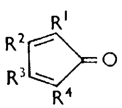
814. *Cyclopentadienes, Fulvenes, and Fulvalenes. Part III.*[1] 2,3,4-*Triphenylcyclopentadienone and Related Products.*

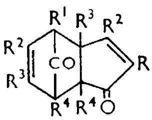
By P. L. Pauson and B. J. Williams.

It is shown that 2,3,4-triphenylcyclopentadienone exists as a stable blue monomer. The anomalous condensation of 1,2,3-triphenylfulvene with *NN*-dimethyl-*p*-nitrosoaniline affords the *p*-dimethylaminoanil of 2-methyl-3,4,5-triphenylcyclopentadienone. The preparation of phenylhydrazones of substituted cyclopentadienones by reaction of the corresponding diazocyclopentadienes with phenyl-lithium is reported.

Previous workers have attempted the preparation of numerous cyclopentadienone derivatives [2-5] and have demonstrated the existence of three types: (1) stable monomers, exemplified by tetracyclone (I; $R^1 = R^2 = R^3 = R^4 = Ph$); (2) those which dimerise too rapidly and irreversibly to permit isolation (though not detection) of the monomer, best exemplified by the parent compound (I; $R^1 = R^2 = R^3 = R^4 = H$); and (3) those of intermediate type showing a temperature-dependent monomer–dimer equilibrium in solution. Allen and Van Allan [3] tried to define the substitution pattern leading to each of these types. *Inter al.* they concluded that only those trisubstituted cyclopentadienones where R^1 and R^4 (in I) are aryl could belong in class (3) and none could belong in class (1).



(I)



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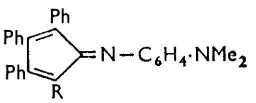
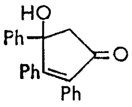
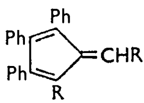


(III)



(IV)



(V)

Among the key examples supporting these rules 2,3,4-triphenylcyclopentadienone (I; $R^1 = R^2 = R^3 = Ph$, $R^4 = H$) was placed in class (2). In our work on 1,2,3-triphenylcyclopentadiene we found this compound to exist as a stable monomer, in conflict with these rules. Our two preparative routes also afforded a dimeric substance, m. p. >310°, that may be the substance previously described [4] as the dimer and said to melt at 258°.

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[1] Part II, preceding paper.

[2] Allen, *Chem. Rev.*, 1945, **37**, 209; de Puy and Lyons, *J. Amer. Chem. Soc.*, 1960, **82**, 631; Hafner and Goliasch, *Angew. Chem.*, 1960, **72**, 781.

[3] Allen and Van Allan, *J. Amer. Chem. Soc.*, 1950, **72**, 5165.

[4] Geissmann and Koelsch, *J. Org. Chem.*, 1938, **3**, 489.

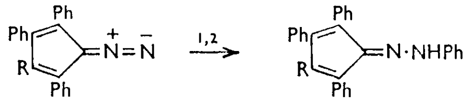
[5] Ziegler and Schnell, *Annalen*, 1925, **445**, 266.

However, its infrared spectrum clearly eliminates the usual structure (II) of the dimers in class (2) and our attempts to convert the monomer into this dimer or *vice versa* were unsuccessful.

By analogy with Ziegler and Schnell's original preparation [5] of tetracyclone, 1,2,3-triphenylcyclopentadiene was converted into the dienone (I; $R^1 = R^2 = R^3 = Ph$, $R^4 = H$) through its *p*-dimethylaminoanil (III; R = H). On hydrolysis with hydrochloric acid this anil afforded a green solid, resolved by chromatography into the above-mentioned " dienone dimer " and the bright blue monomeric ketone (I; $R^1 = R^2 = R^3 = Ph$, $R^4 = H$). A similar mixture was obtained when dehydration of the hydroxy-ketone (IV) by Geissmann and Koelsch's method [4] was repeated. The nature of the " dimer " is being investigated.

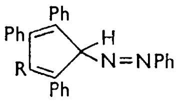
In the tetraphenyl series, the anil (III; R = Ph) may be obtained, not only from the corresponding cyclopentadiene, but also [5a] from the fulvene (V; R = Ph, R′ = H) by condensation with *NN*-dimethyl-*p*-nitrosoaniline. This unusual reaction must involve liberation of formaldehyde. When 1,2,3-triphenylfulvene (V; R = R′ = H) was treated with *NN*-dimethyl-*p*-nitrosoaniline in presence of piperidine the product was not the expected anil (III; R = H), but its homologue (III; R = Me). Its formation must involve, not only condensation at the vacant 4-position of the fulvene (V; R = R′ = H), but also reduction. The new anil (III; R = Me) was characterised by hydrolysis to the known [3] 2-methyl-3,4,5-triphenylcyclopentadienone (I; $R^1 = Me$, $R^2 = R^3 = R^4 = Ph$). The intermediate fulvene (V; R = R′ = H) and its phenyl derivative (V; R = H, R′ = Ph) were readily obtained by condensing 1,2,3-triphenylcyclopentadiene with paraformaldehyde and benzaldehyde respectively.

In the course of this work we also prepared the hitherto unknown phenylhydrazones (VII; R = Ph and H) through the diazocyclopentadienes (VI). Although the formation of a *p*-nitrophenylhydrazone from tetracyclone has been reported,[6] we were unable to obtain the unsubstituted derivative (VII; R = Ph) under the same conditions, confirming earlier reports that it cannot be obtained directly. Like the 1,2,4-triphenyl derivative [1] (VI; R = H) the diazo-compound (VI; R = Ph) was readily obtained by Doering and de Puy's [7,8] method. Both compounds (VI) reacted smoothly with phenyl-lithium. The products are formulated as the hydrazones (VII) rather than the tautomeric azo-compounds (VIII) on the basis of their ultraviolet and infrared spectra. Attempts to convert these phenylhydrazones into the free ketones failed, and our experiments were therefore not extended to the 1,2,3-triphenyl series.



(VI) (VII)

1, PhLi; 2, H_2O.



(VIII)

Experimental

For general remarks see Part I.[8]

5-p-*Dimethylaminoanilino*-1,2,3-*triphenylcyclopentadiene* (III; R = H).—1,2,3-Triphenylcyclopentadiene [8] (2·94 g., 0·01 mole) and *NN*-dimethyl-*p*-nitrosoaniline (2·25 g., 0·015 mole) in boiling benzene (50 ml.), were added slowly to a solution of sodium methoxide [from sodium

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[5a] Taber, Becker, and Spoerri, *J. Amer. Chem. Soc.*, 1954, **76**, 776.

[6] Sonntag, Linder, Becker, and Spoerri, *J. Amer. Chem. Soc.*, 1953, **75**, 2283; Josten, *Ber.*, 1938, **71**, 2230.

[7] Doering and de Puy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.

[8] Part I, *J.*, 1961, 4153.

(0·1 g.) and methanol (5 ml.)]. The mixture, which became dark red, was boiled for a further 10 min. An equal volume of light petroleum was then added, and the mixture set aside overnight. The dark red crystals were filtered off and washed with 1·5N-hydrochloric acid until the filtrate was colourless, and finally with water. After drying, dark red needles of 5-p-*dimethylaminoanilino*-1,2,3-*triphenylcyclopentadiene*, m. p. 194°, were obtained. Recrystallisation from benzene–ligroin did not raise the m. p. (Found: C, 87·2; H, 6·1; N, 6·6. $C_{31}H_{26}N_2$ requires C, 87·3; H, 6·1; N, 6·6%).

Hydrolysis of 5-p-*Dimethylaminoanilino*-1,2,3-*triphenylcyclopentadiene*.—The anil (1·4 g.) was added in portions to boiling 20% hydrochloric acid (100 ml.). The added compound became brownish-yellow and finally green. The mixture was then refluxed for a further ½ hr. Water was added and the green solid (0·9 g.) was filtered off and chromatographed in benzene on alumina. Four coloured bands were obtained: (*a*) A dark red band, eluted with benzene, yielded starting material (0·036 g.). (*b*) A yellow band, eluted with ether–benzene, gave a yellow solid (0·06 g.); this recrystallised from ether to give yellow needles of the "*dienone-dimer*," m. p. >310° (Found: C, 89·1; H, 5·5. $C_{46}H_{32}O_2$ requires C, 89·6; H, 5·2%), $\nu_{max.}$ 1672 cm.$^{-1}$ (C=O). (*c*) A blue band, eluted with ether–benzene, yielded a solid (0·18 g.); recrystallisation from cyclohexane gave blue needles of 2,3,4-*triphenylcyclopentadienone*, m. p. 292—294° [Found: C, 89·9; H, 5·5%; *M* (cryoscopic in benzene), 300. $C_{23}H_{16}O$ requires C, 89·6; H, 5·2%; *M*, 313], $\nu_{max.}$ 1681 cm.$^{-1}$ (C=O), $\lambda_{max.}$ 266, 276, 306, 606, and 940 mμ (log ε 4·17, 4·17, 4·28, 3·28, and 3·01). (*d*) A red band, eluted with ether–benzene, yielded a brown-red uncrystallisable solid (0·06 g.).

Dehydration of 4-*Hydroxy*-2,3,4-*triphenylcyclopent*-2-*enone* (IV) (cf. Geissman and Koelsch[4]).—The hydroxy-ketone (1·5 g.) in acetic acid (10 ml.) and sulphuric acid (1 ml.) was heated to the b. p. with frequent shaking. After ½ hour's refluxing the dark red mixture was poured into water and extracted with ether–benzene. The organic solution was washed to neutrality, dried (Na_2SO_4), and evaporated, to give a dark blue-green solid. This was chromatographed in benzene, giving: (*a*) a yellow band, eluted with benzene–ether, which gave yellow needles (0·083 g.) identical in infrared spectrum with the above "dienone-dimer"; (*b*) a blue band, eluted with benzene–ether and yielding 2,3,4-triphenylcyclopentadienone (0·33 g.), m. p. 292—294°.

Solutions of 2,3,4-triphenylcyclopentadienone are decolorised on addition to solutions of Grignard reagents or alkyl- or aryl-lithiums.

1,2,3-*Triphenylfulvene* (V; R = R′ = H).—Sodium ethoxide [from sodium (0·7 g., 0·03 g.-atom) in ethanol (50 ml.)] was added dropwise to 1,2,3-triphenylcyclopentadiene (1·0 g., 0·0034 mole) and paraformaldehyde (9·0 g., 0·3 mole) in boiling ethanol (150 ml.). The red solution was refluxed for 3 hr. and then evaporated to a small volume, poured into water, and extracted with ether. The red extract was dried (Na_2SO_4) and evaporated to a red gum (1·2 g.). This was extracted with boiling light petroleum (b. p. 60—80°) and the extract was chromatographed on alumina. The main orange band was eluted with light petroleum and recovered, giving 1,2,3-*triphenylfulvene* as bright red needles (0·4 g.), m. p. 151—151·5° unchanged on recrystallisation (Found: C, 94·0; H, 6·4. $C_{24}H_{18}$ requires C, 94·0; H, 6·0%). The fulvene is extremely susceptible to oxidation, and solutions left in contact with the air are rapidly decolorised.

1,2,3,6-*Tetraphenylfulvene* (V; R = H, R′ = Ph).—Sodium methoxide [from sodium (1·1 g., 0·046 g.-atom) and methanol (60 ml.)] was added dropwise to 1,2,3-triphenylcyclopentadiene (1·0 g., 0·0034 mole) and benzaldehyde (2·54 g., 0·024 mole) in boiling methanol (50 ml.). The mixture, which became red, was refluxed for a further 4 hr. After cooling, the red crystals of 1,2,3,6-*tetraphenylfulvene* were filtered off and washed with methanol (1·2 g.). Recrystallised from light petroleum (b. p. 60—80°) they had m. p. 174—175·5° (Found: C, 94·2; H, 5·8. $C_{30}H_{22}$ requires C, 94·2; H, 5·8%).

5-p-*Dimethylaminoanilino*-1-*methyl*-2,3,4-*triphenylcyclopentadiene* (III; R = Me).—1,2,3-Triphenylfulvene (0·092 g., 0·0003 mole) and *NN*-dimethyl-*p*-nitrosoaniline (0·045 g., 0·0003 mole) in pyridine (3 ml.) and piperidine (1 ml.) were left at room temperature for 5 days. The dark red solution was poured into water and the precipitate filtered off, then chromatographed in benzene on alumina. The main purple band was eluted with ether–benzene, and, after evaporation of the solvent, gave a purple solid (0·032 g.). Recrystallisation from benzene–light petroleum gave 5-p-*dimethylaminoanilino*-1-*methyl*-2,3,4-*triphenylcyclopentadiene* as purple needles, m. p. 219—221° (Found: C, 87·1; H, 6·4; N, 6·6. $C_{32}H_{28}N_2$ requires C, 87·2; H, 6·4;

N, 6·4%). This compound depressed the m. p. (194°) of 5-*p*-dimethylaminoanilino-1,2,3-triphenylcyclopentadiene and had a similar, but not identical, infrared spectrum.

2-*Methyl*-3,4,5-*triphenylcyclopentadienone* (I; $R^1 = Me$, $R^2 = R^3 = R^4 = Ph$).—5-*p*-Dimethylaminoanilino-1-methyl-2,3,4-triphenylcyclopentadiene (0·14 g.) was added slowly to boiling hydrochloric acid, the colour changing from deep purple to reddish-brown. Then the mixture was refluxed for a further ½ hr. and diluted with water. The red-brown solid (0·096 g.) was filtered off, washed free from acid, and dried. Recrystallisation from light petroleum (b. p. 60—80°) afforded 5-methyl-2,3,4-triphenylcyclopentadienone as red-brown rods, m. p. 198—199° (lit.,[3] 196°) (Found: C, 89·9; H, 5·9. Calc. for $C_{24}H_{18}O$: C, 89·4; H, 5·6%), $\nu_{max.}$ 1704 cm.$^{-1}$ (C=O), $\lambda_{max.}$ 270 and 322 mμ (log ε 4·32 and 3·93).

Phenylhydrazone (VII; R = H) *of* 2,3,5-*Triphenylcyclopentadienone*.—5-Diazo-1,2,4-triphenylcyclopentadiene (1·92 g., 0·006 mole) in ether (100 ml.) was added dropwise to a stirred solution of phenyl-lithium (0·006 mole) in ether. An immediate deep red-violet colour was produced. The mixture was stirred for a further ½ hr., then a mixture of ice and dilute hydrochloric acid was added. The organic solution was separated, washed to neutrality, and dried (Na_2SO_4). Evaporation gave a dark brown solid. This crystallised from acetone as red-brown needles (0·6 g.) of 2,3,5-*triphenylcyclopentadienone phenylhydrazone*, m. p. 183° (Found: C, 87·4; H, 5·8; N, 7·1. $C_{29}H_{22}N_2$ requires C, 87·4; H, 5·6; N, 7·0%), $\nu_{max.}$ 3335 cm.$^{-1}$ (N–H), $\lambda_{max.}$ 206, 268, and 418 mμ (log ε 4·56, 4·50, and 4·50).

5-*Diazo*-1,2,3,4-*tetraphenylcyclopentadiene* (VI; R = Ph).—To phenyl-lithium in ether [from lithium (0·37 g., 0·053 g.-atom) and bromobenzene (3·92 g., 0·025 mole)], a solution of 1,2,3,4-tetraphenylcyclopentadiene (8·32 g., 0·022 mole) in benzene (200 ml.) was added dropwise. After refluxing for 2 hr., the mixture was cooled and added dropwise in 1 hr. to a stirred solution of toluene-*p*-sulphonyl azide (4·43 g., 0·022 mole) in ether (20 ml.). The colour of the mixture changed from yellow to orange-red in 2 hr. Stirring was continued overnight and the mixture then filtered and poured into water. The organic layer was separated and dried (Na_2SO_4). Removal of the solvent yielded a dark red solid (8·8 g.). Recrystallisation from methanol and then from light petroleum (b. p. 60—80°) gave dark red cubes of 5-*diazo*-1,2,3,4-*tetraphenylcyclopentadiene*, m. p. 152—154° (decomp.) (Found: C, 87·8; H, 5·4; N, 6·8. $C_{29}H_{20}N_2$ requires C, 87·8; H, 5·1; N, 7·1%), $\nu_{max.}$ 2088 cm.$^{-1}$ (diazo), $\lambda_{max.}$ 255 and 333 mμ (log ε, 4·48 and 4·22), insoluble in dilute hydrochloric acid, but giving in concentrated sulphuric acid a deep red solution.

2,3,4,5-*Tetraphenylcyclopentadienone Phenylhydrazone* (VII; R = Ph).—Diazotetraphenylcyclopentadiene (2·93 g., 0·0074 mole) in benzene (100 ml.) was added dropwise to a solution of phenyl-lithium in ether [from lithium (0·12 g., 0·017 g.-atom) and bromobenzene (1·28 g., 0·008 mole)]. The violet solution was stirred for a further hr. and ice and dilute hydrochloric acid were added. The organic layer was separated, washed to neutrality, and dried (Na_2SO_4). Removal of the solvent left a deep purple solid (3·2 g.). Recrystallisation from aqueous dioxan gave *tetracyclone phenylhydrazone*, m. p. 266—268° (Found: N, 5·8. $C_{35}H_{26}N_2$ requires N, 5·9%), $\nu_{max.}$ 3350 cm.$^{-1}$ (N–H), $\lambda_{max.}$ 264 and 420 mμ (log ε 4·46 and 4·52).

Attempted Hydrolysis of 2,3,5-*Triphenylcyclopentadienone Phenylhydrazone*.—2,3,5-Triphenylcyclopentadienone phenylhydrazone (0·39 g.) was added to lævulic acid (18 ml.) and N-hydrochloric acid (2 ml.). Enough chloroform was added to give a clear solution, the mixture was refluxed for 3 hr., then poured into water, and the chloroform layer was separated, washed with sodium hydrogen carbonate solution, and dried (Na_2SO_4). Removal of the solvent and recrystallisation from acetone yielded unchanged starting material (0·2 g.), m. p. 181—183°.

The compound was also recovered unchanged after being added to boiling concentrated hydrochloric acid.

Attempted Hydrolysis of Tetraphenylcyclopentadienone Phenylhydrazone.—(*a*) Tetracyclone phenylhydrazone (0·24 g.) in chloroform (30 ml.) and under a nitrogen atmosphere was treated with pyruvic acid (5 ml.) and a 50% w/v solution of hydrogen bromide in acetic acid (0·5 ml.) at room temperature. The mixture, which became deep blue, was heated at 50—60° for 3 hr. The mixture was cooled and poured into water. The chloroform layer was separated, washed with sodium hydrogen carbonate solution, and dried (Na_2SO_4). Evaporation gave a dark red solid (0·24 g.). Recrystallisation from acetone yielded unchanged starting material, m. p. 266—267°.

(*b*) 50% Sulphuric acid (10 ml.) was added to tetracyclone phenylhydrazone (0·2 g.) in dioxan (40 ml.), and the mixture was refluxed overnight, then poured into water and extracted with chloroform. After drying (Na_2SO_4), the extract was evaporated to a red solid (0·2 g.). Recrystallisation from acetone gave unchanged starting material.

Attempted Reaction of Tetracyclone with Phenylhydrazine.—Concentrated sulphuric acid (2 ml.) was added to phenylhydrazine (0·54 g., 0·005 mole) in dioxan (40 ml.), and the solution was heated to boiling. Tetracyclone (1·9 g., 0·005 mole) in dioxan (40 ml.) was added during 15 min. and the mixture refluxed for a further 2 hr. The mixture was poured into water, and the precipitated brown solid was filtered off, dried, and chromatographed in benzene. The main red band was eluted with benzene and recovered as a dark solid. Recrystallisation from acetone yielded tetracyclone (0·7 g.), m. p. 218°.

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