Anal. Calcd for $C_3H_5FN_2O_5$ (168.09): C, 21.43; H, 3.00; F, 11.30; N, 16.67. Found: C, 21.1; H, 3.1; F, 11.4; N, 16.4.

2-Fluoro-2,2-dinitro-1-phenylethanol (II).—To 50 ml of a $NaOH-KH_2PO_4$ buffer of pH 7[10] was added 2.1 g of freshly distilled benzaldehyde; the mixture was stirred and cooled in an ice bath, 5 g of fluorodinitromethane was added, and stirring and cooling were continued for 1 hr. Methylene chloride, 25 ml, was then added to the mixture, the phases were separated, and the organic phase was dried (MgSO₄) and freed from solvent *in vacuo* at ambient temperature. The residual pale yellow oil was shown by nmr (Table I) to be mainly II. However, small amounts (<10%) of benzaldehyde and fluorodinitromethane were also detected in the nmr spectrum and a carbonyl band (benzaldehyde) was present in the ir spectrum.

1,4-Difluoro-1,1,4,4-tetranitrobutane-2,3-diol (III).—Fifty milliliters of a $NaOH-KH_2PO_4$ buffer solution of pH 7[10] was cooled in an ice bath, and 17.7 g of a 30% aqueous solution of glyoxal was added with stirring, followed by 25 g of fluorodinitromethane. The mixture was stirred for 0.5 hr at 0–5°, then acidified with dilute sulfuric acid, saturated with NaCl, and extracted with four 25-ml portions of ether. The combined extracts were dried (MgSO₄) and the solvent was removed *in vacuo*. The residue was triturated with a small amount of methylene chloride; the mixture was chilled in the freezer and filtered to give 21.5 g of crude III, mp 175–180°. One recrystallization from methylene chloride or benzene gave 20.6 g (67%), mp 178–180° dec; ε in 0.01 N aqueous KOH (382 nm) 38,200.

Anal. Calcd for $C_4H_4F_2N_4O_{10}$ (306.10): C, 15.69; H, 1.31; F, 12.42; N, 18.31. Found: C, 15.8; H, 1.6; F, 12.1; N, 18.1

1,5-Difluoro-1,1,5,5-tetranitropentane-2,4-diol (IV).—A solution of 5.5 g of sodium malonaldehyde[11] in dilute sodium hydroxide (60 ml of water + 1.5 ml of 2 N sodium hydroxide) was cooled to about 0° in an ice–salt bath. With stirring and continued cooling, 15.5 g of fluorodinitromethane was added, most of which dissolved rapidly. A saturated solution of potassium dihydrogen phosphate was then added dropwise until the mixture had a pH of about 7. After 0.5 hr of stirring at 0° the solution was acidified with dilute sulfuric acid and extracted with four 50-ml portions of methylene chloride. The extract was dried (MgSO₄) and the solvent removed *in vacuo*. The remaining oil was held under a vacuum of 1 mm for several hours until it had solidified completely. The product was broken up under and digested thoroughly with 25 ml of chloroform and filtered, and the solid was washed with 5 ml of chloroform; 10.8 g of diol, mp 74–77°, was thus obtained. On chilling the filtrate another 0.6 g, mp 70–83°, was obtained; total crude yield, 57%. This material may be purified by vacuum sublimation (0.2 mm, 70°), followed by recrystallization from chloroform, mp 80–84° (mixture of diastereomers), ε in 0.01 N aqueous KOH (382 nm) 38,800.

Anal. Calcd for $C_5H_6F_2N_4O_{10}$: C, 18.76; H, 1.89; F, 11.87; N, 17.50; mol wt, 320.13. Found: C, 19.0; H, 2.0; F, 11.8; N, 17.6; mol wt (benzene), 312, 313.

1,6-Difluoro-1,1,6,6-tetranitrohexane-2,5-diol (V).—A mixture of 12 g of 2,5-dimethoxytetrahydrofuran, 80 ml of water, and 2 ml of 2 N sulfuric acid was stirred at 55° for 1 hr. The solution was then cooled below 5°, 20 g of fluorodinitromethane was added with stirring, and the mixture was brought to a pH of 7 with saturated sodium bicarbonate solution. Stirring and cooling in an ice bath was continued for 0.5 hr, after which time the reaction mixture was acidified with dilute sulfuric acid and extracted with four 30-ml portions of methylene chloride. The extract was dried, the solvent removed *in vacuo* (1 mm), and the semisolid residue triturated with 30 ml of chloroform. After standing in the refrigerator, 20.2 g of crude diol, mp 70–85°, was collected. After two recrystallizations from chloroform the material (15–17 g, 55–63%) melted at 80–100° (mixture of diastereomers), ε in 0.01 N aqueous KOH (328 nm) 38,000.

Anal. Calcd for $C_6H_8F_2N_4O_{10}$: C, 21.57; H, 2.41; F, 11.37; N, 16.77; mol wt, 345.15. Found: C, 21.8; H, 2.6; F, 10.7; N, 16.7; mol wt (chloroform), 335, 336.

Repeated fractional recrystallization of the mixture of diastereomers from chloroform gave two sharp melting fractions

which were readily distinguishable by their ir spectra (see above): Va, mp 86–87°; and Vb, mp 90–92°, 102–104° (isomorphs).

1,7-Difluoro-1,1,7,7-tetranitroheptane-2,6-diol (VI).—A solution of 40 g of 25% aqueous glutaraldehyde in 100 ml of water was cooled to 0° and 25 g of fluorodinitromethane was added. The mixture was stirred and cooled in an ice bath, and the pH was adjusted to 7 by dropwise addition of a saturated aqueous sodium bicarbonate solution. After stirring at about 0° for 0.5 hr, the solution was acidified with dilute sulfuric acid and extracted four times with a total of 200 ml of methylene chloride. Drying the extract and removing the solvent *in vacuo* gave 28.5 g of crude diol; after one recrystallization from chloroform the yield was 26 g (74%), mp 78–101°, ε in 0.01 N aqueous KOH (382 nm) 37,600.

Anal. Calcd for $C_7H_{10}F_2N_4O_{10}$: C, 24.15; H, 2.90; F, 10.91; N, 16.09; mol wt, 348.18. Found: C, 24.3; H, 2.9; F, 10.7; N, 15.8; mol wt (chloroform), 355, 357.

The pure diastereomers VIa and VIb were obtained by fractional recrystallization of the above mixture from chloroform. The higher melting isomer VIb, mp 99–101°, 106.5–108° (isomorphs), is the more abundant and less soluble and is isolated readily. Either of the isomorphic forms of VIb may be obtained by appropriately seeding saturated solutions of the material in chlofoform. The second diastereomer, VIa, had mp 86–88°.

Registry No.—I, 22692-03-1; II, 25244-34-2; III, 25244-35-3; IV, 25244-36-3; V, 25244-37-5; VI, 25244-38-6; fluorodinitromethane, 7182-87-8.

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Sensitized Photolysis of
cis,cis-3,5-Cycloheptadienone.
On the Intermediacy of
cis,trans-3,5-Cycloheptadienone[1]

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It was shown earlier that direct photolysis of *cis,cis*-3,5-cycloheptadienone (I) leads to decarbonylation and ring opening to a mixture of hexatrienes.[3,4] It is clear that this reaction originates from the excited singlet state (S_1) of I from the observations[4] that (a) triplet quenchers are without effect on this reaction, and (b) triplet sensitization gives a different reaction, isomerization of I to the valence tautomer II. By analogy

I   II   III
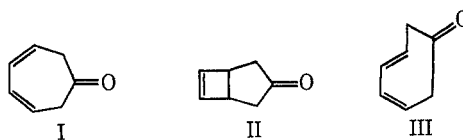
with the course of triplet-sensitized valence isomerization of *cis,cis*-1,3-cyclooctadiene,[5] it was postulated[4]

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(10) Clark and Lubs: 29.63 ml of 0.1 N NaOH and 50 ml of 0.1 M KH₂PO₄ diluted to 100 ml.

(11) T. V. Protopopova and A. P. Skoldinov, *Zh. Obshch. Khim.*, **28**, 240 (1958); *Chem. Abstr.*, **52**, 12754 (1958).

(1) Part XXV of a series on the photochemistry of unsaturated ketones in solution. Part XXIV: D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, No. 19, 1661 (1970).

(2) Alfred P. Sloan Fellow, 1967–1969.

(3) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

(4) D. I. Schuster, B. R. Sckolnick, and F.-T. H. Lee, *ibid.*, **90**, 1300 (1968).

(5) R. S. H. Liu, *ibid.*, **89**, 112 (1967).

that the conversion of I to II involves, initially, sensitized isomerization of I to the highly strained cis,trans-3,5-cycloheptadienone (III), which then undergoes thermally a symmetry-allowed ring closure to II. Because of the strain in III, it would be expected that the thermal ring closure (III → II) should proceed at much lower temperatures than the ring closure of cis,trans-1,3-cyclooctadiene.[5,6]

Experiments were attempted in order to obtain evidence as to the intermediacy of III in the sensitized photolysis of I. In earlier work, low-temperature irradiation of cis-2-cycloheptenone led to the *trans* isomer, identified from its infrared absorption spectrum and by adduct formation with cyclopentadiene and furan.[7] In the case of I, such a study is complicated by the fact that the proposed[4] cis–trans isomerization of I occurs, if at all, only on triplet sensitization, and potential trapping reagents, such as cyclic dienes, would also be expected to act as efficient quenchers of the sensitizer triplets, competing with energy transfer to I. In the event, irradiation of benzophenone in the presence of I and cyclopentadiene (CPD) in ethyl ether at Dry Ice–ethanol temperatures led to partial quenching of the conversion of I → II, but the only new products observed by gas–liquid chromatography (glpc) and column chromatography of the photolysate were CPD dimers.[8] Similar results were obtained when the relative proportions of reactants were varied.

Entirely analogous results were obtained using furan as the potential trapping reagent.[9] The possibility that furan might react with II was eliminated by carrying out the sensitized conversion of I → II in the absence of furan, adding furan and reirradiating. No diminution in the amount of II was observed. Since β-acetonaphthone (E_T = 59 kcal/mol)[11] has a π,π^* configuration in its lowest triplet state, cycloaddition to furan is expected to be unimportant,[10] so that furan should not be consumed in side reactions. Nevertheless, β-acetonaphthone-sensitized irradiation of I at −70° in the presence of furan gave no products attributable to trapping of III, according to glpc and column chromatography.

The failure to trap any reactive intermediate in the sensitized isomerization of I to II implies either that (a) the cis–trans dienone III is not an intermediate, or that (b) III isomerizes thermally to II even at low temperatures much more rapidly than it reacts with either cyclopentadiene or furan. The negative results do not allow an unambiguous decision between these alternatives, although it seems to us more likely that alternative (a) is correct, considering the strain anticipated in III on the basis of inspection of molecular models. It seems probable that the triplet of II, formed by energy transfer from the sensitizer, begins to twist in the direction of forming III with a *trans* double

bond (as with cycloheptenone,[7] cyclooctenone,[12] and even cyclohexenone[13]). However, crossover to the ground-state potential surface leading to II probably occurs before III is reached. The same sort of explanation may hold for the triplet-sensitized reactions of monocyclic cyclohexenones, particularly photocycloadditions leading to *trans*-fused bicyclo[4.2.0]-octane derivatives.[13,14]

In order to determine the triplet energy of I, studies were made with a series of sensitizers at room temperature and at −70°. In addition to sensitization at room temperature by benzophenone and β-acetonaphthone, the conversion I → II was sensitized by chrysene (E_T = 57 kcal/mol),[15] α-acetonaphthone (E_T = 56),[11] biacetyl (E_T = 55),[11] benzil (E_T = 54),[11] fluorenone (E_T = 53),[11] and 1,2,5,6-dibenzanthracene (E_T = 52),[15] but not by benzoquinone (E_T = 53–55)[16] and pyrene (E_T = 49).[11,15] Quantum yields for the sensitized isomerization of I at 366 nm at room temperature were found to be 0.54 for β-acetonaphthone and 0.01 for fluorenone, whereas intersystem crossing efficiencies for these sensitizers are, respectively, 0.84 and 0.93.[17] These data suggest that the triplet energy of I is probably near 59 kcal/mol.

At −70°, sensitized isomerization of I → II could be effected by benzophenone, α- and β-acetonaphthone, and, surprisingly, dibenzanthracene,[18] but not at all by benzil or fluorenone, even on prolonged irradiation. Benzophenone and β-acetonaphthone were ineffective in sensitizing reaction of I in an ether glass at liquid nitrogen temperatures (−196°), under conditions where extensive reaction occurred at −70°. The temperature effect on fluorenone- and β-acetonaphthone-sensitized photolysis of I was studied over the interval 0 to −70°, and a gradual falloff in quantum yield with decreasing temperature (measured at 10° intervals) was observed. Surprisingly, plots of relative quantum yield *vs.* temperature were linear, while more theoretically defensible plots of log Φ *vs.* $1/T$ gave a much poorer linear correlation. Fair linear correlations were also observed between Φ and the reciprocal viscosity of the solvent, ethyl ether.

The quantum yield for sensitized formation of II from I is given by eq 1, where Φ_{ic} is the quantum yield for intersystem crossing of the sensitizer, k_{et} the rate constant for energy transfer, k_{ds} the rate constant for radiationless decay of sensitizer triplets, k_r that for reaction of triplet I to give II, and k_d the sum of rate constants for all decay processes of triplet I. Very little is

$$\Phi = \Phi_{ic}\left(\frac{k_{et}}{k_{et} + k_{ds}}\right)\left(\frac{k_r}{k_r + k_d}\right) \tag{1}$$

known about the expected temperature dependence of each term in eq 1. It is reasonable to assume that the temperature dependence would be most critical for k_{et}, especially when the energy transfer is endothermic, and perhaps also for the partitioning of triplet I, that is,

(6) W. J. Nebe and G. J. Fonken, *J. Amer. Chem. Soc.*, **91**, 1249 (1969); K. M. Shumate, P. M. Neuman, and G. J. Fonken, *ibid.*, **87**, 3996 (1965).

(7) P. E. Eaton and K. Lin, *ibid.*, **87**, 2051 (1965); E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).

(8) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(9) Triplet-sensitized dimerization of furan apparently does not occur, but adduct formation with benzophenone and other triplets is well documented.[10]

(10) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); G. R. Evanega and E. B. Whipple, *Tetrahedron Lett.*, No. 23, 2163 (1967); G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963).

(11) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(12) P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).

(13) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

(14) P. J. Wagner and D. J. Buchek, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

(15) D. P. Craig and J. G. Ross, *J. Chem. Soc.*, 1589 (1954).

(16) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **1**, 21 (1968); see p 127.

(17) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(18) There is the possibility that dibenzanthracene transfers energy from its second triplet state, as is well established for anthracene and some 9,10-disubstituted anthracenes; see R. S. H. Liu and R. E. Kellogg, *J. Amer. Chem. Soc.*, **91**, 250 (1969), and earlier papers cited therein.

for the ratio k_r/k_d. It is tempting to postulate that energy transfer takes place to an upper vibrational level of I so as to allow a vertical Franck–Condon transition to the excited triplet state. Since the diene system of I is twisted,[3,4] flattening of the molecule corresponds to an increase in the ground-state potential energy. The nmr spectrum of I indicates that the α-hydrogens are equivalent at room temperature; *i.e.*, ring flipping is rapid on the nmr time scale at room temperature. The efficiency of energy transfer would be related to the population of the vibrational levels only if decay of sensitizer triplets competes with energy transfer to vibrationally excited ground states of I. Clearly, much more data are necessary to establish whether such an effect can operate in this or other systems. An alternative possibility is that low-energy triplet sensitizers are inducing reaction by a Schenck mechanism[19] involving initial bond formation to I. Such a mechanism has been invoked for sensitized olefin isomerization induced by donors with lowest n,π^* triplet states.[20]

Since the earlier publication,[4] a preliminary value for the quantum yield of the direct photodecarbonylation of I has been measured at 313 nm and found to be 0.31 for disappearance of I. Since intersystem crossing from the excited singlet is clearly unimportant,[4] the inefficiency of the reaction must be attributed either to rapid radiationless decay of the singlet or to reversible formation of an intermediate formed by α cleavage on one side of the double bond.[21,22] Decarbonylation might proceed from such a diradical intermediate, in competition with return to starting material I, or might be the result of a concerted reaction of the excited singlet which competes with α cleavage. Further experiments are necessary to decide between these alternatives. It is certain, however, that all pathways for singlet-state deactivation and reaction are much faster than intersystem crossing to the triplet,[4] although this does not appear to be the case with some unsaturated ketones of comparable symmetry.[23]

Experimental Section

Materials.—*cis,cis*-3,5-Cycloheptadienone was prepared as described previously.[4] Solvents, reagents, and sensitizers were purified by distillation or recrystallization before use.

Photolysis Procedure.—Photolyses of I at room temperature, sensitized and unsensitized, were carried out as described previously.[4] Photolyses at liquid nitrogen (−196°) temperatures were carried out in a Pyrex tube immersed in liquid nitrogen in a large dewar attached at one end to a quartz glass tube. The dewar was placed inside a Rayonet reactor and irradiated with 3650-Å lamps for 4.5 hr. Photolyses at −70° were carried out by immersing a Hanovia immersion cell containing a 450-W high-pressure mercury lamp in a large dewar containing Dry Ice and ethanol. There was an insulating air space around the immersion well provided by a large reaction cell so that water could be circulated within the immersion well without freezing. Samples were in solution in Pyrex tubes surrounding the immersion well outside the insulation but within the dewar. Typical runs involved 40–60 mg of dienone I in 35 ml of ether containing

enough sensitizer to absorb >99% of the incident light. In some runs, Corning 7380 filters were placed between the lamp and the sample tube to restrict the incident light to >340 nm. The progress of the reaction was followed by glpc analysis[4] on a 4-ft column of 5% SE-30 silicone on Chromosorb G.

For the controlled-temperature irradiations between 0 and −70°, the degassed solutions of I, sensitizer, and internal standard were sealed in a 3- or 4-mm Pyrex tube, which was irradiated externally with a Hanovia 450-W lamp inside a Pyrex immersion well through a Corning 7380 filter. The temperature within the tube was maintained using the cooling apparatus for the esr spectrometer, in which a stream of nitrogen at a set temperature was passed around the outside of the sample tube. The heat exchanger for the cooling gas was a Dry Ice–acetone bath. Experiments at lower temperatures with a liquid nitrogen bath for cooling the gas were less reproducible. Analysis by glpc was carried out as above.

Quantum yields for disappearance of I were determined as described earlier,[24] using a Bausch and Lomb high-intensity grating monochromator and ferrioxalate actinometry.

Registry No.—I, 25090-28-2; III, 25090-29-3.

(24) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **90**, 5145 (1968).

Photochemical Rearrangements of α-Benzyloxystyrenes to β-Phenylpropiophenones

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There are a number of examples of photochemical rearrangements of aryl ethers, *e.g.*, the rearrangements of aryl phenyl ethers to arylphenols,[1a,b] that of phenoxycarboxylic acids to hydroxyphenylcarboxylic acids,[2] and that of allyl phenyl ether to allylphenol.[3] They may be initiated by homolytic fission of phenoxy-carbon bonds in electronically excited ether molecules, since phenol is detected in the products. Among them, the photochemical rearrangement of allyl phenyl ether, or Claisen rearrangement, is important since it can be discussed in view of the orbital symmetry.[4]

The rearrangement of α-benzyloxystyrene to β-phenylpropionphenone catalyzed by azobisisobutyronitrile (AIBN) has been known to be intermolecular radical-chain reaction, where ·CH₂Ph acts as a chain carrier.[5a] The rearrangement also occurs on heating at *ca.* 200° in the absence of AIBN. In this case, orbital symmetry arguments may suggest that the shift of 1,3-benzyl radical with continuous overlap is not

(1) (a) D. P. Kelly and J. T. Pinhey, *Tetrahedron Lett.*, 5933 (1966); (b) H.-I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, **88**, 3269 (1966).

(2) D. P. Kelly and J. T. Pinhey, *Tetrahedron Lett.*, 3427 (1964).

(3) (a) M. S. Kharasch, G. Stampa, and W. Nudenberg, *Science*, **116**, 309 (1952); (b) G. Koga, N. Kikuchi, and N. Koga, *Bull. Chem. Soc. Jap.*, **41**, 745 (1968).

(4) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(5) (a) K. B. Wiberg, R. R. Kintner, and E. L. Motell, *J. Amer. Chem. Soc.*, **85**, 450 (1963). (b) It was observed that **1a** was stable but **1c** was rearranged partially to the corresponding photo ketone (**2c**) in a glpc column.

(19) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.*, **71**, 781 (1962).

(20) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **91**, 3265 (1969); J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

(21) P. J. Wagner and R. W. Spoerke, *ibid.*, **91**, 4437 (1969).

(22) In the earlier paper, it was explicitly stated that the results did not exclude a two-step nonconcerted decarbonylation mechanism; see especially footnote 34 in ref 4.

(23) P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, **59**, 5181 (1969).