Fulvenes and Thermochromic Ethylenes. Part 57. The Wittig-Horner Reaction with Fulvene Ketones and Related Ketones[1]

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Very little work has been reported on the Wittig reaction of fulvene ketones such a fluorenone (**1**), 2,3-diphenylindenone (**2**), dibenzo[a;e]cycloheptatrienone (**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-dihydrodibenzo[a;e]cycloheptatrien-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

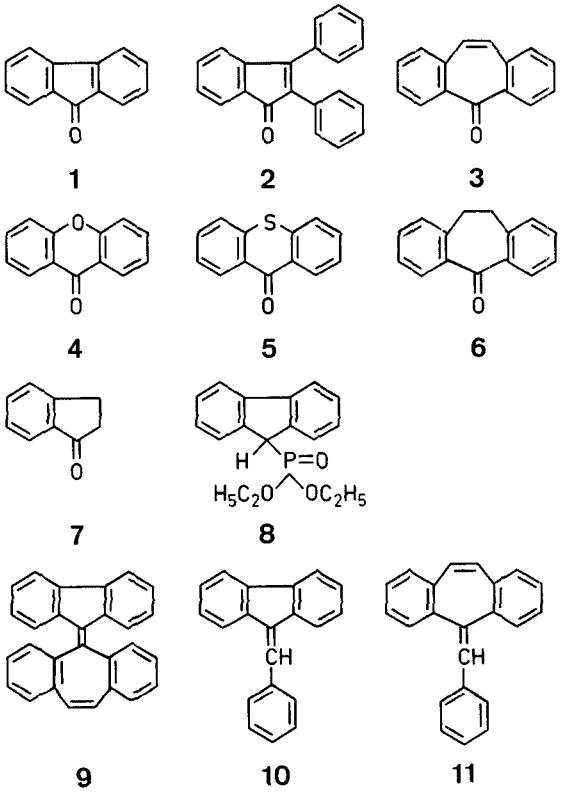
derived from cyclopentadiene, 2,3-diphenylindenone (**2**) and fluorenone (**1**), on the other. It seems that the polarizing power of the anions of the Wittig-Horner reagents obscures the difference in polarity between the fulvene ketones studied.

The reagents employed in this study were:

Triethyl phosphonoacetate, diethyl benzylphosphonate and its *p*-chloro-, *p*-cyano-, *p*-nitro-, and *o*-nitro-derivatives.

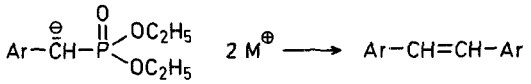
We hoped to find an effect of the larger negativity of the anions containing nitro- and cyano-groups as compared with the parent compound and the *p*-chloro-substituted product. The anions were generated from the Wittig-Horner reagents with sodium hydride, either in diglyme or dimethyl sulfoxide as solvent.

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[2] tetrabenzopentaheptafulvalene (**9**). Indeed, for theoretical reasons this should be the most stable of the products expected in these condensations.

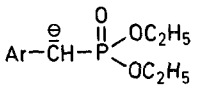


1 **2** **3** **4** **5** **6** **7** **8** **9** **10** **11**

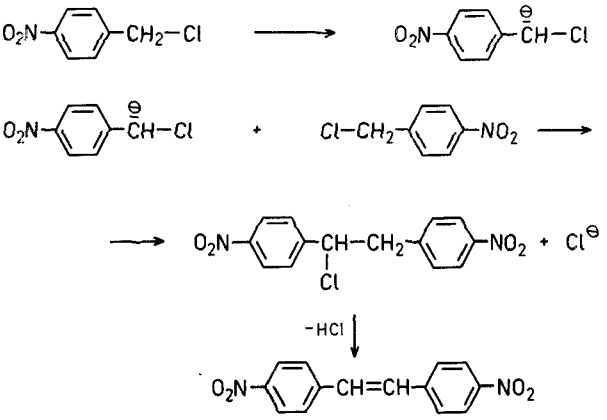
On the whole, the reactions studied were slow. In some cases, this had the consequence that the diethyl benzylphosphonate anions decomposed to the corresponding stilbenes:



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[3]; the mechanism is assumed to be the following:



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[4].

Indan-1-one was transformed into ethyl indan-1-ylideneacetate and 1-benzylideneindane, but a considerable part of the ketone polymerized under the alkaline reaction conditions[5].

The ω-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-methylenefluorene could not be isolated in pure form, as expected[6].

Surprisingly, the decarboxylation of xanthylidene- and thiaxanthylideneacetic acid did not give the (hitherto unknown) methylene derivatives of xanthene and thiaxanthene[7] 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 benzylidenefluorene (**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 hypsochromic 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 vinylog are polarized in opposite directions, the polarization

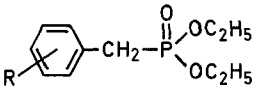
Table 1. Carbonyl Frequencies of Some Fulvene Ketones

Ketone	$\tilde{\nu}_{C=O}$ [cm^{-1}]	Literature
Fluorenone (**1**)	1720	31
2,3-Diphenylindenone (**2**)	1710	32
Dibenzo-[a;e]-cycloheptatrienone (**3**)	1660	33
Xanthone (**4**)	1658	34
Thiaxanthone (**5**)	1629	34
10,11-Dihydrodibenzo-[a;e]-cycloheptatriene-5-one (**6**)	1640	unpublished
Indan-1-one (**7**)	1721	35

thus being influenced by the electronegative nitro group in opposite ways, as has been observed before[8]. 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



R=H, 4-Cl, 4-CN, 2-NO_2, 4-NO_2

were prepared by using the Michaelis-Arbuzov reaction[9] with triethyl phosphonoacetate from sodium diethyl phosphite and ethyl chloroacetate[10].

Diethyl fluorene-9-phosphonate was obtained from triethyl phosphite and 9-bromofluorene[11]; yield: 63%; b.p.$_{0.2}$: 157–160°.

$C_{17}H_{19}PO_3$ calc. C 67.5 H 6.3 P 10.3
found 67.1 6.3 10.0

In the condensation reactions, we employed sodium hydride (50%) in diglyme[12] or in dimethylsulfoxide[13].

Reactions with fluorenone (1):

Ethyl fluorenylideneacetate: 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 (1.8 g) in diglyme (10 ml) was added to the mixture. The blue solution was refluxed for 8 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°/1.7 mm, solidified spontaneously; yield: 2.4 g (96%) (When the reaction mixture was kept at 60° for 1 hr, the yield was 36%). The product was recrystallized from ethanol; m.p. 73° (Lit.[14], m.p. 77°).

IR (KBr): $\tilde{\nu}_{max}$ = 1700 (C=O), 1605 (C=C) cm^{-1}.

UV (C_2H_5OH): λ_{max} = 223 (4.19), 257 (4.56), 284 (3.90), 317 mμ ($\log\varepsilon$ = 3.92).

Hydrolysis with sodium hydroxide in aqueous ethanol afforded free fluorenylideneacetic acid in quantitative yield; from ethanol, m.p. 222° (Lit.[15], m.p. 223.5–224.5°).

IR (KBr): $\tilde{\nu}_{max}$ = 1690 (C=O), 1600 (C=C) cm^{-1}.

UV (C_2H_5OH): λ_{max} = 224 (4.32), 262 (4.40), 284 (4.04), 314 mμ ($\log\varepsilon$ = 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 hydride) was heated at 80° 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°. The oily product was fractionated in vacuo; after some unreacted fluorenone (b.p.$_{0.25}$: 110–120°), benzylidenefluorene distilled at b.p.$_{0.25}$: 173–183°; yield: 1.1 g (42%); from ethanol, m.p. 76° (Lit.[16], m.p. 74.5–76.8°).

UV (C_2H_5OH): λ_{max} = 227 (4.35), 258 (4.29), 326 mμ ($\log\varepsilon$ = 4.09); identical with data given in Lit.[16].

In diglyme, fluorenone did not react with diethyl benzylphosphonate.

9-(4-Nitrobenzylidene)-fluorene was obtained analogously; the reaction mixture was heated at 70–80° for 9 hr; yield: 1 g (66%); m.p. 167–168°, from ethanol, as reported in Lit.[16].

UV (C_2H_5OH): λ_{max} = 224 (4.40), 259 (4.31), 355 mμ ($\log\varepsilon$ = 4.09).

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

IR (KBr): $\tilde{\nu}_{max}$ = 1595, 1515, 1350 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 226 (4.37), 255 (4.29), 357 mμ ($\log\varepsilon$ = 4.07).

$C_{20}H_{13}NO_2$ 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°, from ethanol (Lit.[17], m.p. 192°); 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° (Lit.[18], m.p. 151–152°).

IR (KBr): $\tilde{\nu}_{max}$ = 2210 (C≡N), 1595 (C=C) cm^{-1}.

UV (C_2H_5OH): λ_{max} = 229 (4.36), 257 (4.40), 331 mμ ($\log\varepsilon$ = 4.14).

$C_{21}H_{13}N$ 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° for 14 hr; yield: 36%; from glacial acetic acid, m.p. 148–149° (Lit.[19], m.p. 151°).

UV (C_2H_5OH): λ_{max} = 227 (4.37), 258 (4.30), 328 mμ ($\log\varepsilon$ = 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° (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° (Lit.[20], m.p. 282°); 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°.

IR (KBr): $\tilde{\nu}_{max}$ = 3330 (N–H), 2210 (C≡N), 1610 (C=C), 1600, 1450 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 275 (4.38), 323 mμ ($\log\varepsilon$ = 4.30).

$C_{21}H_{14}N_2$ calc. C 85.7 H 4.8 N 9.5
found 85.6 5.2 9.0

Reactions with Dibenzo[a;e]cycloheptatrienone (3):

The starting material was prepared according to Lit.[21]. Most of the reactions are summarized in Table 2.

Ethyl dibenzo[a;e]cycloheptatrienylideneacetate: 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]cycloheptatrienone (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.$_{0.6}$: 167–170°. The yield was raised to 96% by carrying out the reaction in dimethyl sulfoxide at 100° (30 hr).

IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1705, 1630, 1590 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 231 mμ ($\log\varepsilon$ = 4.28).

$C_{19}H_{16}O_2$ calc. C 83.0 H 5.7
found 82.8 6.1

Dibenzo[a:e]cycloheptatrienylideneacetic acid was obtained by hydrolysis of the ethyl ester with aqueous alcoholic potassium hydroxide; from benzene, colorless crystals, m.p. 202–204° [Lit.[22], m.p. 212° (dec.)].

IR (KBr): $\tilde{\nu}_{max}$ = 3400, 3000, 1690, 1625, 1565 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 231 (4.34), 300^{s}mμ ($\log\varepsilon$ = 4.00).

$C_{17}H_{12}O_2$ calc. C 82.3 H 4.8
found 82.4 4.5

5-Methylene-dibenzo[a;e]cyclodeptatriene (Dibenzoheptafulvene): A mixture of dibenzo-[a;e]-cycloheptatrienylideneacetic acid (0.5 g), quinoline (15 ml), and copper chromite (0.4 g) was heated for 3 hr at 210–220° 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° (Lit.[23], m.p. 119–120°).

UV (C_2H_5OH): λ_{max} = 226 (3.61), 295 mμ (log ε = 4.00).

$C_{16}H_{12}$ calc. C 94.1 H 5.9
found 93.9 5.8

Tetrabenzocyclo pentaheptafulvalene (9): A solution of diethyl fluorene-9-phosphonate (**8**; 3 g) in toluene (5 ml) and a solution of dibenzo-[a;e]-cycloheptatrienone (**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°) 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° (Lit.[2], m.p. 303°).

UV ($CHCl_3$): λ_{max}: 319 mμ (log ε = 4.25).

$C_{28}H_{18}$ 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: Ketone **6** (2.08 g)[23] was condensed with triethyl phosphonoacetate in dimethyl sulfoxide at 100° (25 hr); yield: 80%; b.p.$_{0.5}$: 146 to 152°.

IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1710, 1650, 1600 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 286 mμ (log ε = 4.09).

$C_{19}H_{18}O_2$ calc. C 82.0 H 6.5
found 82.3 6.4

10,11-Dihydrodibenzo[a;e]cycloheptatrienyl-5-ylideneacetic acid 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° (Lit.[24,25], m.p. 172°).

IR (KBr): $\tilde{\nu}_{max}$ = 3400, 1690, 1605 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 260 mμ (log ε = 4.03).

$C_{17}H_{14}O_2$ 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° (Lit.[21], m.p. 63.5–64°).

UV (C_2H_5OH): λ_{max} = 290 mμ (log ε = 3.97).

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

3-Chloro-5-(4-cyanobenzylidene)-dibenzo[a;e]cycloheptatriene: To a suspension of 50% sodium hydride (0.96 g) in dimethyl sulfoxide (25 ml), a solution of diethyl 4-cyanobenzylphosphonate (5.06 g) in dimethyl sulfoxide (5 ml) and a solution of 3-chlorodibenzo-[a;e]-cycloheptatrienone[25,26] (2.4 g) in dimethyl sulfoxide (20 ml) was added. The reaction mixture was heated at 100° 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°.

UV (C_2H_5OH): λ_{max} = 296 mμ (log ε = 4.41).

$C_{23}H_{14}ClN$ 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]cycloheptariene was prepared analogously from 3-chloro-10,11-dihydrodibenzo[a;e]cycloheptatrien-5-one[25] [m.p. 63–65°; IR (KBr): $\tilde{\nu}_{max}$ = 1640 cm^{-1}; UV (C_2H_5OH): λ_{max} = 269 mμ (log ε = 4.16)]; the reaction mixture was heated for 24 hr at 100°. The product was chromatographed as described above, and recrystallized from cyclohexane; yield: 45%; m.p. 194–196°.

UV (C_2H_5OH): λ_{max} = 306 mμ (log ε = 4.34).

$C_{23}H_{16}ClN$ 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-Diphenylindenone (2):

1-(4-Cyanobenzylidene)-2,3-diphenylindene: The reaction between 2,3-diphenylindenone (**2**; 1.41 g of a commercial product) and diethyl 4-cyanobenzylphosphonate (3.8 g) in the presence of sodium hydride (50%, 0.92 g) was carried out in dimethyl sulfoxide (60 ml) at 100° (23 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°.

UV ($CHCl_3$): λ_{max} = 341 mμ (log ε = 4.09).

$C_{29}H_{19}N$ 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°, 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° (from butanol).

UV (C_2H_5OH): λ_{max} = 260 (4.82), 355^{s} mμ (log ε = 4.60).

$C_{28}H_{19}NO_2$ calc. C 83.8 H 4.7 N 3.5
found 83.7 4.9 3.2

A second compound, m.p. 288–289° (from glacial acetic acid), which was isolated in small amounts, was 4,4'-dinitro-*trans*-stilbene.

2,3-Diphenylindenone 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'-dinitro-*trans*-stilbene (m.p. 290°) was isolated.

The positive condensations are summarized in Table 4.

Reactions with Thiaxanthone (5):

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

IR (KBr): $\tilde{\nu}_{max}$ = 1705, 1600 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 230 (4.20), 362 mμ (log ε = 3.42).

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

IR (KBr): $\tilde{\nu}_{max}$ = 3400, 1670, 1600 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 230 (4.25), 266 (4.12), 353 mμ (log ε = 3.42).

$C_{15}H_{10}O_2S$ calc. C 70.9 H 3.9
found 71.2 3.9

Table 2. Reactions with Dibenzo[a;e]cycloheptatrienone (**3**)

Phosphorus compound	Solvent (heating time)	Product		Recrystallized from	Formula	Analysis	IR (KBr) $\tilde{\nu}_{max}$ [cm^{-1}]	UV (C_2H_5OH) λ_{max} [mμ] (log ε)
		Yield %	m. p.					
Diethyl benzyl-phosphonate	DMSO[a] (25 hr)	50	71–73[b]	cyclohexane	$C_{22}H_{16}$	calc. C 94.3 H 5.7 found 94.4 5.7	1595	282 (4.34)
Diethyl 4-nitro-benzylphosphonate	DMSO (4 hr)	56	138–139	isopropanol	$C_{22}H_{15}NO_2$	calc. C 81.2 H 4.6 N 4.3 found 80.8 4.8 4.5	1590	244 (4.30)
Diethyl 2-nitrobenzyl-phosphonate	DMSO (8 hr)	50	142–145	butanol	$C_{22}H_{15}NO_2$	calc. C 81.2 H 4.6 found 81.1 4.6	1590	227 (4.42)
Diethyl 4-cyanobenzyl-phosphonate	diglyme (12 hr)	96	208–211	isopropanol	$C_{23}H_{15}N$	calc. C 90.5 H 4.9 N 4.6 found 89.9 4.9 4.6	2210, 1595	228 (4.35), 294 (4.25)
Diethyl 4-chloro-benzylphosphonate	DMSO (14 hr)	57	154[c]	petroleum ether	$C_{22}H_{15}Cl$	calc. C 84.1 H 4.8 Cl 11.2 found 84.2 4.6 11.2	1595, 820, 780	225 (4.36), 287 (4.26)

[a] No reaction in benzene.
[b] The compound is described as a high-boiling oil: E. D. BERGMANN, M. MAYOT, et. al., Bull. Soc. Chim. France **1951**, 684; cf. forthcoming publication.
[c] A. PULLMAN, B. PULLMAN, E. D. BERGMANN, D. GINSBURG, D. LAVIE, Bull. Res. Council Israel **1** (4), 85 (1952), give m.p. 155°.

Table 3. Reactions with 10,11-Dihydrodibenzo[a;e]cycloheptatrien-5-one (**6**)

Phosphorus compound	Solvent (heating time)	Product		Recrystallized from	Formula	Analysis	IR (KBr) $\tilde{\nu}_{max}$ [cm^{-1}]	UV (C_2H_5OH) λ_{max} [mμ] (log ε)
		Yield %	m. p.					
Diethyl benzyl-phosphonate	DMSO (31 hr)	69	85–87°[a]	isopropanol	$C_{22}H_{18}$	calc. C 93.6 H 6.4 found 93.8 6.6	1485, 1435	284 (4.16)
Diethyl 4-nitro-benzylphosphonate[b]	DMSO (22 hr)	55	141–143°	chromatogr. in hexane	$C_{22}H_{17}NO_2$	calc. C 80.7 H 5.2 N 4.3 found 81.1 5.1 4.1	1590, 1500, 1335	244 (4.29)
Diethyl 4-cyano-benzyl phosphonate	diglyme (11 hr)	30	130°	isopropanol	$C_{23}H_{17}N$	calc. C 89.9 H 5.5 N 4.6 found 89.8 5.7 4.6	2210, 1590	302 (4.25)
Diethyl 4-chloro-benzylphosphonate	DMSO (21 hr)	57	b.p.$_{0.5}$: 196–197°[a]	—	$C_{22}H_{17}Cl$	calc. C 83.5 H 5.4 Cl 11.1 found 82.8 5.9 10.8	1595, 1495, 825, 785	286 (4.15)

[a] The compound is described as an oil: E. D. BERGMANN, M. MAYOT, et al., Bull. Soc. Chim. France **1951**, 684.
[b] The analogous reaction with diethyl 2-nitrobenzylphosphonate did not give defined products either in diglyme or in DMSO.

Table 4. Reactions with Xanthone and Thiaxanthone[a]

Reaction components	Solvent (heating time)	Product		Recrystallized from	Formula	Analysis	IR (KBr) $\tilde{\nu}_{max}$ [cm^{-1}]	UV λ_{max} [mμ] (log ε)
		Yield %	m.p.					
Xanthone and diethyl benzylphosphonate	DMSO (28 hr)	15[b]	109–110°[c]	heptane	$C_{20}H_{14}O$	calc. C 88.9 H 5.2 found 88.6 4.9	1610, 1590	221 (4.60), 340 (4.07)
Xanthone and diethyl 4-cyanobenzylphosphonate	DMSO (29 hr)	88	165–166°	gl.acetic acid	$C_{21}H_{13}NO$	calc. C 85.4 H 4.4 N 4.8 found 85.4 4.4 5.1	2210, 1595	225 (4.40), 360 (4.04)
Xanthone and diethyl 4-chlorobenzylphosphonate	DMSO (29 hr)	53[b]	126–128°[d]	isopropanol	$C_{20}H_{13}ClO$	calc. C 78.9 H 4.3 Cl 11.5 found 78.4 4.7 12.0	1610, 1595, 1455, 820, 760	222 (4.56) 287 (3.91), 344 (4.08)
Thiaxanthone and diethyl benzylphosphonate[e]	DMSO (23 hr)	35	116°[f]	isopropanol	$C_{20}H_{14}S$	calc. C 83.9 H 4.8 found 83.6 5.1	1595	232 (4.24), 274 (4.02), 343 (3.45)
Thiaxanthone and diethyl 4-cyanobenzylphosphonate	DMSO[g] (29 hr)	90	105–108°	gl.acetic acid	$C_{21}H_{13}NS$	calc. C 81.0 H 4.2 N 4.5 found 80.8 4.6 4.2	2210, 1595	237 (4.36), 308 (4.07), 361 (3.96)
Thiaxanthone and diethyl 4-chlorobenzylphosphonate	DMSO (29 hr)	44[h]	162°[f]	gl.acetic acid[i]	$C_{20}H_{13}ClS$	calc. C 75.0 H 4.1 Cl 10.9 found 75.0 4.1 10.4	1585, 1490, 1430, 825, 775, 765	235 (4.37), 297 (4.10), 346 (3.89)

[a] Neither of these ketones reacted with diethyl fluorene-9-phosphonate.
[b] Some xanthone was recovered.
[c] H. E. UNGNADE, E. F. KLINE, E. W. CRANDALL, J. Amer. Chem. Soc. **75**, 3333 (1953), give m.p. 110–111°.
[d] N. P. BUU-HOI, N. D. XUONG, J. Org. Chem. **16**, 1633 (1951), give m.p. 137°.
[e] 4 mol per mol ketone; otherwise practically no condensation product was isolated under the above conditions; 30% of the ketone was recovered.
[f] E. D. BERGMANN, B. PULLMAN, et al., Bull. Soc. Chim. France **1952**, 262, give m.p. 121–122°.
[g] No reaction in diglyme.
[h] Some thiaxanthone was recovered unchanged.
[i] After chromatography on neutral alumina.

Decarboxylation of the acid using copper chromite in quinoline gave only thiaxanthone; from cyclohexane, m.p. and mixed m.p. 203°.

Other reactions are summarid in Table 4.

2-Chloro-9-(4-cyanobenzylidene)-thiaxanthene: A mixture of diethyl 4-cyanobenzylphosphonate (5.06 g), 2-chlorothiaxanthone[28] (2.46 g), 50% sodium hydride (0.96 g), and dimethyl sulfoxide (70 ml) was heated at 100° 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 (schwachsauer, ®Fluka 506 C), benzene serving as eluent; yield: 2.7 g (82%); from isopropanol, m.p.115–117°.

UV (C_2H_5OH): λ_{max} = 238 (4.37), 306 (4.08), 363 mμ (log ε = 3.90).

$C_{21}H_{12}ClNS$	calc.	C 73.0	H 3.5	Cl 10.1	N 4.1
	found	73.2	3.7	10.3	3.8

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

IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1700, 1640, 1600 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 246 (3.77), 284 mμ (log ε = 3.40).

$C_{13}H_{14}O_2$	calc.	C 77.2	H 6.9
	found	76.0	6.7

Indan-1-ylideneacetic acid was prepared by hydrolysis of the ester using aqueous-ethanolic potassium hydroxide; from cyclohexane, m.p. 192–194° (Lit.[29], m.p. 196°).

IR (KBr): $\tilde{\nu}_{max}$ = 3450, 1695, 1635 cm^{-1}.

UV (C_2H_5OH): λ_{max} = 216 (4.11), 232 (4.05), 273 (4.11), 282 (4.10), 305 mμ (log ε = 4.07).

$C_{11}H_{10}O_2$	calc.	C 75.9	H 5.8
	found	75.2	5.8

1-Benzylideneindane: The synthesis was carried out in dimethyl sulfoxide at 100° (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° (Lit.[30], m.p. 73.4–74.4°). 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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