359. *Cyclopropanones and Related Compounds. Part I. Adducts from Reduction of Di-(α-bromobenzyl) Ketone in the Presence of Dipolarophiles* [1]

By R. C. Cookson and M. J. Nye

Zinc–copper couple reduces di-(α-bromobenzyl) ketone (XII) to 1,3,4,6-tetraphenylhexane-2,5-dione (XIII), which is cyclised by alkali to the cyclopentenones (XIV) and (XVI).

The ketone (XII) is reduced by sodium iodide in acetonitrile to 2,3,5,6-tetraphenylcyclohexane-1,4-dione (XVII). During the reaction, bands appear in the infrared spectrum of the solution at 1755 and 1725 cm.$^{-1}$, frequencies near which the allene epoxide (V) and its geometrical isomer might absorb.

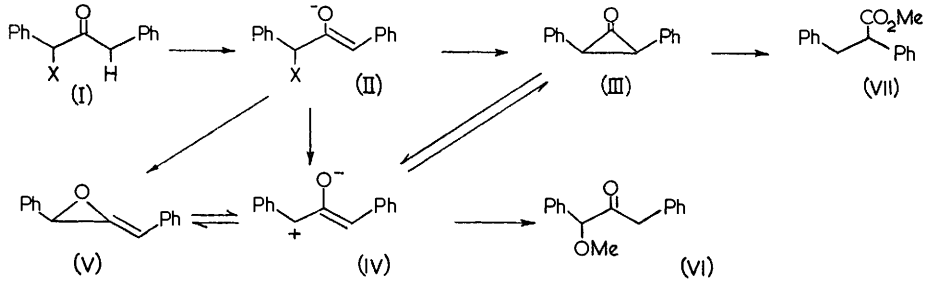
Addition of diethyl azodicarboxylate to the solution results in the adduct (XVIII), perhaps by diversion of an intermediate carbonium-enolate dipole (IV), which otherwise dimerises to (XVII). In the same way, tetracyanoethylene yields 3,4,4-tricyano-2,5-diphenylcyclopent-2-enone (XX). Elimination of hydrogen cyanide forms the electron-deficient cyclopentadienone (XXI) which gives adducts at room temperature with cyclohexene and triphenylphosphine.

The Favorskii rearrangement of α-halogeno-ketones [2] having an enolisable α′-hydrogen atom (*e.g.*, I) * goes through a symmetrical intermediate,[3–5] which was believed [4] to be a cyclopropanone (III). Direct cyclisation of the enolate (II) to the cyclopropanone would produce a stereospecific Favorskii rearrangement,[6] which, however, is not always observed.[7–9] Loss of stereochemistry is explained by Burr and Dewar's mechanism,[10] according to which the enolate anion undergoes S_N1 departure of bromide ion to give the planar dipole (IV), that cyclises to the cyclopropanone (III) if it does not first react with

* The general reactions are illustrated in the dibenzyl ketone system, since it was the one used in our experiments.

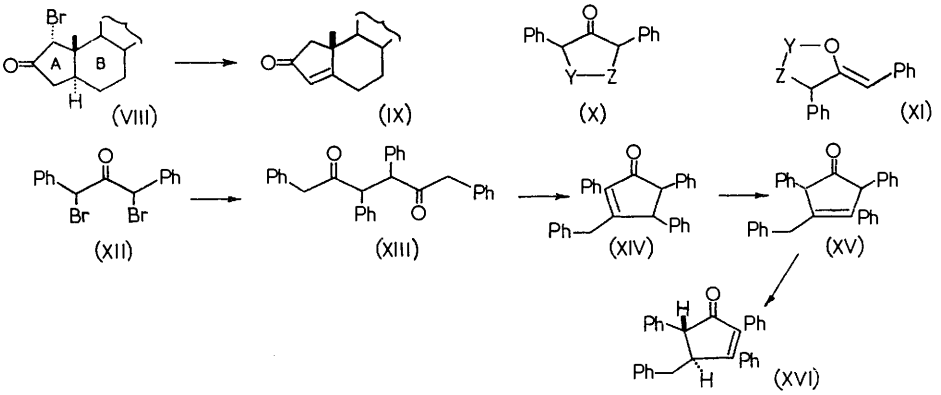
[1] Preliminary Note: Cookson and Nye, *Proc. Chem. Soc.*, 1963, 129. A full account is given by M. J. N., Ph.D. thesis, Southampton, 1963.
[2] Reviewed by Kende, *Org. Reactions*, 1960, **11**, 261.
[3] McPhee and Klingsberg, *J. Amer. Chem. Soc.*, 1944, **66**, 1132.
[4] Loftfield, *J. Amer. Chem. Soc.*, 1950, **72**, 632; 1951, **73**, 4707; 1954, **76**, 35.
[5] Aston and Newkirk, *J. Amer. Chem. Soc.*, 1951, **73**, 3900; Sacks and Aston, *ibid.*, p. 3902.
[6] Stork and Borowitz, *J. Amer. Chem. Soc.*, 1960, **82**, 4307.
[7] Wendler, Graber, and Hazen, *Tetrahedron*, 1958, **3**, 144.
[8] House and Gilmore, *J. Amer. Chem. Soc.*, 1961, **83**, 3972, 3980.
[9] Gaudemer, Parello, Skrobek, and Tchoubar, *Bull. Soc. chim. France*, 1963, 2405.
[10] Burr and Dewar, *J.*, 1954, 1201.

the solvent[11] (*e.g.*, methanol) to give the substitution product (VI). The decrease in stereospecificity with increase in polarity of the medium [8,9] is understandable in terms of this mechanism.



The common α′ substitution and α′β′-elimination in α-halogeno-ketones in polar solvents can also be formulated as proceeding through the carbonium-enolate dipole.[12,13] An example[14] is the elimination of hydrogen bromide from 1-bromo-A-norcholestan-3-one (VIII) with lithium chloride in dimethylformamide to give 92% of the Δ^4-ketone (IX).

If a dipole such as (IV) really can be generated in solution, it should be possible to add it to a suitable dipolarophile[15] (Y = Z) to form an adduct containing a five-membered ring [either (X) or (XI)]. We chose the 1,3-diphenyl derivative because of the ability of the phenyl group to stabilise a system by conjugation by either accepting or releasing electrons, because delocalisation should be helped by symmetrical substitution, and because in the extended conformation (IV) the π-system can be planar. The normal route to the hypothetical intermediate (IV) would be by the action of base on an α-halogeno-ketone (I), but we wished to avoid the presence of base, which might have catalysed undesirable condensations involving the ketone and the dipolarophile. A way to produce an enol in the absence of base is to reduce an α-halogeno-ketone, so that reduction of the αα′-dibromo-ketone (XII) might be expected to give the enol (II) and thence the intermediate (IV, III, or V), or even to undergo concerted loss of both bromine atoms. We also remembered that the classical synthesis of cyclopropanes (cf. III) involves reduction of 1,3-dibromides with zinc.[16]



Reduction of Di-(α-bromobenzyl) Ketone with Metals.—Treatment of the dibromide (XII) with zinc–copper couple in boiling acetonitrile yielded a diketone, the structure (XIII)

[11] Fort, *J. Amer. Chem. Soc.*, 1962, **84**, 2620.
[12] House and Thompson, *J. Org. Chem.*, 1963, **28**, 164.
[13] Many examples and refs. are given in "Steroid Reactions," ed. Djerassi, Holden-Day, San Francisco, 1963, ch. 4, 5, and 13.
[14] Dauben, Boswell, and Templeton, *J. Amer. Chem. Soc.*, 1961, **83**, 5006.
[15] Huisgen, *Proc. Chem. Soc.*, 1961, 357; *Angew. Chem.*, 1963, **75**, 604, 741.
[16] Raphael in "Chemistry of Carbon Compounds," ed. Rodd, Elsevier, 1963, IIA, p. 23.

of which followed from its simple nuclear magnetic resonance (n.m.r.) spectrum [twenty aromatic protons, singlets at τ 6·63 (4), and 5·31 (2)] and its synthesis by condensation of dibenzyl ketone with α-bromodibenzyl ketone (I; X = Br) in the presence of base. The substance had already been made by the latter route,[17] although no structure was put forward: the reaction, however, has analogies.[18] The phenyl groups notably enhance the intensity of the $n \longrightarrow \pi^*$ transition [19] of the diketone (XIII) ($\lambda_{max.}$ 293 mμ, ε 830; cf. dibenzyl ketone [19] $\lambda_{max.}$ 294 mμ, ε 220).

Alkali cyclised the diketone (XIII) to a mixture of two cyclopentenones, one of which (XIV) was formed also in 10% yield during the zinc reduction, no doubt through catalysis by the resulting zinc bromide.† Their infrared spectra were characteristic of cyclopent-2-enones (XIV: $\nu_{max.}$ 1700 and 1640 cm.$^{-1}$; XVI: 1695 and 1625 cm.$^{-1}$), and the two structures were easily assigned on the basis of their ultraviolet spectra (XIV: $\lambda_{max.}$ 217 258, and 315 mμ, ε 27,000, 9200, and 230. XVI: 216, 223, and 295 mμ, ε 24,000, 24,000 and 11,000). The intense band at 295 mμ in (XVI) indicates a 3-phenylcyclopent-2-enone,[20] whereas the band at shorter wavelength, 258 mμ, in the other tautomer (XIV) is compatible with a cross-conjugated 2-phenylcyclopent-2-enone, at the position expected for a simple 1-phenylcyclopentene.[21] (The weaker band at 315 mμ in this case, of course, is not from a $\pi \longrightarrow \pi^*$ transition at all, but from the enhanced $n \longrightarrow \pi^*$ transition.)

These structures are endorsed by the proton magnetic resonance spectra of the two isomers (CCl_4 solutions). Apart from the twenty aromatic protons, the spectrum of (XIV) consists of two quartets: doublets at τ 6·17 and 6·48, J = 3 c./sec. from the *trans* vicinal protons on the cyclopentenone ring, and at τ 5·77 and 6·76, J = 14 c./sec., from the geminal protons of the benzyl group. It is striking that the chemical shifts of the latter differ by as much as one p.p.m. The other isomer (XVI) has a multiplet near τ 6·5 from the two protons (at positions 4 and 5) on the cyclopentenone ring, and the benzyl protons (α and α′) now give rise to two doublets of doublets, the AB part of an ABC spectrum: $\delta_\alpha = \tau$ 7·51, $\delta_{\alpha'} = \tau$ 6·98, $J_{\alpha\alpha'} = 14$, $J_{\alpha 4} = 10$, $J_{\alpha' 4} = 4$ c./sec.

No adducts could be isolated when the dibromide (XII) was reduced with zinc or mercury in the presence of the dipolarophiles, acrylonitrile, tetracyanoethylene, dimethyl fumarate, or diethyl azodicarboxylate. (The adducts formed with furan [1] under these conditions will be described in the second Paper of this series.)

Reduction of Di-(α-bromobenzyl) Ketone with Iodide Ion.—We hoped that most of the disadvantages of reduction by metals (heterogeneity, possible formation of organometallic intermediates, possible transfer of one electron at a time, simultaneous generation of Lewis acids) could be avoided by the use of iodide ion, which allows the maintenance of a strictly neutral solution throughout the reaction.‡ Some justification was later provided by Fort's demonstration [11] that iodide ion in methanol reduces the dibromo-ketone (XII) to the methoxy-ketone (VI), perhaps *via* the dipole (IV).

Reduction of the dibromide (XII) § with sodium iodide in acetone or acetonitrile gave a diketone, analysing for a dimer ($C_{30}H_{24}O_2$) of (IV). Samples from various runs had appreciably different properties, but on equilibration with acid all gave an identical product, with $\nu_{max.}$ 1710 cm.$^{-1}$ (with shoulders at higher and lower ν), $\lambda_{max.}$ 286 mμ, ε 290, signals from

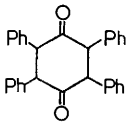
† Dr. G. Subrahmanyam has found that the dibromide is also reduced and cyclised to (XIV) by nickel carbonyl in acetone.

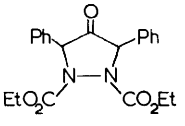
‡ cf. The reduction of 1,3-dibromides, carrying ester or acyl substituents at positions 1 and 3, to cyclopropanes with potassium iodide at room temperature.[16a]

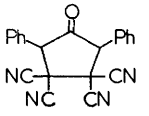
§ The dibromide (XII) can, of course, exist in ±- and *meso*-forms. We did not identify the isomers because similar results were obtained in all experiments whether the pure isomer, m. p. 114°, was used, or a mixture, m. p. *ca.* 81—84°, enriched in the other isomer.

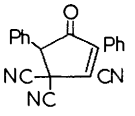
[16a] Kohler and Conant, *J. Amer. Chem. Soc.*, 1917, **39**, 1404.
[17] Smith and Wilson, *J.*, 1955, 1342.
[18] *E.g.*, Chatterjea and Ray, *Chem. Ber.*, 1959, **92**, 998; Stetter and Lauterbach, *ibid.*, 1960, **93**, 603.
[19] Cookson and Wariyar, *J.*, 1956, 2302; Cookson and Hudec, *J.*, 1962, 429, and refs. given there.
[20] Allen and Van Allan, *J. Amer. Chem. Soc.*, 1955, **77**, 2315.
[21] Baddeley, Chadwick, and Taylor, *J.*, 1956, 451.

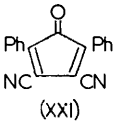
20 aromatic protons and peaks from four protons at τ 5·57 and 5·69 in the ratio 1 : 3·2. Dehydrogenation of all samples, best with air, gave tetraphenylquinol, which could be reversibly oxidised further to tetraphenylbenzoquinone. The dimer must, therefore, be the cyclohexane-1,4-dione (XVII), formed with varying proportions of the five possible stereoisomers but giving a standard equilibrium mixture. Even in Nujol the quinol showed a sharp O–H stretching band at 3600 cm.$^{-1}$ owing to steric prevention of hydrogen-bonding.

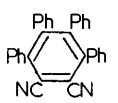

(XVII)

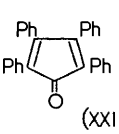

(XVIII)

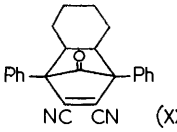

(XIX)

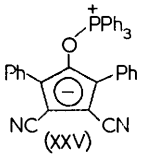

(XX)

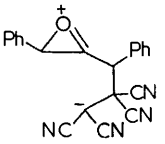

(XXI)

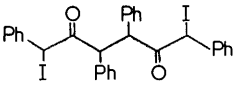

(XXII)

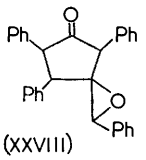

(XXIII)

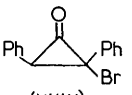

(XXIV)


(XXV)


(XXVI)


(XXVII)


(XXVIII)


(XXIX)

Many attempts to catch the carbonium-enolate dipole (IV), which might have been an intermediate in production of the dimer (XVII), by adding dipolarophiles to the iodide solutions yielded only gums or the dimer (XVII) (sometimes as the quinol or quinone, through oxidation during isolation): dimethyl fumarate, maleic anhydride, acrylonitrile, diethyl acetylenedicarboxylate, dimethylacetylene, bicyclo[2,2,1]heptadiene, vinyl acetate, ethyl vinyl ether, and carbon disulphide, in spite of their differing electron demands, all failed to form isolable adducts. Only tetracyanoethylene and diethyl azodicarboxylate gave crystalline adducts. (Those from dienes [1] will be reported later.)

In accordance with structure (XVIII) the adduct from the azo-ester had in its n.m.r. spectrum, apart from the peaks from the two phenyl and two ethyl groups, only one singlet from two protons at τ 4·69. Like other diethoxycarbonyl-hydrazines [22] the adduct (XVIII) showed two carbonyl stretching frequencies at 1700 and 1770 cm.$^{-1}$, the ketonic carbonyl absorption presumably being obscured by the latter.

Treatment of the dibromide (XII) with sodium iodide in acetone containing tetracyanoethylene gave a 35% yield of the cyclopentenone (XX), apparently formed by elimination of hydrogen cyanide from the primary adduct (XIX), and a trace of the cyclopentadienone (XXI). Under similar conditions using acetonitrile as solvent the only crystalline product was a small quantity of the dienone (XXI): in nitrobenzene or diethylene glycol dimethyl ether no crystalline product could be separated.

The cyclopentenone (XX) had an ultraviolet spectrum (shoulder 239 mμ, ε 6000, $\lambda_{max.}$ 263 mμ, ε 5900, and 341 mμ, ε 11,000) rather similar to that of (XVI): its carbonyl stretching frequency (1740 cm.$^{-1}$) was raised by 40 cm.$^{-1}$ from that of (XVI) by the electron-pull of the cyano-group. Its n.m.r. spectrum had only a singlet at τ 4·88 from one proton, apart from the ten aromatic protons. Although these data leave little doubt about the compound's structure, it was given a rigorous chemical proof.

Many attempts to induce elimination of hydrogen cyanide from (XX) to form (XXI) by treatment with acid or base in solution gave only low yields, if any. However, pyrolysis at temperatures between 180 and 500° caused the required elimination in high

[22] Gilani, Ph.D. Thesis, Southampton, 1963.

yield, at least on a small scale. The product (XXI) was easily recognised as a cyclopentadienone by its characteristic purple colour and absorption spectrum. As the Table shows,

Electronic spectra of some cyclopentadienones in ethanol

	$\lambda_{max.}$ in mμ (ε)		
(XXI)	252 (47,800)	305 (4280)	540 (2820)
(XXIII) [23]	262 (27,800)	333 (7200)	512 (1250)
Tetra-*p*-methoxyphenylcyclopentadienone [23]	370 (31,200)	350 (11,400), 384 (10,400)	560 (1460)

its electronic spectrum is broadly similar to those of the tetra-arylcyclopentadienones,[23] although its visible absorption is more intense. The structure (XXI) follows from the formation of the same tetraphenylphthalonitrile (XXII) by condensation of dienone (XXI) with diphenylacetylene and of tetraphenylcyclopentadienone (XXIII) with dicyanoacetylene. Compounds (XIX), (XX), and (XXI) could not be synthesised by condensation of the monobromo-ketone (I; X = Br) with tetracyanoethylene or of the dibromo-ketone (XII) with tetracyanoethane.

The compound (XXI) is an extreme example of an electron-deficient diene,[24] the usual reactivity of the cyclopentadienone system being reinforced by the electron-demand of the two cyano groups, while the phenyl groups remove any tendency to dimerise.[25] For example, cyclohexene, which reacts very slowly if at all with normal (electron-richer) dienes, adds to (XXI) at room temperature to give the Diels–Alder adduct (XXIV) which showed the typical high-frequency carbonyl band [25] at 1785 cm.$^{-1}$, and lost carbon monoxide when heated.

A related property of (XXI) is its immediate reaction at room temperature with triphenylphosphine to form a pale yellow crystalline 1 : 1 adduct. Rearrangement of neither reactant can have occurred, because dilute nitric acid in acetonitrile oxidised the adduct back to the dienone (XXI) and triphenylphosphine oxide. The adduct can hardly be a charge-transfer complex, for boiling solutions developed no purple tint and the infrared spectrum showed no carbonyl absorption. The phosphorus atom must have added to the electrophilic oxygen atom to give the zwitterion (XXV), a reaction analogous to the formation of enol-phosphonium salts from α-halogeno-ketones.[26]

The Structure of the Intermediate.—The stretching frequencies of the double bonds in the three valency tautomers (III), (IV), and (V) were expected to differ widely: the cyclopropanone (III) should absorb near 1825 cm.$^{-1}$,[27] the allene epoxide (V) perhaps near 1750 cm.$^{-1}$,[28] and the carbonium–enolate dipole (IV), which has rather less than half a double bond between any two atoms, should absorb near 1550 cm.$^{-1}$ or below (cf. RCO_2^- at about 1600 cm.$^{-1}$). The reaction of the dibromo-ketone (XII) with sodium iodide was, therefore, carried out in the cell of an infrared spectrometer, using acetonitrile as solvent, which allows the spectrum to be followed from 1670 to 2000 cm.$^{-1}$. In this way one should be able to observe normal ketones and any appreciable concentration of (III) or (V), but unfortunately not (IV).

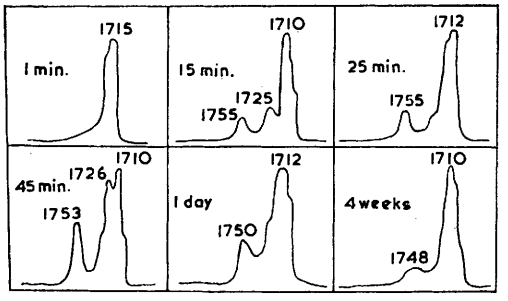
After much experimentation, a suitable method was found in mixing one volume of a saturated solution of the dibromo-ketone (XII) with four volumes of a saturated solution of sodium iodide in acetonitrile. Under these conditions almost two mols. of sodium bromide had separated from solution in one minute, and free iodine (or rather I_3^-) was then slowly liberated in solution. During the reaction the solution developed no detectable electron spin resonance signal. The Figure shows the change in the infrared spectrum

[23] Coan, Trucker, and Becker, *J. Amer. Chem. Soc.*, 1955, **77**, 60.
[24] Pummerer and Fiesselmann, *Annalen*, 1940, **544**, 206; Pummerer and Stieglitz, *Ber.*, 1942, **75**, 1072; Sauer and Wiest, *Angew. Chem.*, 1962, **74**, 269.
[25] Allen, *Chem. Rev.*, 1945, **37**, 209; 1962, **54**, 653.
[26] Trippett, *Quart. Rev.*, 1963, **17**, 413.
[27] De More, Pritchard, and Davidson, *J. Amer. Chem. Soc.*, 1959, **81**, 5874.
[28] Pollard and Parcell, *J. Amer. Chem. Soc.*, 1951, **73**, 2925; Bottini and Roberts, *ibid.*, 1957, **79**, 1462; Gragson, Greenlee, Derfer, and Boord, *ibid.*, 1953, **75**, 3344; Ullman, *ibid.*, 1959, **81**, 5386; Ball and Landor, *Proc. Chem. Soc.*, 1961, 246.

during a typical run: in spite of careful calibration of the spectrometer the exact frequencies were not reproducible, probably due to slight variations in the concentration of the solutions (strong solutions were essential to give sufficient intensity to the transient peaks).

The dibromo-ketone (XII) in acetonitrile absorbed at about 1730 cm.$^{-1}$, and addition of iodine hardly affected the peak. Dibenzyl ketone in acetonitrile absorbed at 1715 cm.$^{-1}$, and addition of sodium iodide did not affect the peak. It therefore seems unlikely that sodium iodide or iodine will cause any large shifts in carbonyl stretching frequencies from their expected positions.

Clearly, the first reaction consists in the fast replacement of successive bromine atoms by iodide ion, so that the peak at 1715 cm.$^{-1}$ after one minute must come from the di-iodo-ketone. The main contributor to the peak at 1710 cm.$^{-1}$ at the end of the reaction is presumably the cyclohexanedione (XVII). The assignment of structures to the molecules responsible for the several other peaks in the spectra at intermediate times of reaction is still a matter for speculation. The two prominent peaks at about 1755 and 1725 cm.$^{-1}$ are particularly intriguing. While one or both might be due to (I; X = I), (XXVII) or



(XXVIII), amongst other possibilities, an explanation worth series consideration is that the band at 1755 cm.$^{-1}$ comes from the allene epoxide (V). Indeed, it is conceivable that the two bands are due to the two stereoisomers, differing in configuration about the double bond, (V) being the more stable.

Burr and Dewar [10] pointed out the unfavourable orbital overlap in the transition-state for internal displacement of bromide from the enolate ion (II) to give the cyclopropanone (III) directly, and, therefore, supposed that the carbonium-enolate dipole (IV) was first formed. The argument is valid for displacement of Br^- by carbon, whose *p*-orbital must be at right angles to the plane of the oxygen and three carbon atoms, but it does not apply to displacement by oxygen. So the allene epoxide (V) might form first, then open to (IV) and re-cyclise to (III). No doubt the detailed course of the reaction will depend on the nature of the ketone and the solvent. That cyclopropanones probably are present under some conditions is implied by the conversion [29] (which we have also observed) of the dibromoketone (XII) into diphenylcyclopropenone with tertiary amines. This reaction is most simply explained by participation of the bromo-cyclopropanone (XXIX).

Either the dipole (IV) or the epoxide (V) ⟶ (XXVI) ⟶ (XIX) could serve as intermediates in formation of the adducts. We defer further discussion until we have presented more evidence in our next Paper.

Experimental

Ultraviolet spectra of ethanol solutions were measured on a Unicam S.P. 700 and infrared spectra (of Nujol mulls unless contraindicated) on a S.P. 200 spectrometer calibrated against a polystyrene film. N.m.r. spectra (CCl_4 solutions unless contraindicated) were measured on a Varian A 60 instrument using tetramethylsilane as internal standard. The reaction of the dibromo-ketone (XII) with sodium iodide was followed on a Unicam S.P. 100 spectrometer.

Petroleum was the fraction of b. p. 60—80°.

[29] Breslow, Posner, and Krebs, *J. Amer. Chem. Soc.*, 1963, **85**, 234.

Di-(α-bromobenzyl) Ketone (XII).—Bromination of dibenzyl ketone gave erratic yields; the total yield of (±)- and *meso*-isomers was usually over 80%, but the yield of pure isomer, m. p. 114°, varied from 0 to 30%. Carbon disulphide,[30] acetic acid, and benzene could be used as solvent.

Bromine (10 ml.) was added dropwise during 1 hr. to a stirred solution of dibenzyl ketone (21 g.) in carbon disulphide (100 ml.), and the solution stirred for a further hr. The solution was washed with sodium thiosulphate solution, twice with sodium bicarbonate solution, and twice with water, dried ($MgSO_4$), and the solvent evaporated. The gummy product was crystallised from ethanol and then benzene to yield needles (3·2 g.), m. p. 109—114°. Two recrystallisations from petroleum–benzene raised the m. p. to 112—114°. ($\nu_{max.}$ 700, 750, and 1715 cm.$^{-1}$, n.m.r.: 10 aromatic protons, 2 protons at τ 4·31).

Evaporation of mother-liquors from the above crystallisation and recrystallisation of the residue from petroleum–benzene yielded crystals (16·1 g.), m. p. 81—84°, [$\nu_{max.}$ 700, 750, and 1715 cm.$^{-1}$, n.m.r.: 10 aromatic protons, 2 protons at τ 4·21 and 4·31 (ratio of integrals 65 : 35)]. Recrystallisation of the fraction, m. p. 81—84°, from petroleum–chloroform yielded fractions melting between 81 and 90°.

Solutions of di-(α-bromobenzyl) ketone, m. p. 81—84°, were refluxed under the following conditions: (i) 24 hr. in benzene plus a little 60% hydrogen bromide. (ii) 24 hr. in acetic acid plus a little 60% hydrogen bromide. (iii) 24 hr. in benzene plus a trace of 2,6-lutidine. (iv) One week in benzene (dried over sodium wire).

In (i), (ii), and (iii) no isomerisation had taken place, but in (iv) crystallisation from petroleum–benzene yielded needles 66%, m. p. 109—111°, and pale brown slabs 16%, m. p. 98—99°. The n.m.r. spectra were the same as for the isomer, m. p. 111—114°.

Reactions with Benzyl α-Chlorobenzyl Ketone (I; X = Cl).—Reaction of the chloro-ketone [31] with 2,6-lutidine [11] or 2,4,6-collidine in carbon tetrachloride or acetonitrile in the presence of dimethyl fumarate or tetracyanoethylene led to no crystalline product.

Action of Zinc–Copper Couple on Di-(α-bromobenzyl) Ketone in Acrylonitrile.—A mixture of ketone (XII) (3·68 g.) and zinc–copper couple [32] (15 g.) was refluxed for 6 hr. in acrylonitrile (dried over sodium sulphate). Sufficient water was added to hydrate any zinc bromide formed in the reaction, and then sodium sulphate to dry the solvent. The solvent was filtered and combined with chloroform extracts of the residue. The solvent was evaporated and the residue chromatographed over silica gel. *1,3,4,6-Tetraphenylhexane-2,5-dione* (XIII) (0·45 g., 22%) was eluted in 50 : 50 benzene–chloroform, m. p. 202—203° (crystallised twice from chloroform) (Found: C, 86·5; H, 6·2. $C_{30}H_{26}O_2$ requires C, 86·1; H, 6·3%).

Action of Zinc–Copper Couple on Di-(α-bromobenzyl) Ketone in Acetonitrile.—A mixture of di-(α-bromobenzyl) ketone (3·68 g.) and zinc–copper couple (25 g.) was refluxed for 1 week in acetonitrile (dried over sodium sulphate). Sufficient water was added to hydrate any zinc bromide formed in the reaction, and then sodium sulphate to dry the solvent. The solvent was filtered and combined with chloroform extracts of the residue. The solvent was evaporated and the residue crystallised from ethanol–chloroform to yield 1,3,4,6-tetraphenylhexane-2,5-dione (1·25 g., 60%). The second crop yielded 3-benzyl-2,4,5-triphenylcyclopent-2-enone (XIV), m. p. 144—148° (crystallised from chloroform–petroleum) (Found: C, 89·7; H, 5·8. $C_{30}H_{24}O$ requires: C, 90·0; H, 6·0%).

Action of Alkali on 1,3,4,6-Tetraphenylhexane-2,5-dione.—The diketone (XIII) (0·42 g.), and potassium hydroxide (0·48 g.), were refluxed for 1·5 hr. in ethanol (30 ml.) and a trace of water. The solution was acidified with dilute hydrochloric acid, and extracted with chloroform. The combined extracts were washed with sodium bicarbonate and water and dried (Na_2SO_4), and the solvent evaporated to yield a pale brown gum. Crystallisation from ethanol gave *3-benzyl-2,4,5-triphenylcyclopent-2-enone* (XIV) (91 mg.), m. p. 150—150·5°, crystallised thrice from ethanol, $\nu_{max.}$ 700, 780, 1640m, and 1700 cm.$^{-1}$ (Found: C, 89·8; H, 5·8%) and *4-benzyl-2,3,5-triphenylcyclopent-2-enone* (XVI), m. p. 130—131°, (43 mg., crystallised twice from ethanol), $\nu_{max.}$ 695, 710, 750, 760, 1625, and 1695 cm.$^{-1}$ (Found: C, 90·0; H, 6·3. $C_{30}H_{24}O$ requires C, 90·0; H, 6·0%).

Preparation of 1,3,4,6-Tetraphenylhexane-2,5-dione.[17]—A saturated solution of potassium hydroxide (570 mg.) was added to dibenzyl ketone ethanol (30 ml.). Immediately, benzyl

[30] Bourcart, *Ber.*, 1889, **22**, 1368.
[31] Prévost and Sommière, *Bull. Soc. chim. France*, 1935, **2**, 1151.
[32] Shank and Schechter, *J. Org. Chem.*, 1959, **24**, 1825.

α-bromobenzyl ketone (3·7 g.) [30] in ethanol (30 ml.) was added. A precipitate quickly formed and was filtered off and crystallised three times from chloroform (2·1 g., 50%), m. p. 201—202°, $\nu_{max.}$ 705, 740, 765, and 1705 cm.$^{-1}$; 1425, 1460, and 1600 cm.$^{-1}$ (in tetrachloroethylene). $\nu_{max.}$ 160 mμ (ε 900), 293 mμ (ε 830) in ethanol. N.m.r.: 20 aromatic protons, singlets at τ 6·63 (4) and 5·31 (2).

Action of Sodium Iodide on Di-(α-bromobenzyl) Ketone.—The dibromo-ketone (XII) (368 mg.) in acetone was quickly mixed with an excess of a saturated solution of sodium iodide in acetone. After 1 min. the precipitate (191 mg.) was filtered off and washed with a little acetone. This solid was analysed for iodide and bromide by using adsorption indicators. The percentage of sodium bromide found was 94%, which gives the number of mols. of sodium bromide liberated from 1 mol. of di-(α-bromobenzyl) ketone as 1·74.

Satisfactory yields of (XVII) were obtained only when acetone was the solvent, and best results were observed when the reaction was done under nitrogen, and crystallisation of the crude product was from acetone, carried out quickly to avoid excessive oxidation. By-products were non-crystalline except for 2,3,5,6-tetraphenylquinol and 2,3,5,6-tetraphenylbenzoquinone, which were obtained occasionally in low yield, and a hygroscopic product which crystallised from the reaction mixture when the solvent was acetonitrile. [This latter compound was also obtained when di-(α-bromobenzyl) ketone was refluxed with activated zinc in acetonitrile. The infrared spectrum had bands at 1600, 1620, 2260m, 2290w, and 3400 cm.$^{-1}$ which are consistent with the structure $Me_3C{=}NH{\cdot}CH_2{\cdot}CN$ hydrate.]

The following procedure was typical. A mixture of di-(α-bromobenzyl) ketone (1 g.), sodium iodide (2 g.), and acetone (40 ml.) was left at room temperature for 1 week under an atmosphere of nitrogen. The solvent was evaporated and the residue extracted with chloroform. The extracts were washed with sodium thiosulphate and water, and dried (Na_2SO_4), and the solvent removed. The residue was crystallised from dry acetone to yield 2,3,5,6-*tetraphenylcyclohexanedione* (XVII) (230 mg.), m. p. 182—183°, $\nu_{max.}$ 705, 710, 720, 760, and 1710 cm.$^{-1}$; $\lambda_{max.}$ 260 (ε 1370) and 286 mμ (ε 388) in ethanol; n.m.r.: 20 aromatic protons, 4 other protons in a doublet at τ 5·57 and 5·69 with ratio of integrations 1 : 10 (Found: C, 85·7; H, 5·8. $C_{30}H_{24}O_2$ requires C, 86·5; H, 5·8%).

A higher yield was obtained when carbon disulphide was present. A mixture of sodium iodide (5 g.), di-(α-bromobenzyl) ketone (1 g.), carbon disulphide (30 ml.), and acetone (30 ml.) was refluxed for 0·5 hr. The mixture was poured into chloroform, and washed with sodium thiosulphate and water, and dried (Na_2SO_4), and the solvent removed. The residual gum was crystallised from acetone giving, after rejection of amorphous material (50 mg.), 2,3,5,6-tetraphenylcyclohexanedione (340 mg., 60%). An experiment on larger scale gave only 30% of 2,3,5,6-tetraphenylcyclohexanedione, but both 2,3,5,6-tetraphenylquinol and 2,3,5,6-tetraphenylbenzoquinone were isolated.

Equilibration of 2,3,5,6-Tetraphenylcyclohexanedione Mixtures.—2,3,5,6-Tetraphenylcyclohexanedione (50 mg.) in acetic acid (10 ml.) and one drop of perchloric acid was refluxed. After 1 hr. the infrared spectrum of the product was constant. The product was obtained by adding chloroform to the solution, washing with sodium bicarbonate and water, drying (Na_2SO_4), removing the solvent, and crystallising the residue from acetone; it had $\nu_{max.}$ 710, 750, 770, and 1710 (shoulders) cm.$^{-1}$; $\lambda_{max.}$ 259 (ε 1450) and 286 mμ (ε 286) in ethanol; n.m.r.: 20 aromatic protons; 4 protons in a doublet at τ 5·57 and 5·69 having ratio of integrations 1 : 3·2.

Equilibration with base was found to be less practicable, as aerial oxidation in basic solution is fast at room temperature.

Oxidation of 2,3,5,6-Tetraphenylcyclohexanedione.—Oxidation to 2,3,5,6-tetraphenylquinol proceeded cleanly when 2,3,5,6-tetraphenylcyclohexanedione (5 mg.) was heated in a melting-point tube at 250° for 15 min. Much longer reaction times were required for larger quantities of reactants. In control experiments carried out under nitrogen 2,3,5,6-tetraphenylcyclohexanedione was recovered. The infrared spectra of the crude uncrystallised product obtained by oxidising two different mixtures of isomers were both identical with the spectrum of 2,3,5,6-tetraphenylquinol obtained by reducing 2,3,5,6-tetraphenylbenzoquinone with stannous chloride.

When oxygen was bubbled through a refluxing solution of 2,3,5,6-tetraphenylcyclohexanedione in benzene for 30 min., very little change occurred, but when solutions of this or 2,3,5,6-tetraphenylquinol were left exposed to air for long periods at room temp., oxidation to 2,3,5,6-tetraphenylbenzoquinone occurred.

Action of Air on 2,3,5,6-Tetraphenylcyclohexanedione in the Presence of Base.—Air was bubbled through 2,3,5,6-tetraphenylcyclohexanedione (1·5 g.) and potassium hydroxide (80 mg.) in ethanol (75 ml.) for 15 min. 2,3,5,6-Tetraphenylquinone (0·5 g.) was filtered off as orange needles, which were contaminated with white needles of 2,3,5,6-tetraphenylquinol. The crude quinone was recrystallised from acetic acid three times, m. p. 305—306° (lit., 311—315° [33]), $\nu_{max.}$ 700, 730, 750, 775, 790, 1595, and 1650 cm.$^{-1}$ (Found: C, 86·6; H, 5·0. $C_{30}H_{20}O_2$ requires C, 87·3; H, 4·9%).

2,3,5,6-*Tetraphenylquinol.*—Stannous chloride dihydrate (57 mg.) in concentrated hydrochloric acid (5 ml.) was added to 2,3,5,6-tetraphenylquinone (103 mg.) in acetic acid (20 ml.). The solution was evaporated to smaller bulk, water added, and 2,3,5,6-tetraphenylquinol (84 mg., 85%) crystallised. It was recrystallised quickly from acetonitrile–chloroform, m. p. 310—320° (m. p. tube sealed in air) (lit.,[33] 322—325°), $\nu_{max.}$ 705, 760, 785m, 1600m, 3600m cm.$^{-1}$ (Found: C, 86·4; H, 5·6. $C_{30}H_{22}O_2$ requires C, 86·9; H, 5·4%).

Action of Sodium Iodide on 1,3-Dibromo-1,3-diphenylpropanone and Diethyl Azodicarboxylate.—A mixture of diethyl azodicarboxylate (2·16 g.), 1,3-dibromo-1,3-diphenylpropanone (3 g.), sodium iodide (15 g.), and acetonitrile (50 ml.) was left at room temp. for 1 day and then refluxed for 1 hr. The mixture was added to water, and extracted with chloroform. The chloroform extracts were washed with water, sodium thiosulphate solution, and water, dried (Na_2SO_4), and the solvent was removed. The residue was chromatographed on silica. Elution with benzene–chloroform 4 : 1 yielded a gum, which crystallised from ethanol to give 1,2-*diethoxycarbonyl*-3,5-*diphenyl*-4-*pyrazolidone* (XVIII) (15%), m. p. 107—108° (crystallised twice from ethanol); $\nu_{max.}$ 700m, 710m, 720, 750m, 765m, 785m, 1250, 1700, and 1770 cm.$^{-1}$; n.m.r.: 10 aromatic protons; 2 proton singlet at τ 4·69, 4 proton quartet at τ 5·77 (J = 7 c./sec.); 6 proton triplet at τ 8·74 (J = 7 c./sec.) (Found: C, 66·1; H, 5·9; N, 7·4. $C_{21}H_{22}N_2O_5$ requires C, 66·0; H, 5·8; N, 7·3%).

Elution with chloroform yielded a gum which crystallised from ethanol to yield 1,2-diethoxycarbonylhydrazine (210 mg.); $\nu_{max.}$ 1250br, 1695, 1745, and 3300 cm.$^{-1}$.

Action of Sodium Iodide on Di-(α-bromobenzyl) Ketone and Tetracyanoethylene.—A mixture of di-(α-bromobenzyl) ketone (920 mg.), tetracyanoethylene (960 mg.), and sodium iodide (3 g.) were refluxed for 1 hr. in acetone (50 ml.). Chloroform was added and the mixture was extracted with water, sodium thiosulphate solution and water, dried (Na_2SO_4), and the solvent evaporated to leave a dark green mass. Chromatography on silica yielded a trace of 3,4-dicyano-2,5-diphenylcyclopentadienone eluted with benzene–chloroform 9 : 1, followed (in benzene–chloroform 4 : 1) by 3,4,4-*tricyano*-2,5-*diphenylcyclopentenone* (XX) (200 mg., 35%), m. p. 164—165·5° (decomp.); $\nu_{max.}$ 690, 700m, 725, 750, 770w, 800, 1610, 1740, and 2250w cm.$^{-1}$; $\lambda_{max.}$ 325 mμ (ε 8900) in chloroform. In ethanol the spectrum showed that reaction was occurring: $\lambda_{max.}$ 275 (ε 14,000), 287sh (ε 12,000), 380 (4200), and 473 mμ (ε 2000); n.m.r. in acetone: 10 aromatic protons, 1 proton at τ 4·88 (Found: C, 78·0; H, 3·7; N, 14·7. C, 77·8; H, 3·9; N, 13·1. C, 78·2; H, 3·8; N, 13·4%; *M*, 330. $C_{20}H_{11}N_3O$ requires C, 77·6; H, 3·6; N, 13·6%; *M*, 309).

Preparation of 3,4-*Dicyano*-2,5-*diphenylcyclopentadienone.*—(a) *Acids and bases. Treatment of* 3,4,4-tricyano-2,5-diphenylcyclopentenone (XX) with either potassium hydroxide or sulphuric acid was tried under numerous conditions by varying solvent, concentrations, temperature and time. In most cases no purple colour was produced, but occasionally both acidic and basic treatments gave 3,4-dicyano-2,5-diphenylcyclopentadienone in yields of less than 10%. 2,6-Lutidine in acetonitrile yielded brown gums.

(b) *Heat.* Pyrolysis of the cyclopentenone (XX) in a flask under a water-pump vacuum and immersed in a heated-oil bath was most successful on the 10-mg. scale with the oil bath at 180°, when the yield of cyclopentadienone (XXI) was then quantitative after 3 hr. Repetition of the experiment on the 1-g. scale produced only 10% conversion after 3 hr., and longer reaction times gave a magenta solid by-product.

The cyclopentenone (XX) in benzene was pyrolysed by passage down a heated column packed with glass beads. The most effective temperature was 500°, when yields varied from 40 to 70% depending on the rate of flow of reactant and nitrogen carrier gas. In most cases the 3,4-*dicyano*-2,5-*diphenylcyclopentadienone* (XXI) was separated by chromatography in benzene on silica gel, from which it was eluted before the cyclopentenone (XX). Further purification was effected by vacuum sublimation at 130° giving (XXI), m. p. 165—172°; $\nu_{max.}$

[33] Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 2478; Hübel and Braye, *J. Inorg. Nuclear Chem.*, 1959, **10**, 250.

695, 745, 760m, 805(doublet), 1720, and 2260 cm.$^{-1}$; $\lambda_{max.}$ 252 (ε 47,800), 305 (ε 4280), and 540 mμ (ε 2820) in hexane (Found: C, 78·7 (81·1); H, 4·3 (4·2); N, 7·4 (9·8). $C_{19}H_{10}N_2O$ requires C, 80·8; H, 3·6; N, 9·9%).

Action of Dimethyl Acetylenedicarboxylate on 3,4,4-Tricyano-2,5-diphenylcyclopentenone.—3,4,4-Tricyano-2,5-diphenylcyclopentenone was refluxed for 1 week with 5 equivs. of dimethyl acetylenedicarboxylate in xylene. The solvent was removed and the residue chromatographed on silica. The fraction eluted with benzene–chloroform (1 : 1) was crystallised from methanol to yield yellow crystals 2%, m. p. 218—222° (crystallised from methanol and ethanol); $\nu_{max.}$ 700, 720m, 755, 765, 775, 785, and 2250 cm.$^{-1}$, $\lambda_{max.}$ 239 (ε 6000sh); 263 (ε 5900); 341 mμ (ε 11,000) (Found: C, 86·3; H, 5·3%).

The fraction eluted with chloroform was crystallised from acetic acid–water to yield *dimethyl 4,5-dicyano-3,6-diphenylphthalate* 15%, m. p. 233·5—234° (crystallised from dilute acetic acid, methanol, and ethanol); $\nu_{max.}$ 710, 770m, 1135, 1235, 1255m, 1725, and 2230 cm.$^{-1}$ (Found: C, 72·5; H, 4·2; N, 7·0. $C_{24}H_{16}N_2O_4$ requires C, 72·7; H, 4·1; N, 7·1%).

Reaction of 3,4-Dicyano-2,5-diphenylcyclopentadienone with Diphenylacetylene.—3,4-Dicyano-2,5-diphenylcyclopentadienone (0·282 g.) and diphenylacetylene (0·9 g.) were heated at 100° for 6 hr. The mixture was then crystallised from benzene–carbon tetrachloride to give *5,6-dicyano-1,2,3,4-tetraphenylbenzene* 0·31 g. (72%), m. p. 254—255° (crystallised twice from benzene–carbon tetrachloride and ethanol) (Found: C, 88·6; H, 5·2; N, 5·9. $C_{32}H_{20}N_2$ requires C, 88·9; H, 4·7; N, 6·5%).

Preparation of 5,6-Dicyano-1,2,3,4-tetraphenylbenzene.—Tetraphenylcyclopentadienone (380 mg.) and dicyanoacetylene [34] (114 mg.) were dissolved in ether (5 ml.) and left at room temp. for 2 days, during which time the pink colour changed to pale brown. The solvent was evaporated and the residue crystallised from chloroform–petroleum ether giving *5,6-dicyano-1,2,3,4-tetraphenylbenzene* (XXII) (236 mg., 55%), m. p. 253·5—255° (crystallised twice from chloroform–petroleum and ethanol); $\nu_{max.}$ 700(doublet), 710, 735, and 2220 cm.$^{-1}$.

Action of 3,4-Dicyano-2,5-diphenylcyclopentadienone on Cyclohexene.—3,4-Dicyano-2,5-diphenylcyclopentadienone (200 mg.) in benzene (25 ml.) and cyclohexene (25 ml.) was left at room temp. for 2 weeks in the dark. The solvent was removed and the residue quickly crystallised from benzene to yield the *adduct* (XXIV) (250 mg.), m. p. 235—238° (preceded by vigorous decomposition without melting above 50°) (crystallised from benzene and chloroform–petroleum); $\nu_{max.}$ 700, 735, 760m, 780m, 800w, 1785, and 2230w cm.$^{-1}$ (Found: C, 81·7; H, 6·2; N, 8·3. $C_{25}H_{20}N_2O$ requires C, 82·4; H, 5·5; N, 7·7%).

The adduct was heated at 250° for 10 min. during which time a gas was evolved: $\nu_{max.}$ of resultant gum, 700, 725, 745, and 2230w cm.$^{-1}$.

Action of 3,4-Dicyano-2,5-diphenylcyclopentadienone on Triphenylphosphine.—3,4-Dicyano-2,5-diphenylcyclopentadienone (200 mg.) and triphenylphosphine (400 mg.) in benzene (50 ml.) was left for 1 hr. at room temp. Pale yellow crystals (190 mg.) were filtered off and recrystallised twice from acetonitrile. The *adduct* (XXV) had m. p. 195—197° (decomp.); $\nu_{max.}$ 685, 700, 735(doublet), 745, 755, and 2200 cm.$^{-1}$ (Found: C, 79·1; H, 4·8; N, 5·3; P, 5·4. $C_{37}H_{25}N_2OP$ requires C, 81·7; H, 4·6; N, 5·1; P, 5·7%).

The adduct (50 mg.) and one drop of concentrated nitric acid in acetonitrile (10 ml.) was heated to 60° and then left to cool for 0·5 hr. Sufficient water was added so that the purple colour produced by the reaction was largely extracted after four extractions with petroleum. The extracts were dried (Na_2SO_4) and the solvent was evaporated to yield 3,4-dicyano-2,5-diphenylcyclopentadienone (12 mg.). The aqueous acetonitrile was then extracted with benzene and the extracts washed with water, dried over sodium sulphate, and the solvent evaporated. The residue was crystallised from cyclohexane to give triphenylphosphine oxide (5 mg.) identified by its m. p., mixed m. p. and infrared spectrum.

M. J. N. gratefully acknowledges a Union Carbide Research Studentship (1961—1963).

THE UNIVERSITY OF SOUTHAMPTON, SOUTHAMPTON. [*Received, March 26th,* 1964.]

[34] Blomquist and Winslow, *J. Org. Chem.*, 1945, **10**, 149.