Vinylcyclopropane Photochemistry. Mechanistic and Exploratory Organic Photochemistry. LXI[1]

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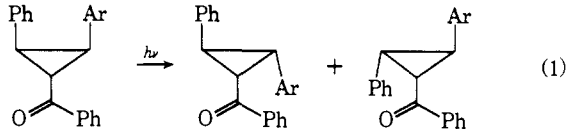
Abstract: *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane (**1**) was synthesized as a methylene analog of the *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane studied earlier. Direct irradiation of this material led to stereoisomerization to *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**2**) and also to a new photochemical transformation. The product of this new reaction has been identified as 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**). The reaction involves three-ring opening followed by a unique 1,3–2,6 cycloaddition. The cis–trans isomer (**2**) was shown not to be a necessary reaction intermediate giving rise to this new product; however, irradiation of the cis–trans isomer (**2**) did slowly give the same new product and the trans–trans isomer (**1**). Interestingly, benzophenone-sensitized irradiation of the *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane isomer (**1**) led to stereoisomerization but to no 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**), thus showing the methanonaphthalene (**3**) to be a singlet product. The direct irradiation quantum yields, both for stereoisomerization and the formation of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**), from **1** were 0.023. The quantum yield of stereoisomerization in the sensitized runs was 0.34. The reaction multiplicities and the molecular details of the mechanisms are discussed. Finally, the role of "free rotors" in dissipating triplet excitation is discussed.

Previously we have studied the photochemistry of cyclopropyl ketones.[1,2a,b] We found a very facile reversible ring opening with stereoisomerization which we ascribed to the n–π* excited state[1,2a,b] (note eq 1)



(1)

Ar = *p*-CN–Ph, *p*-MeO–Ph, or Ph

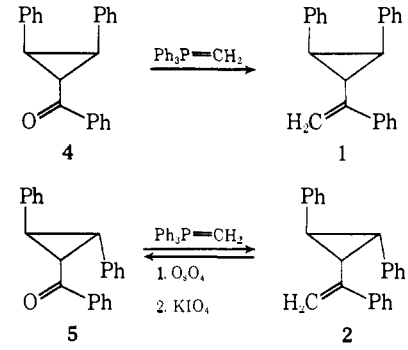
Thus it was of considerable interest to investigate the photochemistry of a methylene analog of one of these cyclopropyl ketones, since such a compound would have no p_y (or n) electrons to be excited and thus no n–π* excited states available.

Secondly, we have recently uncovered a remarkable "free rotor" effect in which triplet excited states dissipate energy by free rotation about π bonds, leading to inhibition of di-π-methane reactivity.[3] Many of these molecules have had methylene (*i.e.*, $=CH_2$) moieties as the free rotor. The present study of a methylene analog promised information on the generality of the free rotor effect.

Synthetic Aspects and Exploratory Photochemical Efforts. The *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**5**) required for this study was synthesized by a Wittig reaction of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**4**) with methylenetriphenylphosphorane (note Chart I).

Irradiation of *trans,trans*-2,3-diphenyl-1-(α-styryl)-cyclopropane (**1**) in cyclohexane with a 450-W Hanovia medium-pressure mercury lamp using a Corex filter and

Chart I. Synthesis of *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane (**1**) and Synthesis and Structure Proof of *cis,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane (**2**)



reversed-phase polystyrene bead liquid–liquid chromatography of the resulting mixture allowed the isolation of two new products, **2** and **3**. One of these products seemed likely to be the *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane stereoisomer (**2**) because of the similarity of its ir and nmr spectra with those of the starting trans–trans compound **1**. This assignment was confirmed by the degradation of **2** to the known[1] *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane (**5**) and by the synthesis of **2** from the same ketone (**5**) by means of the Wittig reaction. Note Chart I.

The second photoproduct **3** was shown to be isomeric with the starting material (**1**) by elemental analysis and molecular weight. It displayed no vinyl proton absorption in its nmr spectrum and only unconjugated benzenoid absorption in its uv spectrum. An analysis of its decoupled 100-MHz spectrum provided suggestive evidence that it was one stereoisomer of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**). Thus the nonaromatic proton absorptions were a 1 H multiplet at τ 6.53 (H-3), a 2 H doublet at τ 6.96 (H-4), and a 3 H complex multiplet extending from τ 8.10 to 8.76 (H-2, H-9). Irradiation of the multiplet at τ 6.53 (H-3) reduced the doublet at τ 6.96 (H-4) to a singlet and simplified the τ 8.10–8.20 portion of the τ 8.10–8.76 multiplet. Irradiation of the doublet at τ 6.96 (H-4) re-

* To whom correspondence should be addressed.

(1) For paper LX see H. E. Zimmerman and T. W. Flechtner, *J. Amer. Chem. Soc.*, **92**, 6931 (1970).

(2) (a) H. E. Zimmerman, S. S. Hixson, and E. F. McBride, *ibid.*, 92, 2000 (1970); (b) H. E. Zimmerman and C. M. Moore, *ibid.*, **92**, 2023 (1970).

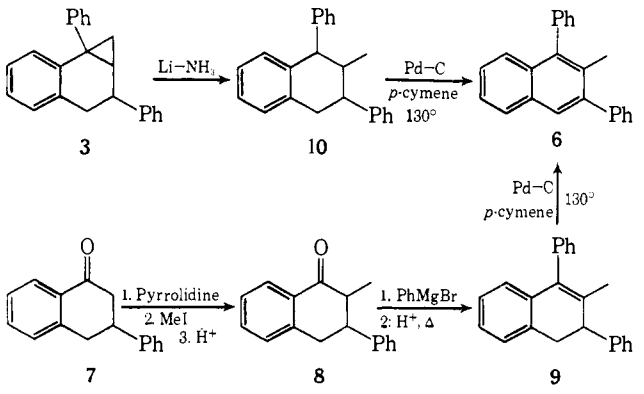
(3) See H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969), for leading references. A very early example is the barrelene to semibullvalene rearrangement.[4]

(4) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).

duced the multiplet at τ 6.53 (H-3) to a doublet. Irradiation of the τ 8.16 portion of the high-field multiplet reduced the multiplet at τ 6.53 (H-3) to a triplet. This nmr evidence implies the presence of the moiety $-CH_2-CHAr-CH-CH_2-$.

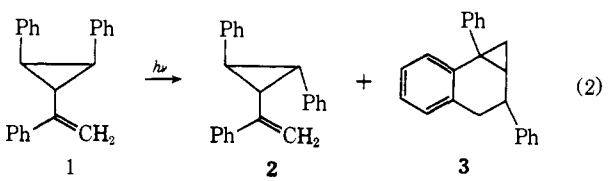
Degradation of this photoproduct (**3**) to 2-methyl-1,3-diphenylnaphthalene (**6**) and comparison with an independently synthesized sample (*vide infra*) confirmed the nmr interpretation. This degradation of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) involved reduction with lithium in liquid ammonia to 1,2,3,4-tetrahydro-2-methyl-1,3-diphenylnaphthalene (**10**) followed by oxidation with palladium on carbon to 2-methyl-1,3-diphenylnaphthalene (**6**). The structure proof is outlined in Chart II.

Chart II. Degradation of 1,2,3,4-Tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) to 2-Methyl-1,3-diphenylnaphthalene (**6**) and Synthesis of 2-Methyl-1,3-diphenylnaphthalene (**6**)



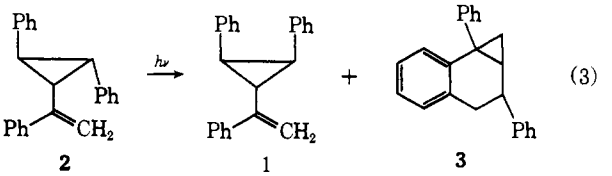
The 2-methyl-1,3-diphenylnaphthalene (**6**) needed for comparison with the material obtained from the degradation of the 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) was synthesized from the known[5] 3-phenyl-1-tetralone (**7**). Methylation of the pyrrolidine enamine of this compound and hydrolysis led to the formation of 2-methyl-3-phenyl-1-tetralone (**8**). Treatment of this ketone with phenylmagnesium bromide and dehydration yielded 3,4-dihydro-2-methyl-1,3-diphenylnaphthalene (**9**). The hydrocarbon **9** was easily oxidized with palladium on carbon to the desired 2-methyl-1,3-diphenylnaphthalene (**6**). This synthesis is described in Chart II.

Hence, the photochemical transformation of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**) may be depicted as in eq 2.



(2)

Irradiation of *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**2**) in cyclohexane with a 450-W Hanovia medium-pressure lamp using a Corex filter slowly produced the *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**) and 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**). The amount of cis–trans isomer (**2**) present always exceeded the amount of the trans–trans isomer (**1**), while the amount of the methanonaphthalene (**3**) increased with increasing conversion. This transformation is shown in eq 3.



(3)

Quantum Yields and Sensitization Experiments. Irradiation of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**) in cyclohexane at 290 nm in our "black box" apparatus[6] and ferrioxalate actinometry[7] revealed that the starting material (**1**) reacted with a quantum yield of $\Phi = 0.052$, *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**2**) appeared with a quantum yield of $\Phi = 0.023$, and 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) appeared with a quantum yield of $\Phi = 0.023$. Sensitization with benzophenone, with the sensitizer capturing more than 99% of the light, afforded a quantum yield of disappearance of the starting material (**1**) of $\Phi = 0.34$ and a quantum yield of appearance of *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**2**) of $\Phi = 0.34$. No 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) was produced in the sensitized irradiations. The direct and sensitized runs are summarized in Table I.

Table I. Direct and Sensitized Irradiations of *trans,trans*-2,3-Diphenyl-(α-styryl)cyclopropane (**1**)

Run[a,b]	Benzophenone concn, M[c,d]	Quantum yields 1	2	3	Conversion, %
1		0.058	0.029	0.023	53
2		0.052	0.023	0.023	23
3	0.031	0.340	0.340	0.000	45
4	0.023	0.345	0.345	0.000	25

[a] Cyclohexane solvent. [b] Direct irradiation runs made with filter transmitting 260–320 nm. [c] Sensitized irradiations made with filter transmitting 303–365 nm. [d] Sensitizer absorbing more than 99% of the light.

Quantitative studies were also carried out on *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**2**). With light input of the same order of magnitude as that employed in the quantum yield determination for the trans–trans isomer **1**, essentially no photoproduct could be detected in direct irradiation. This allowed an upper limit of $\Phi \leq 0.0067$ for the disappearance of **2** to be set.

Interpretative Discussion. The first point to be noted is that cis–trans isomerization occurs both in the direct and in the benzophenone-sensitized irradiations. Since, in the latter, the triplet excited state of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**) is known to be generated, it is certain that the triplet excited state of **1** is capable of undergoing the stereoisomerization process. The sensitized quantum yield of $\Phi = 0.34$ reveals this to be a relatively efficient process.[8] On direct ir-

(5) J. V. Braun and G. Manz, *Ann. Chem.*, **468**, 258 (1929).

(6) Described as apparatus B by H. E. Zimmerman, H. G. Dürr, R. S. Givens, and R. G. Lewis, *J. Amer. Chem. Soc.*, 89, 1863 (1967).

(7) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(8) As has been noted by us earlier,[9] reactions with quantum yields of at least *ca.* 0.05–0.10 or more tend to be synthetically useful and rela-

radiation the same cis–trans isomerization process was observed; however, the efficiency dropped to $\Phi = 0.023$. The excited state involved in this process may well be the triplet again; if so, this would mean that the intersystem crossing efficiency was only 7%. Alternatively, it is quite possible that the singlet is the species reacting on direct irradiation and that the singlet is less capable than the triplet of giving rise to stereoisomerization. The two rationales are operationally indistinguishable with the present information, but both lead to the same conclusion that ring opening of the singlet is an inefficient process.

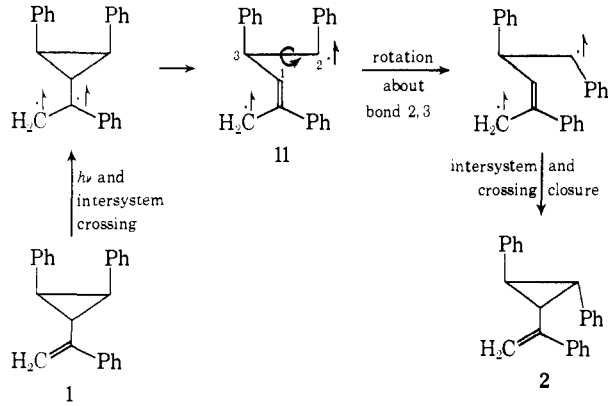
However, the occurrence of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) only in the direct irradiation provides unambiguous evidence that this compound arises from the singlet excited state; the triplet, independently generated by sensitization, is seen to give none of this product.

One might question whether the *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane stereoisomer (**2**) is an intermediate leading to the formation of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**). This is of special concern since a concerted mechanism (*vide infra*) may be written for the formation of the methanonaphthalene (**3**) from the cis–trans isomer (**2**) but not from the *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**). However, since the photolysis of the cis–trans isomer **2** proved to be inefficient overall (*i.e.*, $\Phi \leq 0.0067$, *vide supra*) when irradiated independently compared with the trans–trans reactant (**1**) ($\Phi_{tot} = 0.052$), it is clear that the trans–trans isomer (**1**) reacts directly and that the cis–trans isomer (**2**) is not an intermediate.

Since irradiation of the cis–trans isomer (**2**) did give some stereoisomerization and some methanonaphthalene (**3**) on very prolonged irradiation, it appears that similar reaction pathways are potentially available to this reactant.

Regarding the molecular details of the stereoisomerization, the most reasonable interpretation is that the triplet excited state of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**), represented by **11** in Chart III,

Chart III. Mechanism of Stereoisomerization of *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane (**1**) to *cis,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane (**2**)

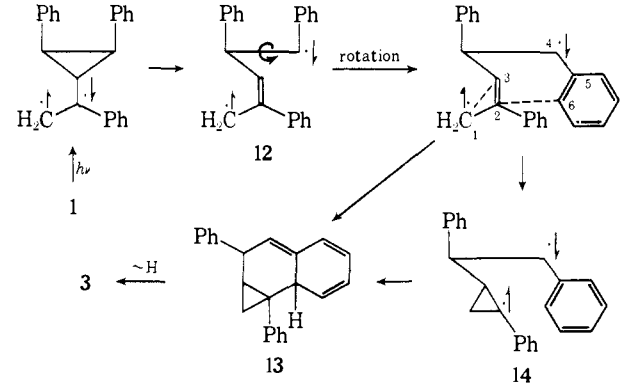


ring opens as depicted and then recloses after free rotation and intersystem crossing. The lower efficiency of stereoisomerization of the cis–trans isomer (**2**) seems most likely ascribable to the considerably lower relief of phenyl-phenyl van der Waals repulsive forces as the bond 1,2 opens. In the case of the trans–trans isomer (**1**), twisting about bond 2,3 may occur concertedly with fission of bond 1,2 and with considerable relief of steric repulsions.

The efficient ring opening of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**) is interesting from another viewpoint. It has been noted[3] that triplet excited states with free rotors present, such as $=CH_2$ groups, have available an energy dissipation process which often leads to lack of photochemical reactivity. In the molecule at hand such a potential free rotor is present but triplet reaction occurs anyway. This is understandable when one considers that the present reaction involves opening of a strained three-ring bond and should have very little, if any, activation energy. This is in contrast with the reactions where free rotors were effective in inhibiting reaction;[3,10a,b] in these cases bond formation, usually generating a strained three ring, was involved in the excited-state reaction process. Hence, in the present instance, the lack of inhibition by a potential free rotor seems due to energy dissipation merely being insufficiently rapid to compete with efficient and rapid ring opening of the triplet.

Finally, the unusual formation of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) can be pictured as involving the singlet diradical-like species **12** in Chart IV. This species cannot be the same as the one

Chart IV. Mechanism of Formation of 1,2,3,4-Tetrahydro-1,2-methano-1,3-diphenylnaphthalene (**3**) from *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane (**1**)



generated from the corresponding triplet (*i.e.*, **11** in Chart III), since the triplet gave none of this product. The reaction of the singlet diradical **12** to form the methanonapthhalene product **3** can be understood as a 1,3–2,6 cycloaddition as shown in this chart, and it is reasonable that the triplet will be less able to participate in such a process involving electron pairing in bond formation. Although the collapse of the singlet diradical **12** to the hydronaphthalene **13** can be drawn as a concerted reaction, it is possible that bond 1,3 formation may precede bond 2,6 formation, thus providing electron density at C-2 and allowing subsequent 2,6-bond formation. Such a two-step conversion has analogy in the photochemical reaction of allyl halides to form cyclopropyl halides.[11]

tively clean. The present reaction proved to proceed cleanly as might be expected from this rule of thumb.

(9) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970).

(10) (a) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969); (b) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **92**, 3474 (1970).

(11) S. J. Cristol and G. A. Lee, *ibid.*, **91**, 7554 (1969).

Another point meriting attention is the relative lack of singlet reactivity of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane (**1**) compared to the efficient triplet process. Thus we know that *ca.* 3.5%, but at most 7%, of the singlet intersystem crosses to the triplet (*vide supra*) and about 3% of the singlet excited state reacts to form the methanonaphthalene **3**, and therefore the balance of 90–94% of the singlet excited state decays to singlet ground state. In the case of the triplet, we know from the sensitized quantum yield of $\Phi = 0.34$ that only 66% of the excited states decay.

This dependence of per cent decay and per cent reaction on multiplicity seems unlikely to derive from the rate of ring opening which one might expect to be relatively independent of multiplicity. If anything, the triplet is of lower energy and both singlet and triplet ring open to species whose energies should differ less than the energies of the cyclic species due to the greater odd electron separation. Hence on purely energetic grounds the singlet should, if anything, ring open faster than the triplet.

A greater rate of decay for the singlet, however, can be understood. The stereoisomerization process demonstrates that ring opening is reversible, and the probability of the opened singlet biradical reclosing prior to conformational changes should be considerably greater than for the triplet in which spins are unpaired and concerted closure to form singlet ground state is limited in rate by the requirement for a multiplicity change.

Experimental Section[12]

Solvent Purification. Cyclohexane used in irradiations was purified in two different ways. In one method, the cyclohexane was stirred for 8 hr with 30% fuming sulfuric acid four times, washed with water, dried with sodium sulfate, and distilled from phosphorus pentoxide onto freshly pressed sodium wire. In the other method, the cyclohexane was passed through an alumina column impregnated with silver nitrate.[13]

trans,trans-**2,3-Diphenyl-1-benzoylcyclopropane.** This compound was prepared by the method of Zimmerman and Flechtner.[1]

trans,trans-**2,3-Diphenyl-1-(α-styryl)cyclopropane.** A slurry of 4.320 g (12.00 mmol) of methyltriphenylphosphonium bromide in 80.0 ml of dry ether was stirred under nitrogen for 20 min before 6.0 ml (*ca.* 12.0 mmol) of *n*-butyllithium in hexane was added. The yellow solution was stirred for 1 hr, then 2.436 g (8.16 mmol) of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane in 20.0 ml of 1:1 benzene–ether was added over 1 hr. The solution was heated at reflux for 30 min, cooled, and poured into 500.0 ml of hexane. The triphenylphosphine oxide was filtered from the solution and the solvent removed *in vacuo* to yield an oil. Crystallization of this oil from methanol yielded 1.850 g (76%) of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane, mp 94.5–95.5°. The spectral data were: ir ($CHCl_3$) 3.40, 6.18, 6.26, 6.71, 6.95, 11.20 μ; nmr ($CDCl_3$) τ 2.35–3.15 (m, 15 H, arom), 4.60, 4.80 (br s, 2 H, $=CH_2$), 7.38 (br s, 3 H, cyclopropyl); uv (cyclohexane) 234 nm max (ε 32,600), 238 nm max (ε 32,600), 243 nm max (ε 29,200), 248 nm max (ε 24,500), 254 nm max (ε 16,600), 261 nm max (ε 11,500), 287 nm max (ε 1900).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.40; H, 6.68.

Direct Irradiation of *trans,trans*-**2,3-Diphenyl-1-(α-styryl)cyclopropane.** A solution of 0.377 g (1.27 mmol) of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane in 250.0 ml of purified cyclohexane was irradiated for 3.5 hr under deoxygenated nitrogen[14] through a Corex filter ($\lambda \geq 260$ nm) with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Nmr spectra taken before and after photolysis showed that *ca.* 80% of the starting material had reacted. The photolysate was concentrated *in vacuo* and chromatographed on a 5 × 150 cm column of polystyrene–divinylbenzene copolymer (2% cross-linked)[15] which had been slurry packed in the upper phase from 1:1 methanol–cyclohexane; the lower phase from this system was the eluent. The eluent absorbance at 260 nm was scanned as 20.0-ml fractions were collected. Fractions 240–256 contained 52 mg of *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane; fractions 257–272 contained 53 mg of this cis–trans isomer and starting material; fractions 286–305 contained 194 mg of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene.

Characterization of 1,2,3,4-Tetrahydro-1,2-methano-1,3-diphenylnaphthalene. The methanonaphthalene was purified by recrystallization from hexane to give a mp of 103–105°. The spectral data were: ir ($CHCl_3$) 3.26, 3.30, 3.42, 6.25, 6.68, 6.90, 9.70, 13.35, 14.35 μ; nmr ($CDCl_3$) τ 2.55–3.10 (m, 14 H, arom), 6.45–6.62 (m, 1 H, benzylic), 7.00 (d, $J = 5.5$ Hz, 2 H, benzylic), 8.10–8.80 (m, 3 H, cyclopropyl); uv (cyclohexane) 318 nm max (ε 270), 292 nm max (ε 380), 278 nm max (ε 1460), 261 nm max (ε 2900), 254 nm max (ε 3150). Molecular weight calcd: 296. Found: 290 (vapor pressure osmometry, $CHCl_3$).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 92.94; H, 7.02.

The 100-MHz nmr spectrum displayed, in addition to the aromatic proton resonances, a multiplet centered at τ 6.53 (H-3), a doublet with further splitting at τ 6.96 (two at H-4), and a complex multiplet extending from τ 8.10 to 8.76 (H-2, two at H-9). In a double resonance experiment, irradiation (300 mV) at τ 6.53 reduced the doublet at τ 6.96 to a broad singlet and simplified the lower field portion of the τ 8.10–8.76 multiplet. Irradiation (315 mV) of the doublet at τ 6.96 reduced the multiplet at τ 6.53 to a doublet ($J = 3$ Hz). Irradiation of the lower field portion of the high field multiplet at τ 8.16 (400 mV) simplified the multiplet at τ 6.53 to a triplet ($J = 5$ Hz). The high-field portion of the τ 8.10–8.76 multiplet could not be clearly observed in the last experiment. No other changes were observed.

Oxidation of *cis,trans*-**2,3-Diphenyl-1-(α-styryl)cyclopropane.** Using the procedures of Baran[16] and Jackson,[17] a solution of 131 mg (0.44 mmol) of crude *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane, 258 mg (2.43 mmol) of sodium chlorate, and 17.3 mg (0.068 mmol) of osmium tetroxide in 10.0 ml of water and 40.0 ml of dioxane was stirred at room temperature for 20 hr. The solution was then diluted with 200.0 ml of ether, washed five times with water, and dried, and the solvent removed *in vacuo* to yield 122 mg of an oil. This crude material was then treated with 233 mg (1.01 mmol) of potassium metaperiodate in 60.0 ml of 38:12:10 ethanol–water–acetone for 20 hr with stirring at room temperature. This solution was diluted with ether, washed five times with water, and dried, and the solvent removed *in vacuo* to yield 140 mg of black oil. This oil was dissolved in 7% ether–hexane and filtered through activated silica gel to yield 48 mg (36% overall) of an oil which crystallized from acetone to give crystals of mp 154–156°, mmp with authentic *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane 153–156°.

cis,trans-**2,3-Diphenyl-1-benzoylcyclopropane.** This compound was synthesized by the method of Zimmerman and Flechtner;[1] mp 156–157°.

cis,trans-**2,3-Diphenyl-1-(α-styryl)cyclopropane.** The treatment of 1.371 g (4.60 mmol) of *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane with the Wittig reagent exactly as described in the synthesis of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane yielded 1.418 g of a red oil. This oil was passed through a silica gel–Norit column slurry packed and eluted with 5% ether–hexane. In 1 l. was obtained 1.278 g (94%) of a water-white oil which solidified on standing. Recrystallization from hexane yielded a white solid, mp 46.5–47°, mmp of this material with the stereoisomerization photoproduct 46–47°. Spectral data were: ir (NaCl) 3.30, 6.15, 6.24, 6.35, 6.68, 9.72, 11.18, 12.90, 13.22, 14.45 μ; nmr ($CDCl_3$) τ 2.50–3.10 (m, 15 H, arom), 4.60, 5.00 (br s, 2 H, $=CH_2$), 7.10–7.52 (m, 3 H, cyclopropyl); uv (cyclohexane) 220 nm max (ε 28,500), 226 nm max (ε 27,900), 292 nm max (ε 152).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.24; H, 6.67.

Reductive Cleavage of 1,2,3,4-Tetrahydro-1,2-methano-1,3-diphenylnaphthalene. To a solution of 381 mg (1.29 mmol) of the

(12) Melting points were obtained on a hot-stage apparatus calibrated with known compounds.

(13) E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).

(14) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(15) We thank the Dow Chemical Company, Midland, Mich., for a generous gift of this substance.

(16) J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).

(17) E. J. Jackson, *Org. React.*, **2**, 341 (1944).

photoproduct in 8.0 ml of ether and 50.0 ml of liquid ammonia was added 37 mg (5.3 mmol) of lithium metal. The red solution was stirred for 45 min, then 880 mg (16.5 mmol) of ammonium chloride was added, the ammonia allowed to evaporate, and the residue dissolved in ether and water. The upper phase was separated and dried, and the solvent removed *in vacuo* to yield a water-white oil. Crystallization of this material from hexane yielded 270 mg (70%) of 1,2,3,4-tetrahydro-2-methyl-1,3-diphenylnaphthalene, mp 130–131°. Spectral data were: ir (KBr) 3.27, 3.30, 3.38, 3.42, 6.25, 6.70, 6.88, 7.28, 8.67, 8.95, 9.24, 9.45, 9.71, 10.50, 11.08, 12.50, 13.18, 13.45, 14.32, 15.60 μ; nmr ($CDCl_3$) τ 2.50–3.42 (m, 14 H, arom), 6.26 (br d, J = 10 Hz, 1 H, benzhydryl), 6.80–8.15 (m, 4 H); uv (cyclohexane) 254 nm max (ϵ 725), 259 nm max (ϵ 850), 264 nm max (ϵ 750), 274 nm max (ϵ 400), 292 nm max (ϵ 30).

Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.68; H, 7.59.

Oxidation of 1,2,3,4-Tetrahydro-2-methyl-1,3-diphenylnaphthalene. This reaction was done by the method of Linstead and Thomas.[18] A slurry of 475 mg (1.59 mmol) of 1,2,3,4-tetrahydro-2-methyl-1,3-diphenylnaphthalene and 1.050 g of 10% palladium on carbon in 40.0 ml of distilled *p*-cymene was heated at reflux for 7 hr while carbon dioxide was bubbled through the solution. After the solution had been cooled and filtered, the *p*-cymene was removed *in vacuo* to yield 334 mg of a yellow oil. Preparative thin-layer chromatography (silica gel G (254), dried at 90° overnight) of 186 mg of this oil and isolation of the second band yielded 53 mg (20%) of a white solid, mp 118–119°. The ir and nmr spectra of this material were directly superimposable upon those of synthetic 2-methyl-1,3-diphenylnaphthalene. A mixture melting point of this material with the synthetic naphthalene was undepressed.

4-Hydroxy-3,4-diphenyl-2-cyclopentenone. This compound was prepared by the method of Japp and Lander.[19] From 500 g (2.37 mol) of benzil was obtained 271.3 g (49%) of 4-hydroxy-3,4-diphenyl-2-cyclopentenone, mp 150–151° (lit.[20] 149°).

Spectral data were: ir ($CHCl_3$) 2.76, 2.94, 5.95, 6.30, 6.39, 6.70, 6.91, 7.56, 9.52, 10.30, 11.65, 14.58, 15.71 μ; nmr ($CDCl_3$) τ 2.35–3.05 (m, 10 H, arom), 3.40 (s, 1 H, vinyl), 6.50 (br s, 1 H, OH), 7.10 (d, J = 1.5 Hz, 2 H, CH_2).

3-Benzoyl-3-phenylpropenoic Acid. Using the procedure of Japp and Lander,[19] 10.0 g (4.30 mmol) of 4-hydroxy-3,4-diphenyl-2-cyclopentenone was converted to 3.780 g (35%) of 3-benzoyl-3-phenylpropenoic acid, mp 143–145° (lit.[19] 142°). Spectral data were: ir (KBr) 3.12, 5.81, 6.18, 6.91, 7.87, 8.26, 8.62, 9.33, 9.80, 10.48, 11.65, 12.95, 13.70, 14.50, and 15.50 μ; nmr ($CDCl_3$) τ 1.50 (br s, 1 H, COOH), 2.30–3.00 (m, 10 H, arom), 3.20 (br s, 1 H, vinyl).

3,4-Diphenylbutanoic Acid. Using the procedure of Japp and Lander,[19] 14.45 g (5.57 mmol) of 3-benzoyl-3-phenylpropenoic acid was converted to 6.477 g (47%) of 3,4-diphenylbutanoic acid, mp 97–98° (lit.[19] 96–97°). The spectral data were: ir ($CHCl_3$) 3.25, 3.42, 5.86, 6.22, 6.68, 6.88, 7.09, 7.72, 8.71, 9.30, 9.70, 14.40 μ; nmr ($CDCl_3$) τ −1.62 (s, 1 H, COOH), 2.38–3.14 (m, 10 H, arom), 6.61 (pentuplet, 1 H, benzylic), 7.22 (d, J = 16 Hz, 2 H, benzylic), 7.33 (d, J = 13 Hz, 2 H, CH_2).

3-Phenyl-1-tetralone. Using the procedure of Newman,[21] 11.45 g (4.78 mmol) of 3,4-diphenylbutanoic acid was treated with 20.8 g (10.0 mmol) of phosphorus pentachloride and then 8.00 g (6.00 mmol) of aluminum trichloride in 100.0 ml of dry benzene to yield 8.612 g of red oil. This oil was chromatographed on a 4.5 × 30 cm silica gel column slurry packed in 2% ether–hexane. Elution was with 2 l. of 4% ether–hexane, 4 l. of 10%, and 5 l. of 20%; 1-l. fractions were collected. Fractions 1 and 2 contained 239 mg of an unidentified solid, mp 118–120°; 3–4 contained 1.038 g of an unidentified oil; 5 and 6, 2.199 g of 3-phenyl-1-tetralone; 8–12, 3.193 g of an oil. Fractions 8–12 were rechromatographed on a similar column slurry packed in 5% ether–hexane. Elution was with 6 l. of 5% ether–hexane and 2 l. of 10%; 1-l. fractions were collected. Fractions 5–8 contained 1.888 g of 3-phenyl-1-tetralone.

The product, 4.087 g (39%), had a mp of 65–66° (lit.[22] 65°). Spectral data were: ir ($CHCl_3$) 3.45, 5.95, 6.23, 6.72, 6.87, 7.80, 8.97, 9.86, 14.40 μ; nmr ($CDCl_3$) τ 1.74–2.00 (m, 1 H, *o*-benzoyl), 2.41–2.85 (m, 8 H, arom), 6.67–7.30 (m, 5 H).

2-Methyl-3-phenyl-1-tetralone. The 3-phenyl-1-tetralone was methylated by the method of Stork.[23] The pyrrolidine enamine was prepared by the treatment of 4.087 g (1.84 mmol) of 3-phenyl-1-tetralone with 12.0 ml (16.8 mmol) of pyrrolidine and 3.653 g (19.2 mmol) of *p*-toluenesulfonic acid hydrate in 65.0 ml of benzene at reflux for 46 hr. Water was removed by the use of a Dean–Stark trap. The benzene solution was then washed with 5% potassium hydroxide and water and dried, and the solvent removed *in vacuo* to yield 4.537 g of crude enamine. The spectral data were: nmr ($CDCl_3$) τ 2.43–3.33 (m, 9 H, arom), 4.92 (d, J = 6 Hz, 1 H, vinyl), 6.17–7.67 (m, 7 H, benzylic and α-pyrrolidino-CH_2), 8.00–8.67 (m, 4 H, β-pyrrolidino-CH_2).

A solution of this material and 15.0 ml (24.4 mmol) of methyl iodide in 40.0 ml of *p*-dioxane was heated at reflux for 4 hr. Then 1.00 ml of acetic acid and 10.0 ml of water were added and the reflux was continued for 4 hr. Benzene was added to the cooled solution, it was washed twice with water and dried, and the solvent removed *in vacuo* to yield 3.382 g of oil. This oil was chromatographed on a 6 × 102 cm silica gel column slurry packed in 5% ether–hexane. Elution was with 6 l. of 5% ether–hexane, 4 l. of 10%, and 6 l. of 20%; 2-l. fractions were collected. Fractions 4 and 5 contained 1.858 g of 2-methyl-3-phenyl-1-tetralone and fractions 6–8 contained 1.139 g of 3-phenyl-1-tetralone.

After recrystallization from ether–hexane, 1.658 g (38%) of 2-methyl-3-phenyl-1-tetralone, mp 60–61°, was obtained. The spectral data were: ir (NaCl) 3.24, 3.29, 3.35, 3.40, 3.46, 5.96, 6.24, 6.71, 6.90, 7.30, 7.64, 7.94, 8.23, 8.68, 8.93, 10.38, 12.90, 13.18, 13.52, 14.31, 14.92, 15.70 μ; nmr ($CDCl_3$) τ 1.80–2.00 (m, 1 H, *o*-benzoyl), 2.44–2.92 (m, 8 H, arom), 6.73–7.33 (m, 4 H), 8.93 (d, J = 7 Hz, methyl); uv (ethanol) 291 nm max (ϵ 3580), 248 nm max (ϵ 11,300).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.45; H, 6.86.

3,4-Dihydro-2-methyl-1,3-diphenylnaphthalene. This reaction was done by the method of Crawfold.[24] To the ethereal phenylmagnesium bromide solution prepared from 3.14 g (20.0 mmol) of redistilled bromobenzene and 506 mg (21.0 mg-atoms) of magnesium in 30.0 ml of ether was added dropwise over 30 min 1.341 g (5.68 mmol) of 2-methyl-3-phenyltetralone in 20.0 ml of ether. This solution was heated at reflux for 5 hr after which 26.0 ml of 2% hydrochloric acid was added, the two-phase system separated, and the ethereal phase washed with water and dried. Removal of the solvent *in vacuo* yielded 1.500 g of an oil.

This oil was dissolved in 100.0 ml of methanol, 3.0 ml of concentrated hydrochloric acid added, and the solution refluxed for 10 min. The solvent was removed *in vacuo* and the resulting brown semisolid was chromatographed on a 6 × 31 cm silica gel column slurry packed in 2% ether–hexane. Elution was with 1 l. of 2% ether–hexane, 2 l. of 5%, and 2 l. of 20%; 1-l. fractions were collected. Fraction 2 contained 765 mg of 2-methyl-3-phenyl-1-tetralone and 3,4-dihydro-2-methyl-1,3-diphenylnaphthalene (1:1); fraction 3 contained 311 mg of the same mixture; and fractions 4 and 5 contained 111 mg of an unidentified oil.

Fraction 3 was chromatographed on a 4 × 30 cm silica gel column slurry packed in 20% benzene–hexane. Elution was with 4 l. of 20% benzene–hexane and 2 l. of pure benzene; 1-l. fractions were collected. Fractions 1 and 2 contained 419 mg of 3,4-dihydro-2-methyl-1,3-diphenylnaphthalene (37%); fractions 5 and 6 contained 335 mg of starting material. The 3,4-dihydro-2-methyl-1,3-diphenylnaphthalene was a water-white oil. Spectral data were: ir (NaCl) 3.20, 3.23, 3.38, 6.24, 6.70, 6.89, 9.32, 9.70, 13.20, 13.71, 14.28, 14.76, 15.12 μ; nmr ($CDCl_3$) τ 2.50–3.45 (m, 14 H, arom), 6.22–7.40 (m, 3 H, benzylic), 8.40 (s, 3 H, methyl); uv (ethanol) 267 nm max (ϵ 10,000), 273 nm max (ϵ 10,300).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.26; H, 6.91.

2-Methyl-1,3-diphenylnaphthalene. Using the procedure of Linstead and Thomas,[18] 155 mg (0.523 mmol) of the 3,4-dihydro-2-methyl-1,3-diphenylnaphthalene in 40.0 ml of distilled *p*-cymene with 181 mg of 10% palladium on carbon was heated at reflux for 2 hr with carbon dioxide bubbling through the solution. Removal of the solvent *in vacuo* after the catalyst had been filtered from the cooled solution afforded 139 mg (90%) of an oil which crystallized upon standing. Recrystallization from hexane afforded 2-methyl-1,3-diphenylnaphthalene, mp 117–118°.

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(20) F. R. Japp and A. Miller, *ibid.*, 21 (1885).
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(22) F. S. Spring, *J. Chem. Soc.*, 1332 (1934).
(23) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
(24) H. M. Crawford, *ibid.*, 61, 608 (1939).

The spectral data were: ir ($CHCl_3$) 3.22, 3.30, 3.40, 6.27, 6.72, 6.95, 7.27, 9.35, 11.22, 14.32, 15.20 μ; nmr ($CDCl_3$) τ 2.03–2.88 (m, 15 H, arom), 7.90 (s, 3 H, methyl); uv (ethanol) 234 nm max (ϵ 52,000), 286 nm max (ϵ 8000).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.96; H, 6.19.

Direct Irradiation of *cis,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane. A solution of 170 mg (0.574 mmol) of *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane in 250.0 ml of purified cyclohexane was irradiated for 2.5 hr under deoxygenated nitrogen[14] through a Corex filter ($\lambda \geq 260$ nm) with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Nmr spectra taken before and after irradiation showed that 50% of the starting material had disappeared and that roughly equal amounts of the *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane and 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene had appeared.

Photolysis Apparatus for Quantum Yields. The "black box" irradiation apparatus[5] used a General Electric AH6 mercury arc in a deep parabolic reflector. The 12-cm beam was filtered through a three-compartment water-cooled solution filter (*vide infra*). The sample cell was maintained at 25 ± 0.2° and deoxygenated nitrogen[14] was bubbled through the photolysis solution.

Filter Solutions. Two filter solution systems were used. Filter I: cell 1, 1 *M* nickelous sulfate in 10% sulfuric acid; cell 2, 2 *M* cobalt sulfate in 10% sulfuric acid; cell 3, 0.1 m*M* bismuth trichloride in 10% hydrochloric acid. Transmission was 0% below 260 nm, between 320 and 335 nm, and above 355 nm. It was 2% at 342 nm (max) and 10% at 290 nm (max). Filter II: cell 1, 0.58 *M* nickelous sulfate in 10% sulfuric acid; cell 2, 1.29 *M* cobalt sulfate in 10% sulfuric acid; cell 3, 54.0 m*M* stannous chloride in 10% hydrochloric acid. Transmission was 0% below 310 nm and above 370 nm and 43% at 338 nm (max).[6]

Actinometry. Incident light was measured by potassium ferrioxalate actinometry[7] before and after each sample run and was monitored for transmission through the sample cell by an actinometer cell behind the sample cell during the sample run. The quantum yield for ferric ion reduction was taken to be 1.25 for the wavelength used.

Quantum Yield Irradiations. The general procedure was as follows. A sample of *trans,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane was dissolved in purified cyclohexane and freshly recrystallized benzophenone (if any) up to a total volume of 730.0 ml. The actinometry and sample irradiation were then carried out and the solvent removed *in vacuo*. The sample was then analyzed by nmr; 10.0 mg of *p*-dioxane served as an internal standard. Very careful electronic integration of the vinyl proton portion of the nmr afforded an accurate determination of the absolute amounts of the *trans,trans*- and *cis,trans*-2,3-diphenyl-1-(α-styryl)cyclopropane stereoisomers present. The entire sample was then subjected to reversed-phase polystyrene bead liquid–liquid chromatography (*vide supra*). The two cyclopropane isomers were collected as one peak and again subjected to nmr analysis. Collection and analysis of separate fractions allowed nearly complete separation; however, the analytical results proved more simply obtained by direct assay of the one combined chromatographic peak. The 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene photoproduct was isolated from the chromatogram and assayed by weight. Its mass accounted for the remainder of the photolysis sample. The nmr analysis was calibrated with known mixtures of the cyclopropane isomers.

Specific data for individual irradiations are given below as follows: weight of hydrocarbon and additive (if any), filter system used, amount of light absorbed, quantum yield for the appearance of the cyclopropyl stereoisomer, mass of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene isolated, quantum yield for the appearance of the methanonaphthalene, total conversion of starting material.

Run QY-1. *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane, 293 mg, no benzophenone, filter I, 9.13 mEinsteins, 0.058, 0.029, 62.6 mg of methanonaphthalene, 0.023, 53%.

Run QY-2. *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane, 302 mg, no benzophenone, filter I, 3.72 mEinsteins, 0.052, 0.023, 25.0 mg of methanonaphthalene, 0.023, 23%.

Run QY-3. *cis,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane, 298 mg, no benzophenone, filter I, 4.50 mEinsteins, less than 0.0067, less than 0.0067, no detectible methanonaphthalene, less than 3%.

Run QY-S1. *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane, 295 mg, 4.069 g of benzophenone, filter II, 1.33 mEinsteins, 0.340, 0.340, no methanonaphthalene, 0, 45%.

Run QY-S2. *trans,trans*-2,3-Diphenyl-1-(α-styryl)cyclopropane, 299 mg, 2.989 g of benzophenone, filter II, 0.710 mEinstein, 0.345, 0.345, no methanonaphthalene, 0, 25%.

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The Structure of Glyoxal in Water

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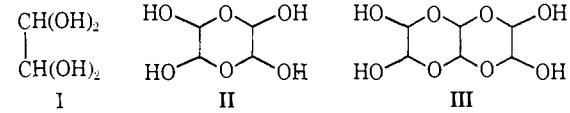
Abstract: The proton magnetic resonance spectrum of aqueous glyoxal is interpreted to show that the principal species present at concentrations below 40% are the hydrated monomer and two dimers whose structures contain a five-membered dioxolane ring.

Glyoxal is generally believed to exist in the form of hydrated oligomers in aqueous solutions, but neither the extent of association nor the structures it produces are known with any certainty. The lowest order oligomers have been assumed, without much evidence, to have the structures I–III.[1]



I II III

The proton magnetic resonance spectrum of aqueous glyoxal (Figure 1), which is partially obscured by the water line unless the temperature is elevated, is quite complicated, giving as many as 12 resolvable lines at 60 MHz and up to 16 in sufficiently strong magnetic fields. None of its lines occurs in the region characteristic of aldehyde protons, and none is affected by isotopic exchange in heavy water. The complex spectrum

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