melts and in ultramarines. The color of ultramarine blue is known to be due to an intense absorption band with maximum at 17,000 cm^{-1}. In the LiCl–KCl eutectic, this band has now been found to have a molar absorptivity in excess of 10^4. The identification of the band as due to the S_3^- ion, based on a quantitative analysis of chemical equilibrium measurements from which the stoichiometry was deduced, strongly supports the suggestion[9,15,16] that this is the sulfur species primarily responsible for the color of ultramarine blue. Furthermore, the identification of the higher energy band in LiCl–KCl eutectic with the S_2^- ion suggests that the absorption feature at 26,000 cm^{-1} in ultramarines[9] is due to the S_2^- species. The oxidation of ultramarine green to ultramarine blue can be rationalized, on the basis of this analysis, as due to an increasing S_3^-/S_2^- ratio in going from the former to the latter pigment.

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(16) S. D. McLaughlan and D. J. Marshall, *J. Phys. Chem.*, **74**, 1359 (1970).

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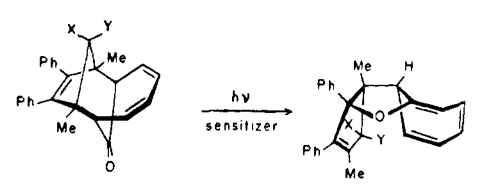
Photochemistry of Tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trienes. I. Selective Photochemically Forbidden Processes

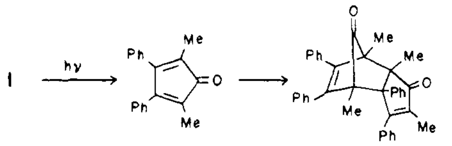
Sir:

Recent interest in the photochemistry of multichromophoric molecules[1] and in the application of orbital symmetry considerations to photochemical reactions[2] prompts us to report a number of new photochemical reactions observed in tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-triene derivatives.[3–5] Remarkably, the new photochemical reactions reported here are all of the photochemically forbidden variety.[5]

Photolysis of **1** in acetone solution produces **2** (67%) as the only major product.[6a] Similar results were obtained with the sensitizers benzophenone and triphenylene.[6b] By contrast, direct photolysis[6c] of **1** in acetonitrile or methanol solution leads to [6 + 4] photodissociation, as evidenced by formation of the cyclopentadienone dimer, **6** (66%).[7] Thermal dissociation of **1** has also been observed at room temperature at a much slower rate than is observed in the photochemical reaction.

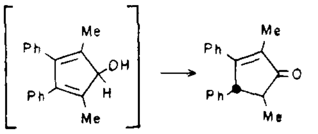


1 (X,Y=O) 2 (X,Y=O)
3 (X=H,Y=OH) 4 (X=H,Y=OH)



5 + Tropone 6

Sensitized photolysis of **3**[6a] produces **4** (45%) as the only major product. Direct photolysis[6c] of **3** produces several unidentified minor products and polymer, but neither the triplet product **4** nor the product expected from dissociation, **8**, are observed in the direct photolysis.[8]



7 8

The formal [8 + 2] adduct **2** was previously isolated by Houk and Woodward as a minor product of the thermal reaction of **5** with tropone.[4] At that time the possibility of formation of **2** by either a direct [8 + 2] combination of reactants, or by a [3,3] sigmatropic shift from [6 + 4] adduct **1** was noted. The previously unknown stereochemistry of the tropone–cyclopentadienone fusion has now been resolved by NOE experiments[9] and by chemical evidence. Thus, sodium borohydride reduction of **2** produced alcohol **4**, the result of borohydride attack from the less hindered side of the carbonyl. Chromic anhydride–pyridine oxidation of **4** regenerated **2** quantitatively. Furthermore, heating **4** for 7.5 hr in refluxing benzene solution or in the crystalline state for 3 days at 100° produced **3** in nearly quantitative yield. The intramolecular nature of this [3s,3s] sigmatropic shift is indicated by the stereospecific formation of **3** uncontaminated by epimer and by the absence of competing formation of **8** which would be expected to be the ultimate product of dissociation of **4** in solution.

Both the reverse Claisen rearrangements of **1** to **2** and of **3** to **4** are photochemically forbidden [3s,3s]

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(1) H. Morrison, J. Pajak, and R. Peiffer, *J. Amer. Chem. Soc.*, **93**, 3978 (1971); H. E. Zimmerman and R. D. McKelvey, *ibid.*, **93**, 3638 (1971); D. O. Cowan and A. A. Baum, *ibid.*, **93**, 1153 (1971), and references therein.

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(4) K. N. Houk and R. B. Woodward, *ibid.*, **92**, 4145 (1970).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(6) [$\lambda_{max}C_6H_{12}$]: **1**, sh 224 (ϵ 9600), 250 (ϵ 12,700), sh 268 (ϵ 9600), sh 320 (ϵ 500), sh 335 (ϵ 300); **3**, sh 220 (ϵ 18,500), sh 259 (ϵ 9900), sh 268 nm (ϵ 8200); **10**, sh 229 nm (ϵ 17,000), 269 nm (ϵ 9700); (a) Rayonet RPR reactor, RUL 2537-Å lamps, quartz vessel, 10–20°, ~10^{-3} *M* in acetone (absorbing ~95% light); (b) RUL 2537-, 3000-, or 3500-Å lamps, ~10^{-3} *M* in acetonitrile containing added sensitizer (absorbing >90% light); (c) RUL 2537-, 3000-, or 3500-Å lamps, ~10^{-3} *M*.

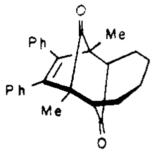
(7) C. F. H. Allen and J. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942); C. F. H. Allen and J. A. Van Allan, *ibid.*, **72**, 5165 (1950).

(8) Formation of **7** by other methods results in rapid tautomerization to **8**: M. A. Ogliaruso, M. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965); K. N. Houk, Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1968.

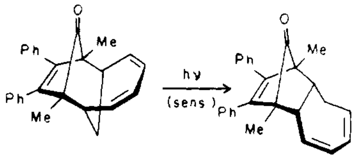
(9) Irradiation of the high-field methyl in **2** results in ~30% enhancement of the intensity of the allylic proton resonance. We thank Professor N. S. Bhacca for carrying out this experiment.

sigmatropic shifts.[10] The photochemical [6 + 4] cycloreversion of **1** is also a photochemically forbidden reaction. Notably, **1**, which undergoes the [6 + 4] cycloreversion upon direct irradiation, thermally dissociates slowly at room temperature, while **3**, which does not photodissociate, is stable above 100°.

Minor modifications of functionality in these systems result in altered photochemical reactivity. In particular, both the diene and stilbene moieties must be present for the [3,3] rearrangement to occur. Thus, the tetrahydro derivative **9**[4] appears quite stable to prolonged irradiation[6c] in the absence of oxygen,[11] in contrast to the more strained 2,3-diphenylnorbornen-7-ones which readily decarbonylate in solution.[12] Moreover, the cyclopentadiene–tropone [6 + 4] adduct displays entirely different photochemical behavior which will be reported at a later date.



9



10

11

Photolysis of the cycloheptatriene [6 + 4] adduct **10**[3,6a,c] results in formation of **11**[3] in about 15% yield in addition to other minor products. However, none of the product expected from dissociation, **6**, is observed in these reactions. This formation of **11** is formally a [1s,5s] sigmatropic carbon shift, a further example of a photochemically forbidden process in these systems.[13] Remarkably, the thermolysis of **10** results in a thermally forbidden [1s,3s] sigmatropic shift, presumably involving a diradical intermediate.[3]

Observation of forbidden reactions is usually considered evidence for diradical or dipolar intermediates. In the present case, the cleavage of the 1,6 bonds in **1**, **3**, and **10** would result in formation of stabilized diradicals. However, the selective collapse of these diradicals to different products when generated from excited states of different multiplicities would constitute spin correlation effects of unexpected proportions.[14] Alternative mechanistic rationales for these reactions involving different diradical intermediates or concerted mechanisms are the subject of continuing studies.

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(11) In the presence of traces of oxygen or iodine, **9** undergoes conversion to a phenanthrene derivative, a well-documented reaction of *cis*-stilbene singlets: F. R. Stermitz, "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 247.

(12) C. M. Anderson, J. B. Bremner, H. H. Westberg, and R. N. Warrener, *Tetrahedron Lett.*, 1585 (1969); I. W. McCay and R. N. Warrener, *ibid.*, 4779 (1970); B. Fuchs, *Isr. J. Chem.*, **6**, 517 (1968), and references therein.

(13) The conversion of **10** to **11** involving a sequence of photochemically allowed [1s, 3s] sigmatropic shifts cannot be discounted at this time.

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Reactions of Dihydronicotinamides. I. Evidence for an Intermediate in the Reduction of Trifluoroacetophenone by 1-Substituted Dihydronicotinamides

Sir:

Many oxidation–reduction reactions of models for the nicotinamide coenzymes involve direct hydrogen transfer without exchange with solvent protons, and show none of the properties of radical-chain processes.[1] Such reactions, and the related enzymic processes, are therefore usually considered to be "hydride transfers,"[2] although the evidence does not demonstrate that the transfer of the proton and two electrons is concerted. We present here evidence which requires that one particular "hydride transfer," the reduction of trifluoroacetophenone to trifluoromethylphenylcarbinol by some 1-substituted-1,4-dihydronicotinamides[3,4] be a two-step process.

The reaction was studied in 25% (v/v) isopropyl alcohol–water with 0.1M triethanolamine–0.1 M triethanolamine hydrochloride buffer and an ionic strength of 0.50 M at 50.0 ± 0.2°. In the presence of excess trifluoroacetophenone, the disappearance of dihydronicotinamide (spectrophotometric at 355 nm) follows first-order kinetics over three half-lives.[4] The first-order rate for a given dihydronicotinamide is the sum of two terms[4] (eq 1). The first term is due to hydration of the dihydronicotinamide and is the rate observed in the absence of ketone.[5] The second is due to the reduction of the ketone; >95% of the carbinol predicted by kinetics can be detected by glpc analysis at the end of a reaction.[4] The oxidation–reduction involves direct transfer of hydrogen, and is not affected by the addition of free-radical chain inhibitors.[3] Although trifluoroacetophenone is extensively hydrated in aqueous solution,[6] the formation of free ketone is not at all rate determining in our experiments, which show clear first-order dependence on dihydronicotinamide concentration.

$$k_{\text{obsd}} = k_{\text{hyd}} + k_{\text{r}}[\text{trifluoroacetophenone}] \qquad (1)$$

The calculated second-order constants k_{r} for the reduction of trifluoroacetophenone by three dihydronicotinamides and 4-monodeuteriodihydronicotin-

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(1) See, for instance: (a) D. Mauzerall and F. H. Westheimer, *J. Amer. Chem. Soc.* **77**, 2261 (1955); (b) R. H. Abeles, R. F. Hutton, and F. H. Westheimer, *ibid.*, **79**, 712 (1957); (c) B. E. Norcross, P. E. Kleindienst, Jr., and F. H. Westheimer, *ibid.*, **84**, 797 (1962); (d) K. A. Schellenberg and G. W. McLean, *ibid.*, **88**, 1077 (1966); (e) R. W. Huffmann and T. C. Bruice, *ibid.*, **89**, 6243 (1967).

(2) H. Sund in "Biological Oxidations," T. P. Singer, Ed., Wiley-Interscience, New York, N. Y., 1968, pp 621–624.

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(4) J. J. Steffens, Ph.D. Thesis, Massachusetts Institute of Technology, 1971; J. J. Steffens and D. M. Chipman, in preparation.

(5) C. C. Johnston, J. L. Gardner, C. H. Seulter, and D. E. Metzler, *Biochemistry*, **2**, 689 (1963).

(6) R. Stuart and R. Van der Linden, *Can. J. Chem.*, **38**, 399 (1960).