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# REDUCTION OF 2,3,4,5-TETRAPHENYLCYCLOPENTADIENONE (TETRACYCLONE)

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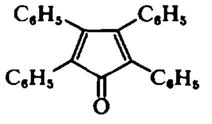
**Abstract**—A convenient route for the reduction of tetracyclone (**1**) to 1,2,3,4-tetraphenylcyclopentadiene (**2**) is to heat a mixture of **1**, hydrazine hydrate (excess), and hydrazine dihydrochloride in diethylene glycol for 4 h. In the absence of the solvent diethylene glycol the product obtained was shown from the IR, NMR and mass spectral data to be the enone **3**.

## INTRODUCTION

Considerable attention[1] has been focussed on the CO group reduction of tetracyclone (**1**). Although tetracyclone (**1**) can be obtained in a one step synthesis[1] from benzil and dibenzyl ketone, the reduction of **1** to **2** by well known methods of CO group reduction has not afforded the desired product **2** in any appreciable yield.[1-3] Various other methods tried by several workers resulted in a variety of products.[1] Sonntag *et al*[3] reported that pyrolysis of **1** with zinc gave a 5% yield of **2** whereas the reduction of **1** using LAH gave **2** in a yield of 18%. Recently Cava and Narasimhan[4] reported that the reduction of **1** using LAH and $AlCl_3$ gave pure **2** in a yield of 46%. We now report our results on the reduction of **1** by conventional methods for reducing a CO group to a methylene group.



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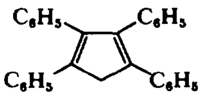

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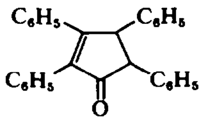

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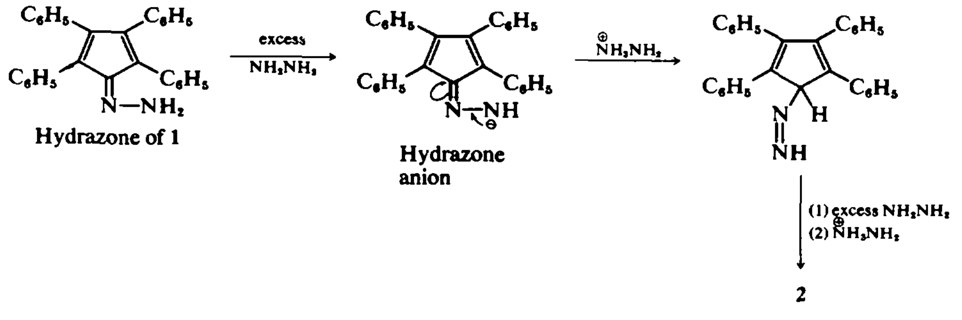
## RESULTS AND DISCUSSION

Attempts to reduce **1** by the Wolff–Kishner method and its Huang–Minlon modification[5] failed to give the desired product **2**. Since the lack of reactivity of the CO group of tetracyclone (**1**) may be due to steric hindrance by the phenyl groups acidic conditions[6] were employed in an effort to increase the yield of the hydrazone of **1**. The mixture of **1**, excess hydrazine hydrate (98%) and hydrazine dihydrochloride were heated under reflux for 4 h. The product obtained was found to be not the hydrazone of **1** as expected but 2,3,4,5-tetraphenylcyclopent-2-en-1-one (**3**) which may have arisen by the diimide reduction of C—C double bond.[7] The latter experiment when repeated with diethylene glycol as solvent and when heated under reflux for 2½ h gave 1,2,3,4-tetraphenylcyclopentadiene (**2**) (80%) contaminated with the hydrazone of **1** (as shown by the NMR and mass spectra). The impurities were conveniently removed on a column of alumina (Experimental). When the period of reflux was prolonged (4 h) there was no detectable impurity of the hydrazone of **1**, and almost pure **2** was obtained. It is probable that the hydrazone of **1** does not require potassium or sodium hydroxide as an additional base to induce its decomposition since the negative charge which develops on the $C_1$ atom of the hydrazone anion[8] is delocalised.

We repeated Cava and Narasimhan's[4] method of conversion of **1** to **2** and obtained **2** in a yield of 78%. But we find that this method gives **2** contami-



nated with its dimer as shown by the mass spectra. When 1 was reduced with LAH in a mixture of dibutyl ether and diethyl ether[3] we obtained the enone 3 as the major product.

*Mass spectral fragmentation of* **3**. Bergmann *et al*[9] gave the structure of the product they obtained on reducing **1** with LAH in dioxane as 2,3,4,5-tetraphenylcyclopentan-1-one. In a subsequent report without further experimental work Bergmann[10] has re-named the product formed in the above reaction as 2,3,4,5-tetraphenylcyclopent-2-en-1-one (**3**). We have obtained further confirmatory evidence for the structure of the product formed in the LAH reduction of **1** to be the enone **3**, (Experimental). The mass spectrum of **3** (Fig 1) needs special mention in view of the communication by Beynon *et al.*[11] They have suggested that tetracyclone (**1**) might readily eliminate carbon monoxide on electron impact to give the cation of tetraphenylcyclobutadiene. They have proved this by determining the mass spectrum of tetracyclone. They have also suggested that tetraphenylcyclobutadiene which may be formed in the mass spectrometer could subsequently react with residual oxygen or water vapour during the period the sample of **1** was in the spectrometer to give tetraphenylfuran. The cation corresponding to the parent molecular ion of tetraphenylfuran was observed in the mass spectrum of **1** by Beynon *et al.*[11] Similarly the cations with *m/e* 358 and 374 obtained in the mass spectrum of **3** (Fig 1) could be interpreted as being the structures **4** and **5** and could be postulated to arise by the mechanism given in Chart 1.

## EXPERIMENTAL

All m.ps are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 257 spectrometer. NMR spectra were recorded on a Varian HA-100 spectrometer with TMS as internal standard. Mass spectra were recorded on a AEI-MS 9 spectrometer.

### 1,2,3,4-*Tetraphenylcyclopentadiene* (**2**)

*Method A*. A mixture of **1** (4·0 g, 0·0104 mole), hydrazine hydrate (40 ml of 98–100% w/w), hydrazine dihydrochloride (7·0 g, 0·101 mole) and diethylene glycol (150 ml) was heated under reflux for 2½ h at 135–140° (inside temp). The colourless soln was cooled and the crude product was filtered off. The NMR spectra of the crude product showed signals at 2·8 $\tau$ (m, due to aromatic ring protons), 5·75 $\tau$ (s, due to $=NNH_2$ protons) and 5·94 $\tau$ (s, due to $=C{-}CH_2{-}C=$ protons). In the mass spectra a

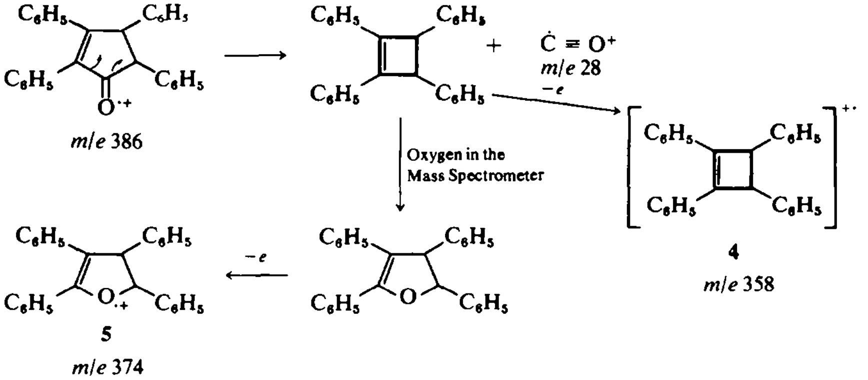


CHART 1

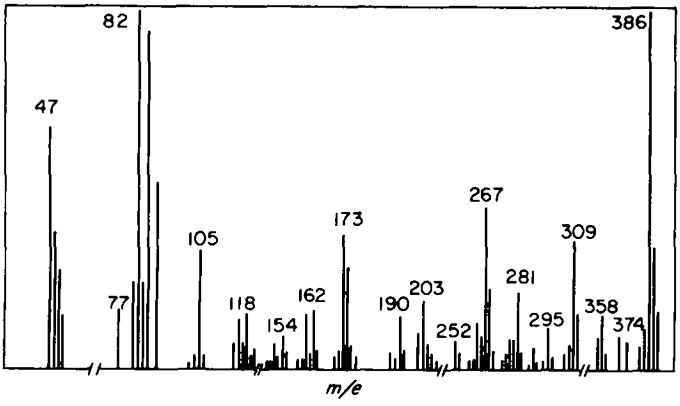


Fig 1.

peak at *m/e* 370 corresponding to the parent molecular ion of the diene **2** and also a peak at *m/e* 398 corresponding to the parent molecular ion of the hydrazone of **1** were obtained. The crude product was chromatographed on alumina and the light petroleum eluates were collected and solvent evaporated. The solid product obtained was crystallised from hexane to give the diene **2** (3·08 g, 80%), m.p. 179° (Lit.,[3] m.p. 180°), IR (KBr) 3000 (CH), 1600 (C=C), 1575 (C=C), 1440 (aromatic C=C), 770 and 690 cm$^{-1}$ (monosubstituted benzene), NMR ($CDCl_3$) 2·8 τ (20H, m), 5·94 τ (2H, s); MS, $M^+$ 370: MW calc. 370·49. When the period of reflux was extended to 4 h the crude product obtained was shown to have no contamination of the hydrazone of **1**. Almost pure **2** was obtained.

*Method B*. Tetracyclone **1** (2·0 g, 0·0052 mole) was added to a stirred mixture of dry ether (40 ml), $AlCl_3$ (1·25 g, 0·0094 mole), and LAH (0·8 g, 0·021 mole) in a 100 mole round bottomed flask. The colour of the ketone disappeared in less than 10 min and the mixture was heated under reflux for 45 min. The excess hydride was decomposed by the addition of dil HCl. Evaporation of the dried ($MgSO_4$) ethereal extract left a residue which was crystallised from n-hexane to yield **2** (1·5 g, 78%), m.p. 178° (Lit,[3] m.p. 180°). IR and NMR spectra of the product obtained by this method were identical with those of the product obtained by the method A. In the MS there were peaks beyond *m/e* 370, the peak with the highest *m/e* value was at 740.

2,3,4,5-*Tetraphenylcyclopenten*-2-1-*one* (**3**)

*Method A*. A mixture of **1** (4·0 g, 0·0104 mole), hydrazine hydrate (40 ml of 98–100% w/w), hydrazine dihydrochloride-7·0 g, 0·101 mole) were heated under reflux for 4 h at 135–140° (inside temp). The soln was allowed to cool and was poured into water. The product was filtered, dried and was crystallized from rectified spirit to yield **3** (2·9 g, 72%), m.p. 162° (Lit,[3] 162°), IR ($CHCl_3$ solution) 3000 (CH), 1680 (C=O), 1616 (C=C), 1575 and 1440 cm$^{-1}$ (aromatic C=C); NMR ($CDCl_3$) 2·8 τ (20H, m), 5·48 τ (1H, d, $J = 2$ c/s), 6·28τ (1H, d, $J = 2$ c/s); MS, $M^+$ 386; MW calc. 386·49.

*Method B*. Tetracyclone (2·0 g, 0·0052 mole) in dry di-n-butyl ether (200 ml) was added dropwise (in about 1 h) with stirring to a soln of finely powdered LAH (2·0 g, 0·053 mole) in dry diethyl ether (200 ml). The mixture was stirred vigorously for 1 h and then heated under reflux till the soln was almost colourless. After cooling, dil HCl (75 ml) was added. The ethereal soln was washed with water and was dried ($CaCl_2$). The residue on evaporation of the solvent was crystallised from rectified spirit to give **3** (1·5 g, 75%), m.p. 162° (Lit,[3] m.p. 162°). The IR, NMR, and mass spectra of the product was identical with those for the product obtained by the method A.

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## REFERENCES

[1] M. A. Ogliaruse, M. G. Romanelli and E. I. Becker, *Chem. Rev.* **65**, 261 (1965)
[2] W. Dilthey, W. Braun and O. Trösken, *J. Pract. Chem.* **139**, 1 (1933)
[3] N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, *J. Am. Chem. Soc.* **75**, 2283 (1953)
[4] M. P. Cava and K. Narasimhan, *J. Org. Chem.* **34**, 3641 (1969)
[5] N. B. Chapman, S. Sotheeswaran and K. J. Toyne, *Ibid.* **35**, 917 (1970)
[6] W. Nagata and H. Ttazaki, *Chem. & Ind.* 1194 (1964)
[7] S. Hunig, H. R. Muller and W. Thier, *Angew. Chem.* **4**, 275 (1965)
[8] H. H. Szmant, *Ibid.* **7**, 120 (1968)
[9] E. D. Bergmann, G. Berthier, D. Ginsburg, Y. Hirshberg, D. Lavie, S. Pinchas, B. Pullmann and A. Pulmann, *Bull. Soc. Chim. Fr.* **18**, 661 (1951)
[10] E. D. Bergmann, *Ibid.* **19**, 703 (1952)
[11] J. H. Beynon, R. F. Curtis and A. E. Williams, *Chem. Comm.* **8**, 237 (1966)