

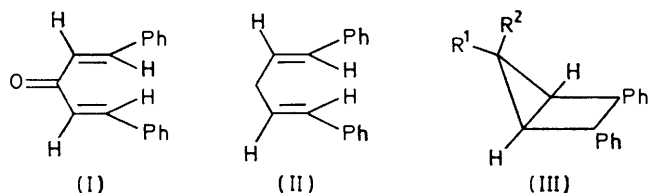
## Electrocyclic Reactions. Part X.<sup>1</sup> Photochemical Cyclisation of *trans,trans*-Dibenzylideneacetone

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Photolysis of *trans,trans*-dibenzylideneacetone (1,5-diphenylpenta-1,4-dien-3-one) in benzene solution at *ca.* 300 nm gave, as the major product by head-to-head staggered [ $\pi 2_s + \pi 2_s$ ] cycloaddition, the truxinic-type dimer (IV), whose structure has been established by both chemical and physical methods. As minor products, four stereoisomeric trimers have been isolated; these appear to be derivatives of tri(cyclobuta)[*a,d,g*]nonane-3,6,9-trione (XII), and their structures and modes of formation are discussed.

UNLIKE phorone, *trans,trans*-dibenzylideneacetone (I) is structurally incapable of undergoing deconjugation on irradiation, and *trans,trans*-dibenzylidenemethane (II) on irradiation gives *cis,anti*-, *trans*-, and *cis,syn*-2,3-diphenylbicyclo[2.1.0]pentanes [as (III); R<sup>1</sup> = R<sup>2</sup> = H].<sup>2</sup> In the hope of realising a unimolecular photocyclisation of *trans,trans*-dibenzylideneacetone to bicyclo[2.1.0]pentanones [as (III); R<sup>1</sup>R<sup>2</sup> = :O], we have re-examined its photochemical behaviour.

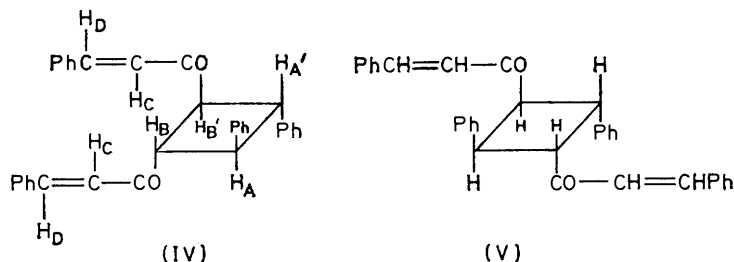


Ciamician and Silber<sup>3</sup> found that irradiation of yellow *trans,trans*-dibenzylideneacetone (I) with sunlight in

irradiation of the crystalline complex of *trans,trans*-dibenzylideneacetone with uranyl chloride and acetic acid, [(I)<sub>2</sub>·UO<sub>2</sub>Cl<sub>2</sub>·(AcOH)<sub>2</sub>],<sup>6</sup> and shown to have the truxillic-type structure (V) by oxidation with chromium trioxide-acetic acid to  $\alpha$ -truxillic acid<sup>6</sup> and by X-ray crystallography.<sup>7</sup> The same dimer was obtained<sup>6</sup> by irradiation of the crystalline complex of *trans,trans*-dibenzylideneacetone with tin(IV) chloride and benzene, [(I)<sub>2</sub>·SnCl<sub>4</sub>·C<sub>6</sub>H<sub>6</sub>].

Irradiation of *trans,trans*-dibenzylideneacetone (I) in benzene under nitrogen at *ca.* 300 nm at 25 °C gave a complex mixture, from which by successive column chromatography on silica impregnated with silver nitrate and on neutral aluminium oxide, followed by fractional crystallisation, five cyclic compounds were isolated; none was of the bicyclo[2.1.0]pentane type (III; R<sup>1</sup>R<sup>2</sup> = :O).

The principal photoproduct was the dimer (IV),  $\nu_{\max}$  1 675 (CO-C=C) and 1 600 cm<sup>-1</sup> (aromatic C=C); the



ethanol yielded a colourless dimer, m.p. *ca.* 135°, and Praetorius and Korn<sup>4</sup> observed that irradiation with sunlight in acetic acid in the presence of uranyl chloride gave another colourless dimer, m.p. 245°. The former dimer was obtained pure (m.p. 139–140°) by Pitts *et al.*<sup>5</sup> and shown to be of the truxinic type by oxidation with boiling aqueous potassium permanganate to give  $\delta$ -truxinic acid; we have now proved that this dimer has formula (IV) by oxidation with chromium trioxide-acetic acid to give  $\delta$ -truxinic acid and by physical means (see later). The latter dimer was also obtained by

<sup>1</sup>H n.m.r. spectrum (see Experimental section) showed a multiplet for twenty aromatic protons, two doublets each for two *trans*-vinyl protons (2H<sub>C</sub>, 2H<sub>D</sub>; *J* 16 Hz), and an AA'BB' system for four cyclobutane protons. The detail of the AA'BB' system is shown in Figure 1 together with the results of iterative computer analysis.<sup>8</sup> As has been pointed out,<sup>9,10</sup> vicinal coupling constants cannot be used to derive the stereochemistry of cyclobutane derivatives on account of the flexibility of the ring. However, the long-range coupling constants (<sup>4</sup>*J*)

<sup>1</sup> Part IX, C. W. Shoppee and Y.-S. Wang, *J.C.S. Perkin I*, 1976, 695.

<sup>2</sup> E. Block and H. W. Orf, *J. Amer. Chem. Soc.*, 1972, **94**, 8438; E. Block, H. W. Orf, and R. E. K. Winter, *Tetrahedron*, 1972, **28**, 4483.

<sup>3</sup> G. Ciamician and P. Silber, *Ber.*, 1909, **42**, 1386.

<sup>4</sup> P. Praetorius and F. Korn, *Ber.*, 1910, **43**, 2744.

<sup>5</sup> G. W. Rechtenwald, J. N. Pitts, jun., and R. L. Letsinger, *J. Amer. Chem. Soc.*, 1953, **75**, 3028.

<sup>6</sup> H. Stobbe and E. Färber, *Ber.*, 1925, **58**, 1548.

<sup>7</sup> N. W. Alcock, N. Herron, T. J. Kemp, and C. W. Shoppee, *J.C.S. Chem. Comm.*, 1975, 785.

<sup>8</sup> A. A. Bothner-By and S. M. Castellano in 'Computer Programs for Chemistry,' vol. 1, ed. D. F. Detar, Benjamin, New York, 1968.

<sup>9</sup> J. Laing, A. W. McCulloch, D. G. Smith, and A. G. McInnes, *Canad. J. Chem.*, 1971, **49**, 574.

<sup>10</sup> G. Montadu and S. Caccamese, *J. Org. Chem.*, 1973, **38**, 710.

appear<sup>11</sup> to be characteristic of stereochemistry, with  $^4J_{trans}$  negative (0.25–1.77 Hz) and  $^4J_{cis}$  positive (0.6–7.4 Hz); this criterion supports the all-*trans*-structure

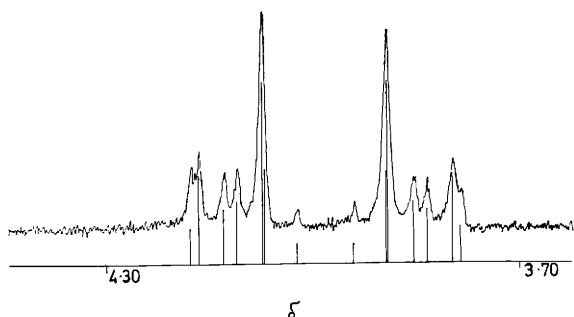


FIGURE 1 Portion of 100 MHz  $^1\text{H}$  n.m.r. spectrum of the dimer (IV) (9% w/v in  $\text{CDCl}_3$ ). The theoretical spectrum corresponds to the final output of the iterative portion of the LAOCN3 program<sup>8</sup> used to analyse this spectrum as an AA'BB' system and to the following parameters:  $\delta_A$  3.853,  $\delta_B$  4.113,  $J_{AA'}$  9.24,  $J_{AB}$  -0.06,  $J_{AB'}$  9.32,  $J_{BB'}$  9.24 Hz. The r.m.s. error is 0.060 Hz and the largest deviation for any single line is 0.096 Hz. Lines less than 0.2 Hz apart were considered unresolved and were assigned the same frequency

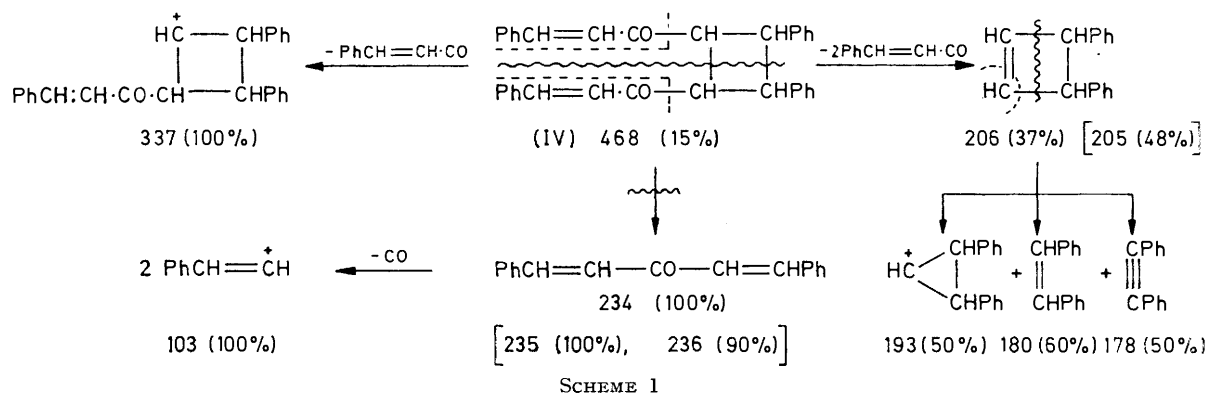
(IV), for although the very small value for  $^4J$  (-0.06 Hz; Figure 1) makes the significance of the determination of

acid in  $\text{CDCl}_3$  showed, besides resonances due to aromatic protons, an AA'BB' multiplet which was analysed by the iterative LAOCN3 procedure<sup>8</sup> to give the following parameters:  $\delta_A$  3.17,  $\delta_B$  3.41,  $J_{AA'}$  9.59,  $J_{AB'}$  9.51,  $J_{AB}$  0.01,  $J_{BB'}$  9.59. The r.m.s. error was 0.136 and the largest deviation for any single line was 0.275 Hz.

The extreme insolubility of  $\delta$ -truxinic acid in deuteriochloroform prevented us from obtaining a spectrum of high quality, and this is reflected in the relatively large errors and the probably spurious equality between two sets of coupling constants, but it is clear that the values of vicinal and long-range coupling constants for  $\delta$ -truxinic acid are almost identical to those for compound (IV) (Figure 1); hence no isomerisation by prototropy took place during the oxidation.<sup>5</sup>

The  $^{13}\text{C}$  n.m.r. spectrum (see Experimental section) is also consistent with structure (IV). The mass spectrum showed the parent peak at  $m/e$  468 and a consistent fragmentation pattern (Scheme 1). No trace was found of the truxillic-type dimer (V) of Praetorius and Korn<sup>4</sup> and Stobbe and Färber,<sup>6</sup> nor of the other five theoretically possible dimers (VI)–(X).

A concerted photochemical excited-state cycloaddition of an  $m$ -electron system ( $m = 2$ ) to an  $n$ -electron system



sign tenuous, nevertheless the small absolute value is consistent with the all-*trans*-structure (IV). The  $^1\text{H}$  n.m.r. spectrum of a sample of  $\delta$ -truxinic acid, m.p. 175°,

( $n = 2$ ) is symmetry-allowed for  $[\pi 2_s + \pi 2_s]$  and  $[\pi 2_a + \pi 2_a]$  processes,<sup>12</sup> with the stereochemical consequences set out in the Table. If the photochemical dimerisation

Photochemical process	Geometry of addenda	Stereochemical type of dimer
$[\pi 2_s + \pi 2_s]$	Head-to-head, staggered (A)	$\delta$ -Truxinic (IV)
	Head-to-tail, staggered	$\epsilon$ -Truxillic (VI)
$[\pi 2_a + \pi 2_a]$	Head-to-head, staggered	$\omega$ -Truxinic (VII)
	Head-to-tail, staggered	$\eta$ -Truxillic (VIII)
$[\pi 2_s + \pi 2_s]$	Head-to-head, eclipsed (B)	$\beta$ -Truxinic (IX)
	Head-to-tail, eclipsed	$\alpha$ -Truxillic (V)
$[\pi 2_a + \pi 2_a]$	Head-to-head, eclipsed	$\mu$ -Truxinic (X)
	Head-to-tail, eclipsed	$\alpha$ -Truxillic (V)

obtained by oxidation of compound (IV) with potassium permanganate<sup>5</sup> was also re-analysed because the reported<sup>10</sup> data for this compound were incomplete and refer to a solution in pyridine. The 90 MHz  $^1\text{H}$  n.m.r. spectrum for a ca. 0.5% solution of  $\delta$ -truxinic

of *trans,trans*-dibenzylideneacetone (I) in solution is a concerted reaction, then the dimer (IV) results from a head-to-head union of two staggered molecules (A) by a  $[\pi 2_s + \pi 2_s]$  process; formation of the dimer (V) requires head-to-tail union of two eclipsed molecules (B), so orientated in the uranyl chloride and tin(IV) chloride complexes, by either a  $[\pi 2_s + \pi 2_s]$  or a  $[\pi 2_a + \pi 2_a]$  process.

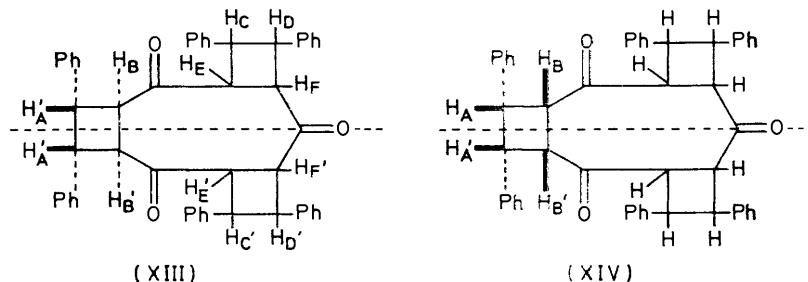
The four minor photoproducts isolated are colourless

<sup>11</sup> A. Gamba and R. Mondelli, *Tetrahedron Letters*, 1971, 2133.

<sup>12</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, p. 66.



the  $^1\text{H}$  n.m.r. spectrum of [(XIII) or (XIV)] in  $\text{C}_6\text{D}_6$  showed, besides the resonances due to 20 aromatic protons, six signals of equal intensity (2 H each) between  $\delta$  3 and 5 (Figure 2). Two of these (signals A and B in Figure 2) were recognized as a symmetrical AA'BB' pattern, thus leaving the remaining four signals (C—F)



as a doubled up unsymmetrical four-spin system. Analysis by use of the LAOCN3 method<sup>8</sup> gave the parameters

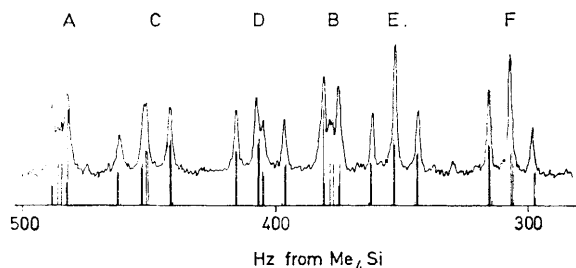


FIGURE 2 Portion of 100 MHz  $^1\text{H}$  n.m.r. spectrum of the trimer [(XIII) or (XIV)] (7% w/v in  $\text{C}_6\text{D}_6$ ). The theoretical spectrum under the A and B portion corresponds to the final output of the iterative portion of the LAOCN3 program<sup>8</sup> used to analyse these signals as an isolated AA'BB' system and to the following parameters:  $\delta_A$  3.779,  $\delta_B$  4.859,  $J_{AA'}$  5.89,  $J_{AB}$  0.21,  $J_{AB'}$  6.11,  $J_{BB'}$  5.79 Hz. The r.m.s. error is 0.064 Hz and the largest deviation of any single line is 0.16 Hz (one line; all other lines are within  $\pm 0.088$  Hz of the computed values). The theoretical spectrum under the remaining portions of the spectrum (C—F) corresponds to that generated by the non-iterative portion of LAOCN3<sup>8</sup> (the spectrum was too degenerate for meaningful iterative analysis) and to the following parameters:  $\delta_F$  3.063,  $\delta_E$  3.520,  $\delta_D$  4.054,  $\delta_C$  4.515,  $J_{FE}$  9.30,  $J_{FD}$  8.90,  $J_{FC}$  0.20,  $J_{ED}$  0.20,  $J_{EC}$  9.40,  $J_{DC}$  10.50 Hz

listed in Figure 2, which were assigned as shown in structure (XIII). The assignment of signals A, C, and D to benzylic protons is based on the presence of small broadening due to benzylic coupling,<sup>17</sup> which was confirmed by appropriate decoupling experiments. The assignment of the remaining signals follows from the magnitudes of coupling constants (Figure 2), but the interchange of  $\text{H}_C$  and  $\text{H}_D$  with a simultaneous interchange of  $\text{H}_E$  and  $\text{H}_F$  is equally probable. The analysis was confirmed by the more tightly coupled spectrum of a solution in  $\text{CDCl}_3$  (Figure 3). Coupling constants in both solvents are well within the limits of the range expected from changes in the average conformation.

The small magnitude of the long-range coupling constant in the unique cyclobutane ring ( $J_{AB'}$ ) suggests<sup>11</sup> a *trans*-relation between  $\text{H}_A$  and  $\text{H}_{B'}$ , thus making structure (XIII) more probable than (XIV). By the same

argument  $\text{H}_C$  and  $\text{H}_F$  are probably *trans*, but this information is insufficient for a complete description of the stereochemistry of [(XIII) or (XIV)].

The  $^1\text{H}$  n.m.r. data (see Experimental section) for another cyclic trimer (A), m.p. 265—268°,  $\nu_{\text{max}}$  1 695 and 1 600  $\text{cm}^{-1}$ , show that this molecule lacks symmetry, so

that the twelve hydrogen atoms in the three cyclobutane rings all possess different environments. Various structures of type (XII) complying with this requirement can be devised, but we have no evidence that this trimer possesses any one of them.

Similarly, the  $^1\text{H}$  n.m.r. data (see Experimental section) for another cyclic trimer (B), m.p. 294—295°,  $\nu_{\text{max}}$  1 705, 1 695, and 1 600  $\text{cm}^{-1}$ , highly insoluble in organic solvents, are consistent with a cyclic trimer of type (XII) but do not specify the stereochemistry.

A fourth cyclic trimer (C), m.p. 210—214°, of extreme insolubility and probably not obtained in pure homogeneous condition, gave a  $^1\text{H}$  n.m.r. spectrum similar to that of the cyclic trimer (B), m.p. 294—295°, and probably

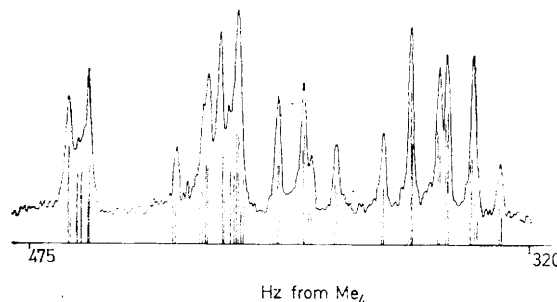


FIGURE 3 Portion of 100 MHz  $^1\text{H}$  n.m.r. spectrum of the trimer [(XIII) or (XIV)] (7% w/v in  $\text{CDCl}_3$ ). The theoretical spectrum corresponds to the final outputs of the iterative portions of the LAOCN3 program<sup>8</sup> which was used to analyse the twelve-spin system in two portions: (i) an AA'BB' system with the following parameters:  $\delta_A$  4.131,  $\delta_B$  4.602,  $J_{AA'}$  7.05,  $J_{AB'}$  -0.18,  $J_{AB}$  6.14,  $J_{BB'}$  6.56 Hz (r.m.s. error is 0.041; largest deviation of any single line 0.078 Hz); (ii) a four-spin system designated FEDC with the following parameters:  $\delta_F$  3.393,  $\delta_E$  3.565,  $\delta_D$  3.903,  $\delta_C$  4.199,  $J_{EF}$  9.07,  $J_{DF}$  8.26,  $J_{CF}$  -0.69,  $J_{DE}$  -0.65,  $J_{CE}$  9.26,  $J_{CD}$  10.66 Hz (r.m.s. error 0.098; largest deviation of any single line 0.282 Hz)

has a structure of type (XII), with  $\nu_{\text{max}}$  1 715, 1 695sh, and 1 600  $\text{cm}^{-1}$ .

The photochemical formation of the 'unique' cyclobutane ring of the trimer (XIII) requires, as the initial step (i) head-to-head [ $\pi 2_s + \pi 2_s$ ] cycloaddition of two

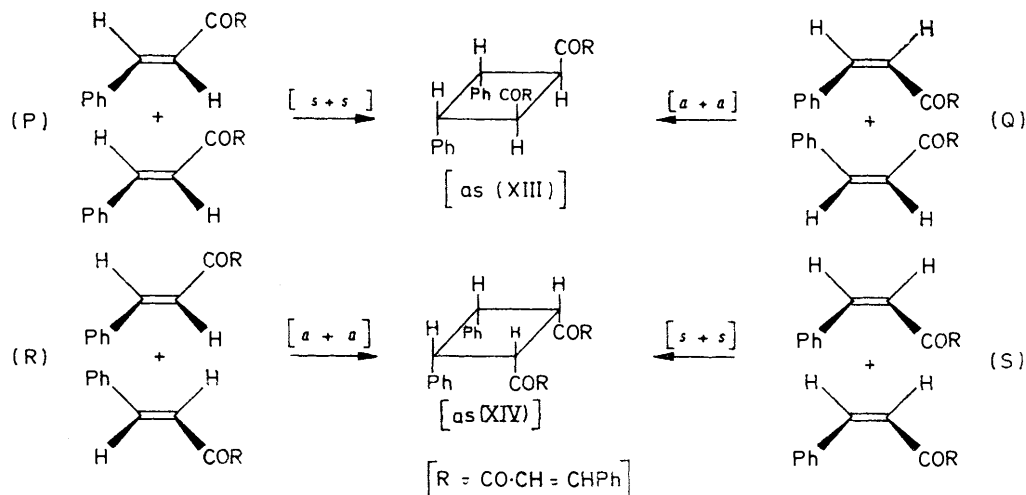
<sup>17</sup> S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

eclipsed molecules of *trans,trans*-dibenzylideneacetone (P), or (ii) photochemical conversion of *trans,trans*-dibenzylideneacetone into the *cis,trans*-isomer followed by head-to-head  $[\pi 2_a + \pi 2_a]$  cycloaddition of two staggered molecules (Q). Similarly, photochemical formation of the 'unique' cyclobutane ring of the trimer (XIV) requires, as the initial state, (i) head-to-head  $[\pi 2_a + \pi 2_a]$  cycloaddition of two staggered molecules of

truxinic-type photodimers [(VII), (IX), and (X)] which were not isolated but may have been formed and removed by photochemical cycloaddition as in Scheme 3.

## EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345. M.p.s were determined with a Thomas 40 hot-stage apparatus, and are corrected. I.r. spectra (solutions

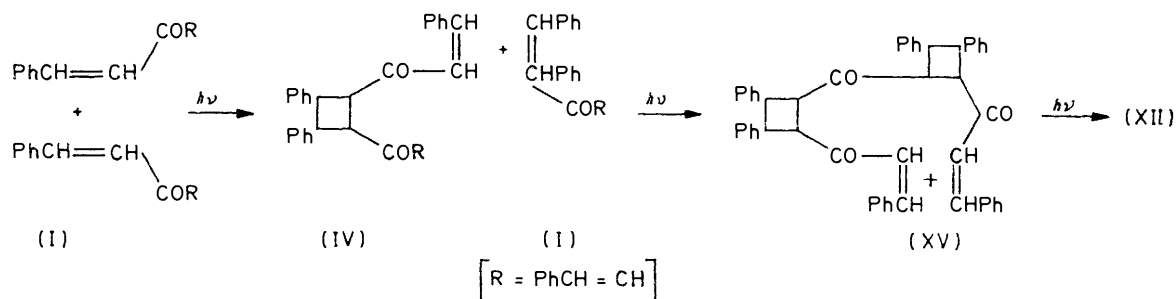


*trans,trans*-dibenzylideneacetone (R), or (ii) head-to-head  $[\pi 2_s + \pi 2_s]$  cycloaddition of two eclipsed molecules of photochemically generated *cis,trans*-dibenzylideneacetone (S).

A mechanism for the photochemical formation of cyclic trimers of type (XII) encounters serious difficulties on account of entropy factors. However, three consecutive photochemical  $[\pi 2_s + \pi 2_s]$  or  $[\pi 2_a + \pi 2_a]$  cycloadditions could lead to stereoisomeric structures of the required type [(I) + (I)  $\rightarrow$  (IV); (IV) + (I)  $\rightarrow$  (XV)  $\rightarrow$  (XII) (Scheme 3)]. Alternatively, more simply

in chloroform \* unless otherwise specified) were determined with Beckman IR 18 and IR 33 spectrometers. N.m.r. spectra were recorded with a Varian XL100-15 or XL100-12, or a Bruker HX 30 instrument for solutions in deuteriochloroform unless otherwise specified, with tetramethylsilane as internal reference. Mass spectra were measured with a Varian MAT 311 double-focus spectrometer coupled to a Varian SS102 16K computer. Column chromatography was performed with silica gel impregnated with silver nitrate prepared according to the procedure of Block and Orf,<sup>2</sup> or aluminium oxide (Woelm; neutral).

*trans,trans*-1,5-Diphenylpenta-1,4-dien-3-one (dibenzyl-



SCHEME 3

and therefore more probably, a bimolecular photochemical  $[\pi 2_s + \pi 2_s]$  or  $[\pi 2_a + \pi 2_a]$  cycloaddition of the photodimer (IV) could also lead to trimeric structures of the required type [(IV) + (I)  $\rightarrow$  (XV)  $\rightarrow$  (XII) (Scheme 3)]. In both sequences the photodimer (IV) could be replaced by one of the other three possible

ideneacetone (I) had m.p. 112–113° (from ethyl acetate),  $\nu_{\max}$  (CCl<sub>4</sub>) 1 675 cm<sup>-1</sup>,  $\delta$  7.42 (m, 10 ArH), 7.74 (d, H <sub>$\beta$</sub> , *J* 16 Hz), and 7.06 (d, H <sub>$\alpha$</sub> , *J* 16 Hz).

*Photolysis of trans,trans-Dibenzylideneacetone (I).*—(a) A saturated homogeneous solution of the ketone (I) (1.5 g) in hexane at ca. 35 °C (550 ml) was irradiated with a Hanovia high-pressure quartz mercury-vapour lamp (No. 6515-34) in a quartz apparatus in nitrogen at ca. 30 °C for 80 h. Filtration gave a pale yellow solid (0.5 g),  $\nu_{\max}$  (CCl<sub>4</sub>) 1 710,

\* Chloroform solutions give carbonyl bands ca. 15 cm<sup>-1</sup> to lower wavenumber than those observed in carbon tetrachloride.<sup>15</sup>

1 690, 1 655, and 1 600  $\text{cm}^{-1}$ , and evaporation of the filtrate gave a yellow semi-solid (1 g),  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1 695, 1 680sh, 1 660, and 1 610  $\text{cm}^{-1}$ . The hexane-soluble material (1 g) was chromatographed on silica gel-silver nitrate (36 g; column  $2.5 \times 19$  cm) in hexane. Elution with benzene-hexane (1:1; 600 ml) gave a viscous yellow oil (0.35 g); elution with benzene-hexane (4:1; 300 ml) and with benzene (1 l) gave yellow semisolids which were combined (0.35 g). The viscous yellow oil was rechromatographed on neutral aluminium oxide (15 g; column  $1.3 \times 19$  cm) in benzene. Elution with benzene (600 ml) gave a pale yellow solid (0.25 g), which by washing with ether gave colourless material (0.2 g), m.p. 137—139°; this by recrystallisation from methylene chloride-ether and then from ethyl acetate gave the dimer (IV) as prisms, m.p. 139—140° (lit.,<sup>5</sup> 139.5—140°),  $\nu_{\text{max}}$  1 675, 1 645, and 1 600  $\text{cm}^{-1}$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.32 (m, 20 ArH), 6.75 (d, 2 vinyl  $\text{H}_C$ ,  $J$  16 Hz), and 3.97 (m, 4 cyclobutane  $\text{H}_A\text{H}_A\text{H}_B\text{H}_B$ ) (irradiation at  $\delta$  7.3 caused the doublet centred at  $\delta$  6.75 to collapse to a singlet),  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 7.04 (m, 20 ArH), 6.72 (d, 2 vinyl  $\text{H}_C$ ,  $J$  16 Hz), and 7.48 (d, 2 vinyl  $\text{H}_D$ ,  $J$  16 Hz), (see also Figure 1),  $\delta_{\text{C}}$  153.4 [(C=C)—C=O], 150.0 and 142.9 (ArC), 139.1, 137.3, 136.8, 135.9, 135.7, and 133.7 (ArCH), 85.6 and 84.3 (CH=CH), and 57.4 and 56.2 (2 cyclobutane CH); for mass spectrum see text [Found (after drying at 20 °C and 0.01 mmHg): C, 87.0; H, 6.15; O, 6.9%;  $M^+$ , 468. Calc. for  $(\text{C}_{17}\text{H}_{14}\text{O})_2$ : C, 87.15; H, 6.0; O, 6.85%;  $M$ , 468]. The yellow semisolids were rechromatographed on neutral aluminium oxide (15 g; column  $1.3 \times 19$  cm) in benzene. Elution with benzene (150 ml) gave a colourless solid (70 mg); the ether-soluble portion yielded colourless needles (60 mg), m.p. 224—232°,  $\nu_{\text{max}}$  1 700 and 1 600  $\text{cm}^{-1}$ , of the trimer [(XIII) or (XIV)], and the ether-insoluble portion furnished the trimer (XIIB) (10 mg), m.p. 285—290°,  $\nu_{\text{max}}$  1 705, 1 695, and 1 600  $\text{cm}^{-1}$ . Further elution with benzene (150 ml) gave a pale yellow solid (50 mg), which was rubbed and washed with ether to afford the trimer (XIIA), m.p. 266—268°,  $\nu_{\text{max}}$  1 695 and 1 600  $\text{cm}^{-1}$ . Irradiation of (I) (5.7 g) suspended in hexane for 72 h gave similar results.

(b) The ketone (I) (20 g), dissolved in thiophen-free benzene (150 ml) and isopropanol (450 ml), was irradiated as in (a) but through a Pyrex filter ( $\lambda$  280—360 nm); separation of a colourless solid was observed within 15 h. After 93 h, the precipitate was filtered off and washed with ether to give the crude trimer (XIIC) (0.6 g), m.p. 198—202°,  $\nu_{\text{max}}$  1 715, 1 695sh, and 1 600  $\text{cm}^{-1}$ ,  $\nu_{\text{max}}$  (Nujol) 1 718 and 1 600  $\text{cm}^{-1}$  (see later). The filtrate was evaporated to give an orange semisolid (19 g), which was chromatographed on neutral aluminium oxide (450 g; column  $4.5 \times 47$  cm) in benzene. Elution with benzene ( $12 \times 500$  ml) gave 12 fractions; further elution with ether-benzene mixtures yielded gummy orange material (9.3 g), from which crystalline material was not obtained. Fraction 1 was very small; fraction 2 (0.7 g), by trituration with ether, gave a colourless solid (120 mg), which after washing with ether and two crystallisations from ethyl acetate furnished the trimer (XIIB) (30 mg), m.p. 294—295°,  $\nu_{\text{max}}$  1 705, 1 695, and 1 600  $\text{cm}^{-1}$ , insoluble in most solvents except ethyl acetate and chloroform,  $\delta_{\text{H}}$  7.2 (m, 30 ArH), 3.2—4.8 (m, 12 cyclobutane H, each with a different chemical shift), mass spectrum (see Scheme 2):  $m/e$  702 ( $M^+$ ), 572 and 571 ( $M^+ - \text{PhCH}=\text{CHCO}^+$ ), 522, 505, 469 and 468 (7 and 12%; also the dimer), 338 and 337 (14 and 49%), 235 (13%), 234 (38%; monomer), 233 (31%), 206 and 205 (22 and 13%), 193 (11%), 191 (7%), 186 and 185 (11 and 72%), 181, 180, 179, and 178 (7, 46, 23, and 8%),

167 (11%), 165 (11%), 157 (7%), 132 (15%), 131 (100%;  $\text{PhCH}=\text{CHCO}^+$ ), 129 and 128 (9 and 9%), 115 (7%), 105 (7%), 103 (28%;  $\text{PhCH}=\text{CH}^+$ ), 91 (36%;  $\text{PhCH}_2^+$ ), and 77 (7%;  $\text{Ph}^+$ ) [Found: C, 86.9; H, 6.05%;  $M^+$  702.277.  $(\text{C}_{17}\text{H}_{14}\text{O})_3$  requires C, 87.2; H, 6.0%;  $M$ , 702.3134]. Evaporation of the ethereal washings yielded colourless crystals (160 mg), m.p. 224—234°; this crude mixture of trimers (XIIA) and [(XIII) or (XIV)] was ground up and washed with ether. The ether-insoluble portion was twice recrystallised from ethyl acetate to give the trimer (XIIA) as needles, m.p. 263—265°,  $\nu_{\text{max}}$  1 695 and 1 600  $\text{cm}^{-1}$ ,  $\delta_{\text{H}}$  7.0br (m, 30 ArH) and 3.2—5.0 (m, 12 cyclobutane H, each with a different chemical shift),  $m/e$  702 ( $M^+$ ) 571 ( $M^+ - \text{PhCH}=\text{CHCO}^+$ ), 522, 505, 470, 469, and 468 (2, 5, and 6%; also the dimer), 365 (3%), 338 and 337 (5 and 16%), 322 (1%), 320 (1%), 247 and 246 (3 and 3%), 236 and 235 (2 and 15%), 234 (40%; monomer), 233 (25%), 207, 206, 205, 204, and 203 (3, 17, 8, 1, and 1%), 193 (10%), 186 and 185 (3 and 22%), 181, 180, 179, and 178 (4, 13, 22, and 5%), 167 (4%), 165 (6%), 157 (4%), 132 (9%), 131 (100%;  $\text{PhCH}=\text{CHCO}^+$ ), 129 and 128 (5 and 5%), 115 (4%), 105 (3%), 103 (20%), 91 (21%), and 77 (6%) [Found: C, 87.4; H, 6.25%;  $M^+$ , 702.  $(\text{C}_{17}\text{H}_{14}\text{O})_3$  requires C, 87.2; H, 6.0%;  $M$ , 702]. The ether-soluble portion was recrystallised from methylene chloride-pentane to give crystals (50 mg), m.p. 236—238°, which by recrystallisation from methylene chloride-ether afforded the trimer (XIII) or (XIV) (35 mg), m.p. 237—239°, mixed m.p. with trimer (XIIA) ca. 254°,  $\nu_{\text{max}}$  1 705sh, 1 695, and 1 600  $\text{cm}^{-1}$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.05br (m, 30 ArH) and 4.02 (m, 12 cyclobutane H),  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 7.05br (m, 30 ArH) and 3.96 (m, 12 cyclobutane H) [discussed in detail in the text],  $m/e$  702 ( $M^+$ ) 572 and 571 ( $M^+ - \text{PhCH}=\text{CHCO}^+$ ), 563, 531, 522, 505, 470, 469, and 468 (3, 6, and 7%; also the dimer), 365 (3%), 338 and 337 (6 and 20%), 322 (1%), 320 (1%), 275 (1%), 247 and 246 (2 and 3%), 236 and 235 (1 and 12%), 234 (40%; monomer), 233 (25%), 207, 206, 205, and 204 (2, 14, 7, and 1%), 193 (9%), 191 (3%), 186 and 185 (3 and 23%), 181, 180, 179, and 178 (3, 19, 10, and 4%), 167 (4%), 165 (6%), 157 and 156 (4 and 1%), 132 (10%), 131 (100%;  $\text{PhCH}=\text{CHCO}^+$ ), 129 and 128 (4 and 5%), 115 (4%), 105, 104, 103, and 102 (3, 2, 18, and 2%), 91 (18%), and 77 (4%) [Found: C, 87.5; H, 6.3%;  $M$ , 702.  $(\text{C}_{17}\text{H}_{14}\text{O})_3$  requires C, 87.2; H, 6.0%;  $M$ , 702]. Fraction 3 (0.86 g) yielded no crystalline material. Fractions 4—12 (total 2.45 g) all showed the same i.r. spectrum, with  $\nu_{\text{max}}$  1 675  $\text{cm}^{-1}$ , and the dimer (IV) could be obtained from each by washing with ether (total 1.65 g); m.p. and mixed m.p. 138—140°. The precipitate of the crude trimer (XIIC) (0.6 g), m.p. 198—202°,  $\nu_{\text{max}}$  1 715, 1 695sh, and 1 600  $\text{cm}^{-1}$ ,  $\nu_{\text{max}}$  (Nujol) 1 718 and 1 600  $\text{cm}^{-1}$ , was extremely insoluble in all organic solvents except chloroform and acetic acid; attempted crystallisation from acetic acid-benzene gave a little of the trimer (XIIB), m.p. 287—290°; the recovered trimer (XIIC), m.p. 210—214°, showed  $\delta_{\text{H}}$  (poor quality spectrum because of low solubility) 7.3 (m, 30 ArH) and 3.1—4.9 (m, 12 cyclobutane H, each with a different chemical shift),  $m/e$  702 ( $M^+$ ) 684, 595, 572, 571 ( $M^+ - \text{PhCH}=\text{CHCO}^+$ ), 556, 555, 554, 553, 536, 525, 522, 505, 469 and 468 (5 and 6%; also the dimer), 467 (3%), 465 (3%), 439 and 438 (2 and 5%), 338, 337, 336, 335, and 334 (4, 13, 6, 9, and 2%), 319 and 318 (4 and 7%), 286 (3%), 257 (2%), 236, 235, 234 (monomer), 233, 232, and 231 (10, 14, 6, 6, and 14%), 222 (5%), 217 (3%), 215 (3%), 206, 205, 204, 203, and 202 (3, 7, 7, 6, and 5%), 193, 192, and 191 (3, 3, and 4%), 181, 180, 179, and 178 (3, 16, 11, and 6%), 165 (5%), 145 (3%), 133, 132, and 131 (8, 11, and 100%;  $\text{PhCH}=\text{CHCO}^+$ ),

CHCO<sup>+</sup>), 129 and 128 (2 and 3%), 117 (3%), 115 (5%), 105, 104, and 103 (4, 7, and 24%; PhCH=CH<sup>+</sup>), 91 (20%; PhCH<sub>2</sub><sup>+</sup>), and 77 (8%; Ph<sup>+</sup>) [Found (after drying at 60 °C and 0.01 mmHg): C, 86.9; H, 6.2%; *M*<sup>+</sup>, 702. (C<sub>17</sub>H<sub>13</sub>O)<sub>3</sub> requires C, 87.2; H, 6.0%; *M*, 702]. Two more similar photolyses of (I) (20 and 35 g) gave further quantities of the dimer (IV) and the trimers (XIIA—C) and [(XIII) or (XIV)]; in the latter case the weight of aluminum oxide (1 kg) and the eluant volumes (3.5 l) were inconveniently large.

*Oxidation of the Dimer (IV) to δ-Truxinic Acid.*—The dimer (IV) (1.0 g) dissolved in acetic acid (20 ml) was treated with 2% chromium trioxide in acetic acid (50 ml) at 25 °C for 20 h. The usual work-up with chloroform and separation

<sup>18</sup> R. Stoermer and F. Bacher, *Ber.*, 1922, **55**, 1882.

<sup>19</sup> M. Freedman, Y. Mohadger, J. Rennert, S. Soloway, and I. Waltcher, *Org. Prepn. and Procedures*, 1969, **1**, 267.

into neutral and acidic fractions gave some unchanged dimer. The acidic fraction, a colourless solid (0.7 g), was boiled with water; the water-insoluble material (0.26 g), by recrystallisation from methanol, gave δ-truxinic acid, m.p. 173° (lit.,<sup>5</sup> 174—175°; lit.,<sup>18,19</sup> 175°); the water-soluble material was benzoic acid (0.28 g), m.p. 118°, mixed m.p. 118—121°, i.r. spectrum identical with that of an authentic sample.

One of us (C. W. S.) acknowledges the support of the Robert A. Welch Foundation, Houston, Texas, U.S.A., and another (Y-s. W.) the tenure of a Welch Postdoctoral Research Fellowship. This work was also supported by the Australian Research Grants Committee.

[6/246 Received, 5th February, 1976]