(5)$ Å^3, $Z = 2$, $D_c = 1.236$ g cm^{-1}, θ values 2.91–27.48°, absorption coefficient μ (Mo-K$_\alpha$) = 0.08 mm^{-1}, $F(000) = 336$. The unique reflections measured were 4419, of which 2091 reflections with threshold expression $I > 3\sigma(I)$ were used in the structural analysis. Convergence for 256 variable parameters by least-squares refinement on F^2 with $\omega = 1/[\sigma^2(F_o{}^2) + 0.10000\ F_o{}^2]$. The final agreement factors were $R = 0.041$ and $wR = 0.074$ with a goodness-of-fit of 0.906.

(Z)-(3,3-Diphenyl-2-oxoindan-1-ylidene)acetonitrile (**7c**, $C_{23}H_{15}NO$)

Yield 17%; pale yellow crystals; mp 177–178°C ($CHCl_3$/*n*-hexane); IR: $\bar{\nu} = 2214$ (C≡N), 1743 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.98$ (s, =CH), 7.08–7.32 (m, 10 ArH), 7.32 (d overlapped, $J = 7.2$ Hz, ArH at C-4), 7.50, 7.55 (2 dt, $J = 7.5$, 1.2 Hz, 2 ArH at C-5 and C-6), 7.69 (d, $J = 7.2$ Hz, ArH at C-7) ppm; MS: m/z (%) = 321 (M$^+$, 69).

*Crystallographic Data of **7c***

$C_{23}H_{15}NO$, $M_r = 321.379$, monoclinic, crystallizes in space group $P2_1/c$, $a = 8.8281(2)$, $b = 16.8513(4)$, $c = 13.7453(3)$ Å, $V = 1707.86(7)$ Å^3, $Z = 4$, $D_c = 1.25$ g cm^{-1}, θ values 2.91–25.35°, absorption coefficient μ (Mo-K$_\alpha$) = 0.08 mm^{-1}, $F(000) = 672$. The unique reflections measured were 3446, of which 2092 reflections with threshold expression $I > 3\sigma(I)$ were used in the structural analysis. Convergence for 226 variable parameters by least-squares refinement on F^2 with $\omega = 1/[\sigma^2(F_o{}^2) + 0.10000\ F_o{}^2]$. The final agreement factors were $R = 0.039$ and $wR = 0.074$ with a goodness-of-fit of 1.254.

Triphenylphosphine Oxide

Yield quantitative; colorless crystals; identified by mp and mixed mp with an authentic sample.

*Reaction of Dione **1** with Acetylmethylene(triphenyl)-phosphorane* (**3a**)

A solution of 0.6 g **1** (2 mmol) and 1.27 g **3a** [38] (4.2 mmol) in 20 cm^3 dry benzene was stirred at room temperature for about 30 h. Then, the volatile material was evaporated under reduced pressure and the residue was chromatographed on silica gel, using acetone and petroleum ether (bp 60–80°C) as eluent to produce isomer **9a**, **12**, triphenylphosphine, and triphenylphosphine oxide besides a compound which easily decomposed and could not be isolated in pure form.

(E)-3,3-Diphenyl-1-(2-methyl-2-oxoethylindene)indan-2-one (**9a**, $C_{24}H_{18}O_2$)

Yield 20%; yellow crystals; mp 143–144°C ($CHCl_3$/*n*-hexane); IR: $\bar{\nu} = 1731$, 1682 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.44$ (s, *Me*), 6.95 (s, =CH), 7.06–7.36 (m, 11 ArH), 7.42, 7.50 (2dt, $J = 7.5$, 1.2 Hz, 2 ArH at C-5 and C-6), 8.84 (d, $J = 7.8$ Hz, ArH at C-7) ppm; MS: m/z (%) = 338 (M$^+$, 100).

(E)-3-(3,3-Diphenyl-2-oxoindan-1-ylidene)-4-(triphenyl-λ^5-phosphanylidene)hexane-2,5-dione (**12**, $C_{45}H_{35}O_3P$)

Yield 18%; deep red crystals; mp 147–148°C (benzene/*n*-hexane); IR: $\bar{\nu} = 1712$, 1681 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.10$, 2.00 (2s, 2*Me*), 7.00–7.78 (m, 28 ArH), 8.23 (d, $J = 7.2$ Hz, ArH at C-7) ppm; MS: m/z (%) = 654 (M$^+$, 3).

Triphenylphosphine and Triphenylphosphine Oxide

Yields quantitative; colorless crystals; identified by mp and mixed mp with an authentic samples.

*Preparation of a Single Crystal of **12***

A single crystal X-ray diffraction of **12** was prepared from acetone solution with molecular formula $C_{45}H_{35}O_3P \cdot C_3H_6O$ and molecular weight 712 (*i.e.* the crystal contains one mole of acetone).

*Crystallographic Data of **12***

$C_{45}H_{35}O_3P \cdot C_3H_6O$, $M_r = 712.834$, triclinic, crystallizes in space group P_1, $a = 9.4780(5)$, $b = 9.8221(6)$, $c = 22.4452(12)$ Å, $V = 1967.9(2)$ Å^3, $Z = 2$, $D_c = 1.205\,\mathrm{g\,cm^{-1}}$, θ values 2.910–22.213°, absorption coefficient μ (Mo-K$_\alpha$) = $0.11\,\mathrm{mm^{-1}}$, $F(000) = 754$. The unique reflections measured were 5689, of which 2119 reflections with threshold expression $I > 3\sigma(I)$ were used in the structural analysis. Convergence for 478 variable parameters by least-squares refinement on F^2 with $\omega = 1/[\sigma^2(F_o{}^2) + 0.10000\ F_o{}^2]$. The final agreement factors were $R = 0.054$ and $wR = 0.098$ with a goodness-of-fit of 2.351.

*Reaction of Dione **1** with Benzoylmethylene(triphenyl)-phosphorane* (**3b**)

A mixture of 0.6 g **1** (2 mmol) and 1.6 g **3b** [38] (4.2 mmol) in 20 cm^3 dry benzene was heated under reflux for about 35 h. After removal of the volatile materials under reduced pressure, the residue was chromatographed on silica gel, using *n*-hexane and ethyl acetate as eluent. The isomer **9b**, **14**, **15**, triphenylphosphine, and triphenylphosphine oxide were obtained.

(E)-3,3-Diphenyl-1-(2-oxo-2-phenylethylidene)indan-2-one (**9b**, $C_{29}H_{20}O_2$)

Yield 44%; yellow crystals; mp 183–184°C [benzene/petroleum ether (40–60°C)]; IR: $\bar{\nu} = 1736, 1658$ (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 7.14$–8.08 (m, 18 ArH), 7.62 (s, =CH), 8.57 (d, $J = 8.1$ Hz, ArH at C-7) ppm; MS: m/z (%) = 400 (M$^+$, 92).

[(2R,3S*)-3-Benzoyl-8,8-diphenyl-3,8-dihydro-2H-indeno[2,1-b]furan-2-yl]phenylmethanone* (**14**, $C_{37}H_{26}O_3$)

Yield 12%; colorless crystals; mp 253–254°C (benzene/*n*-hexane); IR: $\bar{\nu} = 1745, 1674$ (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 4.10, 4.18$ (2d, $J = 7.8$ Hz, H^a and H^b), 6.70–7.93 (m, 24 ArH) ppm; MS: m/z (%) = 518 (M$^+$, 8).

1,4-Diphenyl-2-(3,3-diphenyl-2-hydroxy-3H-inden-1-yl)but-2-ene-1,4-dione (**15**, $C_{37}H_{26}O_3$)

Yield 30%; red crystals; mp 108–109°C (CHCl$_3$/*n*-hexane); IR: $\bar{\nu} = 3421$ (OH), 1728, 1685 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 4.85$ (s, OH exchangeable with D$_2$O), 7.13–7.40 (m, 24 ArH and =CH) ppm; MS: m/z (%) = 518 (M$^+$, 19).

Triphenylphosphine and Triphenylphosphine Oxide

Yields quantitative; colorless crystals; identified by mp and mixed mp with an authentic samples.

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