Fulvenes and Thermochromic Ethylenes. Part 57.
The Wittig-Horner Reaction with Fulvene Ketones and Related Ketones

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Very little work has been reported on the Wittig reaction of fulvene ketones such as fluoronone (1), 2,3-diphenylindenone (2), dibenzofulvencycloheptatrienone (3) or the isosters of the latter, xanthone (4), and thiaxanthone (5); the ketones 3–5 often show highly attenuated carbonyl properties which should be reflected in their behaviour towards Wittig reagents. We have studied the Wittig-Horner reaction of these ketones and, for comparison of 10,11-dihydrodibenzofulvencycloheptatrien-5-one (6) and indan-1-one (7). We expected that the more polar the carbonyl group would be as, e.g., indicated by its IR absorption (see Table 1), the easier should be the reaction with the Wittig-Horner reagents. However, it turned out that there was no significant difference between dibenzocycloheptatrienone, xanthone, and thiaxanthone on the one hand and the ketones
derived from cyclopentadiene, 2,3-diphenylidenone (2) and fluorenone (1), on the other. It seems that the polarizing power of the anions of the Wittig-Horner reagents obscures the difference in polarity between the fulvene ketones studied.

The reagents employed in this study were:


We hoped to find an effect of the larger negativity of the anions containing nitro- and cyano-groups as compared with the parent compound and the p-chloro-substituted product. The anions were generated from the Wittig-Horner reagents with sodium hydride, either in diglyme or dimethyl sulfoxide as solvent.

We have also tried the condensation of fulvene ketones with diethyl fluorene-9-phosphonate (8); however, only the ketone 3 forms the expected product, the known tetrabenzopentalenaldehyde (9). Indeed, for theoretical reasons this should be the most stable of the products expected in these condensations.

![Chemical structures](image)

On the whole, the reactions studied were slow. In some cases, this had the consequence that the diethyl benzylphosphonate anions decomposed to the corresponding stilbenes:

\[ \text{ArO} \overset{\Phi}{\text{CH}} \overset{\Phi}{\text{OCCH}_3} \overset{\Phi}{\text{OCCH}_3} \xrightarrow{2\text{eq.} M^+} \text{Ar} \overset{\Phi}{\text{CH=CH=CH}} \text{Ar} \]

This decomposition took place with the p-nitro- and p-cyano-derivatives, in which the negative charge of the species would very probably be spread over the whole molecule.

The transformation of 4-nitrobenzyl chloride, for example, into 4,4′-dinitrostilbene under the influence of alkali is well known\(^1\); the mechanism is assumed to be the following:

\[ \text{O}_2\text{N} \overset{\Phi}{\text{CH}} \overset{\Phi}{\text{CH}} \overset{\Phi}{\text{Cl}} \xrightarrow{\text{HCl}} \text{O}_2\text{N} \overset{\Phi}{\text{CH=CH}} \overset{\Phi}{\text{CH}} \overset{\Phi}{\text{Cl}} \]

By analogy, the above reaction would lead to the elimination of diethyl phosphite.

In no case in which the fulvenes or fulvene-like compounds prepared could theoretically exist in two stereoisomeric forms, was more than one isomer isolated.

Anthraquinone did not react at all in the Wittig-Horner reactions, and anthrone was recovered as anthraquinone. Anthrone is known to be readily oxidized in alkaline medium\(^2\).

Indan-1-one was transformed into ethyl indan-1-yldeneacetate and 1-benzylideneneindene, but a considerable part of the ketone polymerized under the alkaline reaction conditions\(^3\).

The p-carboxy derivatives of the fulvenes prepared were easily decarboxylated using copper chromite in quinoline. Thus, 5-methylene-dibenzo[a;e]cycloheptatriene and its 10;11-dihydro derivative could be prepared, whereas 9-methylenelfuorene could not be isolated in pure form, as expected\(^4\).

Surprisingly, the decarboxylation of xanthilylidene- and thiaxanthilylideneacetic acid did not give the (hitherto unknown) methylene derivatives of xanthene and thiaxanthene\(^5\) but, through autoxidation, xanthone and thiaxanthone, respectively.

The study of the spectra of the fulvenes and fulvene analogs prepared led to some unexpected observations. The longest-wavelength band of benzylidenelfuorene (10) undergoes a bathochromic shift when a nitro group is introduced into the 4-position of the benzylidene moiety, whereas a cyano group or a chlorine atom exerts practically no effect at all. In the case of 5-benzylidenebenzo[a;e]cycloheptatriene (11), nitro groups effect a hypochromic shift; here, too, the cyano group and chlorine do not significantly affect the spectrum. This difference may well be related to the fact that in 10 and 11 the fulvene system and its vinyllog are polarized in opposite directions, the polarization

<table>
<thead>
<tr>
<th>Ketone</th>
<th>(\nu_{\text{cm}^{-1}})</th>
<th>Literature</th>
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</thead>
<tbody>
<tr>
<td>Fluorenone (1)</td>
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<tr>
<td>2,3-Diphenyldienone (2)</td>
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<tr>
<td>Dibenzo[a;e]-cycloheptatriene (3)</td>
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<td>Xanthone (4)</td>
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<td>Thiaxanthone (5)</td>
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<tr>
<td>10,11-Dihydrodibenzo[a;e]-cycloheptatriene 5-one (6)</td>
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<tr>
<td>Indan-1-one (7)</td>
<td>1721</td>
<td>35</td>
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</table>

Table 1. Carbonyl Frequencies of Some Fulvene Ketones
thus being influenced by the electronegative nitro group in opposite ways, as has been observed before. The derivatives of dibenzo[a,e]cycloheptatriene and its 10,11-dihydro derivative have practically identical spectra.

In conclusion, it can be said that the Wittig-Horner reaction provides an additional synthetic route to fulvenes and fulvene analogs of various types.

The diethyl benzylphosphonates

were prepared by using the Michelines-Artunov reaction with triethyl phosphonoacetate from sodium diethyl phosphite and ethyl chloroacetate.

Diethyl fluorene-9-phosphonate was obtained from triethyl phosphite and 9-bromofluorene; yield: 65%; b.p. c. 150°C.

In the condensation reactions, we employed sodium hydride (50%) in diglyme or in dimethylsulfoxide.

Reactions with fluorenone (1):

Ethyl fluorenylidenacetate: A solution of triethyl phosphonoacetate (2.24 g) in diglyme (5 ml) was added to a suspension of 50% sodium hydride (0.48 g) in diglyme (20 ml). After 1 hr, a solution of fluorenone (1.3 g) in diglyme (10 ml) was added to the mixture. The blue solution was refluxed for 5 hr and then decomposed with water (150 ml). The aqueous layer was extracted thoroughly with ether. The extracts were combined and the ether evaporated. The oily residue, which boiled at 188-189°C/1.7 mm, solidified spontaneously; yield: 2.4 g (96%); (When the reaction mixture was kept at 60°C for 1 hr, the yield was 36%). The product was recrystallized from ethanol; m.p. 73°C (Lit. 13, m.p. 77°C).

IR (KBr): 1700 (C = O), 1605 (C = C) cm⁻¹

UV (C₂H₅OH): λ max = 223 (4.19), 257 (4.56), 284 (3.90), 317 μm (log ε = 3.92).

Hydrolysis with sodium hydroxide in aqueous ethanol afforded free fluorenylideneacetic acid in quantitative yield; from ethanol, m.p. 222°C (Lit. 13, m.p. 225-226°C).

IR (KBr): 1690 (C = O), 1600 (C = C) cm⁻¹

UV (C₂H₅OH): λ max = 224 (4.32), 262 (4.40), 284 (4.04), 314 μm (log ε = 4.05).

9-Benzylidenefluorene: In a nitrogen atmosphere, a suspension of 50% sodium hydride (0.48 g) in dimethyl sulfoxide (25 ml), distilled over calcium chloride, was heated at 80°C until the evolution of hydrogen ceased. Then, a solution of diethyl benzylphosphonate (2.28 g) in dimethyl sulfoxide (5 ml) and a solution of fluorenone (1.8 g) in dimethyl sulfoxide (20 ml) were added at room temperature, and the mixture was heated for 30 hr at 100°C. The oily product was fractionated in vacuo; after some unreacted fluorenone (b.p. 25°C/110-120°C), benzylidenefluorenone distilled at b.p. 25°C/113-183°C; yield: 1.1 g (42%); from ethanol, m.p. 76°C (Lit. 13, m.p. 74.5-76.8°C).

UV (C₂H₅OH): λ max = 227 (4.35), 258 (4.29), 326 μm (log ε = 4.09); identical with data given in Lit. 13.

In diglyme, fluorenone did not react with diethyl benzylphosphonate.

9-(2-Nitrobenzylidene)-fluorene was obtained analogously; reaction mixture was heated at 70-80°C for 9 hr; yield: 1 g (66%); m.p. 167-168°C, from ethanol, as reported in Lit. 13.

UV (C₂H₅OH): λ max = 224 (4.40), 259 (4.31), 355 μm (log ε = 4.09).

9-(2-Nitrobenzylidene)-fluorene was obtained analogously; yield: 0.69 g (46%); from butanol, yellowish crystals, m.p. 188-191°C.

IR (KBr): ν max = 1595, 1515, 1530 cm⁻¹

UV (C₂H₅OH): λ max = 226 (4.37), 255 (4.29), 357 μm (log ε = 4.07).

C₂H₁₇NO₃ calc. C 80.3 H 4.3 N 4.7

found 79.6 4.3 4.1

In diglyme as solvent, no condensation took place; fluorenone was recovered, and diethyl 2-nitrobenzylphosphonate was converted into 2,2-dinitro-trans-stilbene, m.p. 194°C, from ethanol (Lit. 13, m.p. 192°C); elemental analysis in good accordance with calculated values.

9-(4-Cyanobenzylidene)-fluorene was prepared from the corresponding components in diglyme as solvent. The mixture was refluxed for 12 hr and the product, after dilution with water, taken up in ether. The resulting oil crystallized immediately; yield: 1.2 g (43%); from isopropanol, m.p. 151°C (Lit. 16, m.p. 151°C).

IR (KBr): ν max = 2210 (C = N), 1595 (C = C) cm⁻¹

UV (C₂H₅OH): λ max = 229 (4.36), 257 (4.40), 331 μm (log ε = 4.14).

C₂H₃N calc. C 90.3 H 4.7 N 5.0

found 89.6 4.9 5.0

9-(4-Chlorobenzylidene)-fluorene was prepared from the components in dimethyl sulfoxide. The reaction was carried out at 100°C for 14 hr; yield: 36%; from glacial acetic acid, m.p. 148-149°C (Lit. 14, m.p. 151°C).

UV (C₂H₅OH): λ max = 227 (4.37), 258 (4.30), 328 μm (log ε = 4.12).

With diethyl fluorene-9-phosphonate, fluorenone could not be induced to react.

2-Amino-9-(4-cyanobenzylidene)-fluorene was obtained analogously from 2-aminofluorenone and diethyl 4-cyanobenzylphosphonate in dimethyl sulfoxide at 100°C (25 hr). The product was dissolved in benzene and chromatographed on neutral alumina, pentane serving as eluent. A first fraction was identified as 4,4'-dinitrostilbene; from benzene, m.p. 279-281°C (Lit. 16, m.p. 282°C); elemental analysis in good accordance with calculated values. On subsequent elution with hexane, a red product was obtained; yield: 0.4 g (40%); from benzene, m.p. 206-208°C.

IR (KBr): ν max = 3330 (N-H), 2210 (C = N), 1610 (C = C), 1450 cm⁻¹

UV (C₂H₅OH): λ max = 275 (4.38), 323 μm (log ε = 4.30).

C₂H₁₄N₂ calc. C 85.7 H 4.8 N 9.5

found 85.6 5.2 9.0

Reactions with Dibenzo[a,e]cycloheptatriene (3):

The starting material was prepared according to Lit. 13. Most of the reactions are summarized in Table 2.

Ethyl dibenzo[a,e]cycloheptatrienylidenacetate: To a suspension of 50% sodium hydride (0.24 g) in diglyme (15 ml), a solution of triethyl phosphonoacetate (1.12 g) in diglyme (5 ml) and a solution of dibenzo[a,e]cycloheptatriene (1.03 g) in diglyme (20 ml) were added, and the mixture was refluxed for 11 hr. The product was a viscous oil; yield: 0.7 g (51%); b.p. 167°C (20°C).

IR (CHCl₃): ν max = 1705, 1630, 1590 cm⁻¹

UV (C₂H₅OH): λ max = 231 μm (log ε = 4.28).

C₁₂H₁₂O₂ calc. C 83.0 H 5.7

found 82.8 6.1

Dibenzo[a,e]cycloheptatrienylidenacetic acid was obtained by hydrolysis of the ethyl ester with aqueous alcoholic potassium hydroxide; from benzene, colorless crystals, m.p. 202-204°C (Lit. 13, m.p. 212°C (dec.).

IR (KBr): ν max = 3400, 3000, 1690, 1625, 1565 cm⁻¹

UV (C₂H₅OH): λ max = 231 (4.34), 300 μm (log ε = 4.00).

C₁₂H₁₂O₂ calc. C 82.3 H 4.8

found 82.4 4.5
5-Methylene-dibenzo[a;e]cycloheptatriene (Dibenzoheptafulvene): A mixture of dibenzo[a;e]-cycloheptatrienylidenecarboxylic acid (0.5 g), quinoline (15 ml), and copper chromite (0.4 g) was heated for 3 hr at 210–220°C and then poured into 10% hydrochloric acid (60 ml). Extraction of the product with ether gave an almost quantitative yield of a solid which was recrystallized from methanol; m.p. 118–120°C (Lit., m.p. 119–120°C).

UV (C₂H₅OH): λ_max = 226 (3.61), 295 μm (log e = 4.00).

C₁₈H₁₂ calc. C 94.1 H 5.9
found 93.9 5.8

Tetrazenocyclo pentahexafulvene (9): A solution of diethyl fluorene-9-phosphonate (8.3 g) in toluene (3 ml) and a solution of dibenzo[a;e]-cycloheptatriene (3; 1.03 g) in toluene (20 ml) were successively added, with stirring and at room temperature, to a suspension of 50% sodium hydride (0.48 g) in toluene (25 ml). The mixture was refluxed for 10 hr and poured into water (200 ml). The precipitate (9) was filtered off (0.25 g; from benzene/heptane, m.p. 301–302°C) and the benzene solution dried and evaporated. The residue was dissolved in benzene and chromatographed on neutral alumina, benzene serving as eluent. The first fraction was identified as 9; yield: 0.45 g (29%); from benzene/heptane, m.p. 301–302°C (Lit., m.p. 303°C).

UV (CHCl₃): λ_max = 319 μm (log e = 4.25).

C₂₈H₁₈ calc. C 94.9 H 5.1
found 94.7 5.2

The second fraction was unreacted starting ketone (0.45 g). In diglyme or dimethyl sulfoxide, no condensation could be achieved.

Reactions with 10,11-Dihydrodibenzo[a;e]cycloheptatrien-5-one (6):

Ethyl 10,11-dihydrodibenzo[a;e]cycloheptatrien-5-ylideneacetate: Ketene (6.208 g) was condensed with triethyl phosphonoacetate in dimethyl sulfoxide at 100°C (25 hr); yield: 80%e; b. p. n.s.: 146 to 152°C.

IR (KBr): 6. λ_max = 1710, 1650, 1600 cm⁻¹.

UV (C₂H₅OH): λ_max = 286 μm (log e = 4.09).

C₁₈H₁₈O₂ calc. C 82.0 H 6.5
found 82.3 6.4

10,11-Dihydrodibenzo[a;e]cycloheptatrien-3-ylidenecarboxylic was obtained from the ester by hydrolysis with aqueous-ethanolic sodium hydroxide; the reaction was slow. The oily product crystallized after trituration with cyclohexane: from cyclohexane, m.p. 165–166°C (Lit., 164–165°C, m.p. 172°C).

IR (KBr): 6. λ_max = 3400, 1690, 1605 cm⁻¹.

UV (C₂H₅OH): λ_max = 260 μm (log e = 4.03).

C₁₈H₁₈O₂ calc. C 81.6 H 5.6
found 81.4 5.9

5-Methylene-10,11-dihydrodibenzo[a;e]cycloheptatriene was obtained by decarboxylation of the preceding acid in the manner described for the preparation of dibenzoheptafulvene; yield: 75%; from ethanol, m.p. 61°C (Lit., m.p. 63.5–64°C).

UV (C₂H₅OH): λ_max = 290 μm (log e = 3.97).

Analogous condensation reactions of ketone 6 are summarized in Table 3.

3-Chloro-5-(4-cyanoxybenzylidene)-dibenzo[a;e]cycloheptatriene: To a suspension of 50% sodium hydride (0.90 g) in dimethyl sulfoxide (25 ml), a solution of diethyl 4-cyanobenzyolphosphonate (5.06 g) in dimethyl sulfoxide (5 ml) and a solution of 3-chlorodibenzo[a;e]-cycloheptatrienone (2.4 g) in dimethyl sulfoxide (20 ml) was added. The reaction mixture was heated at 100°C for 23 hr. The solid reaction product was chromatographed in benzene on alumina (schwachsauer, Fluka 506-C); and recrystallized from cyclohexane; yield: 1.5 g (68%); m.p. 146–148°C.

UV (C₂H₅OH): λ_max = 296 μm (log e = 4.41).

C₁₃H₁₃ClO₂N calc. C 81.4 H 4.1 N 4.1 Cl 10.3
found 81.4 4.4 3.8 10.3

3-Chloro-5-(4-cyanobenzylidene)-10,11-dihydrodibenzo[a;e]cycloheptatriene was prepared analogously from 3-chloro-10,11-dihydrodibenzo[a;e]cycloheptatrien-5-one25 (m. p. 63–65°C; IR (KBr): ν_max = 1640 cm⁻¹; UV (C₂H₅OH): λ_max = 269 μm (log e = 4.16)); the reaction mixture was heated for 24 hr at 100°C. The product was chromatographed as described above, and recrystallized from cyclohexane; yield: 45%; m. p. 194–196°C.

UV (C₂H₅OH): λ_max = 306 μm (log e = 4.34).

C₁₃H₁₃ClN calc. C 80.8 H 4.7 N 4.1 Cl 10.4
found 80.5 4.5 4.0 10.4

Reactions with 2,3-Diphenylindene (2):

1-(4-Cyanobenzylidene)-2,3-diphenylindene: The reaction between 2,3-diphenylindene (2; 1.41 g of a commercial product) and diethyl 4-cyanobenzyolphosphonate (3.8 g) in the presence of sodium hydride (50%); 0.92 g) was carried out in dimethyl sulfoxide (60 ml) at 110°C (2 hr). The crude product was dissolved in hexane and chromatographed on neutral alumina, benzene serving as eluent. The product thus obtained was recrystallized from isopropanol; yield: 0.5 g (60%); red crystals, m. p. 202–204°C.

UV (CHCl₃): λ_max = 341 μm (log e = 4.09).

C₆₂H₄₃N calc. C 91.3 H 5.0 N 3.7
found 91.0 5.0 3.5

1-(4-Nitrobenzylidene)-2,3-diphenylindene was prepared analogously. After a reaction time of 12 hr at 100°C, the yield was 55%. The crude product in hexane was chromatographed on alumina (schwachsauer; Fluka C) and eluted with benzene. The first fraction consisted of red crystals, m. p. 211°C (from butanol).

UV (C₂H₅OH): λ_max = 260 (4.82), 355 μm (log e = 4.60).

C₆₂H₄₃NO₂ calc. C 83.8 H 4.7 N 4.5
found 83.7 4.9 3.2
A second compound, m. p. 288–298°C (from glacial acetic acid), which was isolated in small amounts, was 4,4-dimino-trans-stilbene.

2,3-Diphenylindene did not react with triethyl phosphonoacetate in dimethyl sulfoxide.

Reactions with Xanthone (4):

Condensation with triethyl phosphonoacetate: No conditions were found to effect the reaction in diglyme. Using a 3:1 excess of the ester in dimethyl sulfoxide, a very small amount (~3%) of the expected product was formed, as indicated by the IR spectrum, but we could not isolate the product in pure form. Also in other cases, the reaction was often sluggish or did not proceed at all. Thus, the usually very active diethyl 2- and 4-nitrobenzylphosphonates did not react; in the latter case, a large quantity of 4,4-dimino-trans-stilbene (m. p. 290°C) was isolated.

The positive condensations are summarized in Table 4.

Reactions with Thiazanhone (5):

Ethyl thiazanthonylidenecarboxylate: The condensation of thiazanhone with triethyl phosphonoacetate was carried out in dimethyl sulfoxide (diglyme; no reaction was observed); after 30 hr at 100°C; 20% of unreacted ketone 5 was recovered; the yield of the product was only 46%. The product was a viscous liquid which solidified quickly; after ethanol, yellowish crystals, m. p. 35–36°C.

IR (KBr): ν_max = 1705, 1600 cm⁻¹.

UV (C₂H₅OH): λ_max = 230 (4.20), 362 μm (log e = 3.42).

Thiazanthonylidenecarboxylic acid was prepared by hydrolysis of the ester using aqueous-ethanolic sodium hydroxide; yellowish crystals, m. p. 155–156°C.

IR (KBr): ν_max = 3400, 1670, 1600 cm⁻¹.

UV (C₂H₅OH): λ_max = 230 (4.25), 266 (4.12), 353 μm (log e = 3.47).

C₁₃H₁₃O₂S calc. C 70.9 H 3.9
found 71.2 3.9
Table 2. Reactions with Dibenzo[a:ej]cycloheptatrienone (3)

<table>
<thead>
<tr>
<th>Phosphorus compound</th>
<th>Solvent (heating time)</th>
<th>Product</th>
<th>Recrystallized from</th>
<th>Formula</th>
<th>Analysis</th>
<th>IR (KBr) $\nu_{max}$ [cm$^{-1}$]</th>
<th>UV (C$_2$H$<em>5$OH) $\lambda</em>{max}$ [mp] (log e)</th>
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<td>Diethyl benzyl-phosphonate</td>
<td>DMSO* (25 hr)</td>
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<td>71–73$^b$</td>
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<td>Diethyl 4-nitro-benzylphosphonate</td>
<td>DMSO* (4 hr)</td>
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<td>227 (4.42)</td>
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<td>Yield %</td>
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<td>2210, 1595</td>
<td>228 (4.35), 294 (4.25)</td>
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<td>Yield %</td>
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$^a$ No reaction in benzene.

Table 3. Reactions with 10,11-Dihydrodibenzo[a:ej]cycloheptatrien-5-one (6)

<table>
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<th>Formula</th>
<th>Analysis</th>
<th>IR (KBr) $\nu_{max}$ [cm$^{-1}$]</th>
<th>UV (C$_2$H$<em>5$OH) $\lambda</em>{max}$ [mp] (log e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl benzyl-phosphonate</td>
<td>DMSO (31 hr)</td>
<td></td>
<td></td>
<td>C$<em>{22}$H$</em>{18}$</td>
<td>calc. C 93.6 H 6.4</td>
<td>1485, 1435</td>
<td>284 (4.16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yield %</td>
<td>m. p.</td>
<td></td>
<td>found</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85–87$^a$</td>
<td></td>
<td>93.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl 4-nitro-benzylphosphonate$^b$</td>
<td>DMSO (22 hr)</td>
<td></td>
<td></td>
<td>C$<em>{22}$H$</em>{17}$NO$_2$</td>
<td>calc. C 80.7 H 5.2 N 4.3</td>
<td>1590, 1500, 1335</td>
<td>244 (4.29)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yield %</td>
<td>m. p.</td>
<td></td>
<td>found</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>141–143$^c$</td>
<td></td>
<td>81.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl 4-cyanobenzyl phosphonate</td>
<td>diglyme (11 hr)</td>
<td></td>
<td></td>
<td>C$<em>{23}$H$</em>{12}$N</td>
<td>calc. C 89.9 H 5.5 N 4.6</td>
<td>2210, 1590</td>
<td>302 (4.25)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yield %</td>
<td>m. p.</td>
<td></td>
<td>found</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>130$^c$</td>
<td></td>
<td>89.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl 4-chlorobenzylphosphonate</td>
<td>DMSO (21 hr)</td>
<td></td>
<td></td>
<td>C$<em>{22}$H$</em>{13}$Cl</td>
<td>calc. C 83.5 H 5.4 Cl 11.1</td>
<td>1595, 1495, 825, 785</td>
<td>286 (4.15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yield %</td>
<td>m. p.</td>
<td></td>
<td>found</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>196–197$^a$</td>
<td></td>
<td>82.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^b$ The analogous reaction with diethyl 2-nitrobenzylyphosphonate did not give defined products either in diglyme or in DMSO.
<table>
<thead>
<tr>
<th>Reaction components</th>
<th>Solvent (heating time)</th>
<th>Yield %</th>
<th>Recrystallized from</th>
<th>Product</th>
<th>Formula</th>
<th>Analysis</th>
<th>IR (KBr)</th>
<th>UV (λ_max [mp] (log e))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthone and diethyl benzylphosphonate</td>
<td>DMSO (28 hr)</td>
<td>15&lt;sup&gt;a&lt;/sup&gt;</td>
<td>109–110&lt;sup&gt;ac&lt;/sup&gt;</td>
<td>heptane</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O</td>
<td>calc. C 88.9 H 5.2</td>
<td>1610, 1590</td>
<td>221 (4.60), 340 (4.07)</td>
</tr>
<tr>
<td>Xanthone and diethyl 4-cyanobenzylphosphonate</td>
<td>DMSO (29 hr)</td>
<td>88</td>
<td>165–166&lt;sup&gt;a&lt;/sup&gt;</td>
<td>glacial acid</td>
<td>C&lt;sub&gt;21&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;NO</td>
<td>calc. C 85.4 H 4.4 N 4.8</td>
<td>2210, 1595</td>
<td>225 (4.40), 360 (4.04)</td>
</tr>
<tr>
<td>Xanthone and diethyl 4-chlorobenzylphosphonate</td>
<td>DMSO (29 hr)</td>
<td>53&lt;sup&gt;a&lt;/sup&gt;</td>
<td>126–128&lt;sup&gt;ac&lt;/sup&gt;</td>
<td>isopropanol</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;ClO</td>
<td>calc. C 78.9 H 4.3 Cl 11.5</td>
<td>1610, 1595, 1455, 820, 760</td>
<td>222 (4.56), 287 (3.91), 344 (4.08)</td>
</tr>
<tr>
<td>Thiaxanthone and diethyl benzylphosphonate&lt;sup&gt;e&lt;/sup&gt;</td>
<td>DMSO (23 hr)</td>
<td>35</td>
<td>116&lt;sup&gt;f&lt;/sup&gt;</td>
<td>isopropanol</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;S</td>
<td>calc. C 83.9 H 4.8</td>
<td>1595</td>
<td>232 (4.24), 274 (4.02), 343 (3.45)</td>
</tr>
<tr>
<td>Thiaxanthone and diethyl 4-cyanobenzylphosphonate</td>
<td>DMSO&lt;sup&gt;g&lt;/sup&gt; (29 hr)</td>
<td>90</td>
<td>105–108&lt;sup&gt;a&lt;/sup&gt;</td>
<td>glacial acid</td>
<td>C&lt;sub&gt;21&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;NS</td>
<td>calc. C 81.0 H 4.2 N 4.5</td>
<td>2210, 1595</td>
<td>237 (4.36), 308 (4.07), 361 (3.96)</td>
</tr>
<tr>
<td>Thiaxanthone and diethyl 4-chlorobenzylphosphonate</td>
<td>DMSO (29 hr)</td>
<td>44&lt;sup&gt;a&lt;/sup&gt;</td>
<td>162&lt;sup&gt;ef&lt;/sup&gt;</td>
<td>glacial acid&lt;sup&gt;e&lt;/sup&gt;</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;ClS</td>
<td>calc. C 75.0 H 4.1 Cl 10.9</td>
<td>1585, 1490, 1430, 825, 775, 765</td>
<td>235 (4.37), 297 (4.10), 346 (3.89)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Neither of these ketones reacted with diethyl fluorene-9-phosphonate.
<sup>b</sup> Some xanthone was recovered.
<sup>e</sup> 4 mol per mol ketone; otherwise practically no condensation product was isolated under the above conditions; 30% of the ketone was recovered.
<sup>g</sup> No reaction in diglyme.
<sup>h</sup> Some thiaxanthone was recovered unchanged.
<sup>i</sup> After chromatography on neutral alumina.
Decarboxylation of the acid using copper chromite in quinoline gave only thixanthonone; from cyclohexane, m.p. and mixed m.p. 203°C.

Other reactions are summarized in Table 4.

2-Chloro-9-(4-cyanobenzylidene)-thixanthonone: A mixture of diethyl 4-cyanobenzylophosphate (5.86 g), 2-chlorothixanthonone28 (2.46 g), 50% sodium hydride (0.96 g), and dimethyl sulfoxide (70 ml) was heated at 100°C for 30 hr. Then, the reaction mixture was poured into water and the crystalline product isolated by filtration. It was dissolved in hexane and chromatographed on alumina (schwachauer, Fluka 506 C, benzene serving as eluent; yield: 2.7 g (82%); from isopropanol, m.p.115–117°C.

UV (C₂H₅OH): λmax = 238 (4.37), 306 (4.08), 363 μg (log ε = 3.90).
C₃₃H₃₃CINS calc. C 73.0 H 3.5 CI 10.1 N 4.1
found 73.2 3.7 10.3 3.8

Ethyl Indan-1-ylidenacetate: Indan-1-one (7; 1.32 g) and triethyl phosphateacetate (2.24 g) were condensed in the presence of 50% sodium hydride (0.48 g) in diglyme (45 ml) as solvent at 100°C (3 hr). The product was an oil; yield: 1.1 g (54%); b. p. 0.5: 104–108°C.

IR (CHCl₃): fmax = 1700, 1640, 1600 cm⁻¹.
UV (C₂H₅OH): λmax = 246 (3.77), 284 μg (log ε = 3.40).
C₁₃H₁₄O₂ calc. C 77.2 H 6.9
found 76.0 6.7

Indan-1-ylidenacetic acid was prepared by hydrolysis of the ester using aqueous-ethanolic potassium hydroxide; from cyclohexane, m.p. 192–194°C (Lit.27, m.p. 196°C).

IR (KBr): fmax = 3450, 1695, 1635 cm⁻¹.
UV (C₂H₅OH): λmax = 216 (4.11), 232 (4.05), 273 (4.11), 282 (4.10), 305 μg (log ε = 4.07).
C₁₃H₁₁O₂ calc. C 75.9 H 5.8
found 75.2 5.8

1-Benzylidenenadine: The synthesis was carried out in dimethyl sulfoxide at 100°C (3 hr). The reaction mixture was poured into water and the precipitated product recrystallized from aqueous ethanol; yield: 0.8 g (39%); m.p. 71–74°C (Lit.29, m.p. 73.4–74.4°C).

The elemental analysis was in good accordance with the calculated values.

Only resinous material, but no defined products were isolated from the analogous reactions of indan-1-one with various substituted diethyl benzylphosphonates.

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26 The ketone had m.p. 106–108°C, whilst Lit.28 gives both m.p. 109–111°C and m.p. 91–93°C; IR (KBr): υmax = 1640 cm⁻¹; UV (C₂H₅OH): λmax = 314 μg (log ε = 4.14).