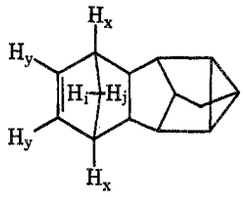


Figure 6.

ments are analogous to the work of Franzus[8] whose studies characterized this type of ring system.

We may conclude that $Ni(CO)_4$ is a unique catalyst having the ability to produce different types of norbornadiene dimers as a function of the type of excitation. Furthermore, all four Diels–Alder dimers structures are now firmly assigned and nmr interpretation of these types of structures is somewhat facilitated. Ring current effects in cyclopropane are implicated in deshielding an equatorial proton.

Experimental Section

General.—The nmr spectra were obtained from a Varian A-60 spectrometer while all the spin decoupling was done on a Varian HA-60 spectrometer. Gas chromatography information was determined by a Varian Aerograph Model 1740, and preparative separations were done on an Aerograph Autoprep Model A-700. A Varian CH-5 mass spectrometer with a gas chromatograph attached was used for mass spectral data. Norbornadiene was purchased from Frinton, purified (according to gc analysis) by recrystallizing the $AgNO_3$ complex of it in ethanol, and recovered by thermal decomposition under vacuum. The $Ni(CO)_4$ (toxic), obtained from Matheson, was distilled once prior to use.

Thermal Reaction.—To 8.5 ml of norbornadiene (7.73 g, 83.9 mmol) under oxygen-scrubbed N_2 in a flask fitted with reflux condenser and Hg bubbler was added $Ni(CO)_4$ (0.145 g, 0.849 mmol). The solution was brought to reflux (85–87°) and held there for 6.5 hr. Analysis by gc (6-ft column, 5% SE-30 on Gas-Chrom Z, 100–120 mesh) showed two dimer peaks in the ratio (peak heights) of 3:1. The dimers (3.17 g, 17.2 mmol) constituting a 41% conversion of norbornadiene [2030% yield based on $Ni(CO)_4$] were removed from solution by distillation under vacuum. Comparison of the nmr spectrum of the mixture with those of dimers I and II reported in the literature[3e] proved their identity. The integration of the olefin proton peaks in the nmr spectrum also showed a relative ratio of 3:1 I:II.

Photochemical Reaction.—Under vacuum (<0.015 mm) purified norbornadiene was transferred into a calibrated flask and 8.5 ml (7.73 g, 83.9 mmol) was transferred into a Vycor tube (10-mm i.d., 20-cm length). $Ni(CO)_4$ (0.145 g, 0.849 mmol) was added to the norbornadiene *via* syringe through a septum above the tube which was then sealed under vacuum and irradiated for 4.5 days in a "merry-go-round" tube holder by a Hanovia 450-W Hg lamp in a quartz, water-cooled jacket. From gc analysis (6-ft column, 5% SE-30 on Gas-Chrom Z, 100–120 mesh; 6-ft column, 20% Carbowax 20M on Chromosorb W, 80–100 mesh) the contents of the tube were found to contain dimers, 90% of which were the two pseudo-Diels–Alder dimers (peak height ratio of 2:1). Also detected were a trace of CO insertion product (parent peak in mass spectrum at m/e 212) and some trimer (parent peak at m/e 276). Separation of the products by vacuum distillation produced 0.876 g (4.75 mmol) of dimers [11% conversion of norbornadiene or 559% yield based on $Ni(CO)_4$] and 43 mg (0.156 mmol) of trimer. The dimers were separated on a 20-ft column, 20% Carbowax 20M on Chromosorb W, 80–100 mesh, 190°. The nmr spectrum of the original mixture of dimers (ratio of olefin proton integrations was 2:1 VI:VII) was the same as the combination of the nmr spectrum of each of the components. When Pyrex and quartz tubes were used rather than Vycor, both ratios and amounts as well as number of products were essentially the same from gc information.

Investigation of Interconversion of Dimers.—A mixture of pseudo-Diels–Alder dimers (5.15 g), the predominant one being VI, and $Ni(CO)_4$ (91 mg) were heated at 92° for 26 hr under nitrogen. An nmr spectrum showed the dimer mixture to be unchanged. Likewise, a mixture of dimers I and II (6.33 g) and $Ni(CO)_4$ (104 mg) were sealed under vacuum and irradiated as above for 1 week. The nmr analysis showed no change in dimer contents.

Silver Nitrate–Dimer Complex for Crystal Structure.—To dimer VI a saturated aqueous $AgNO_3$ solution was added and the resulting white precipitate collected. After being washed with water the precipitate was recrystallized from absolute ethanol and crystals were used for structure determination.

X-Ray Data.—This compound crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 17.554(9) Å, b = 6.908(4) Å, c = 11.031(5) Å, and β = 103.10(3)°.

A unique data set was collected by the θ–2θ scan technique on a GE XRD-5 diffractometer using zirconium-filtered Mo K_α radiation. Two crystals were used to collect 1181 pieces of data, of which 841 were found to be more than twice the standard deviation of the intensity and were thus considered observed. The data were reduced and corrected for absorption.

The structure was solved by the conventional heavy atom method. Hydrogens were located from the difference map. The structure was refined using full matrix least squares, treating hydrogen atoms isotropically and nonhydrogen atoms anisotropically, to an R value of 3.3%.[12]

Registry No.—I, 2957-68-8; II, 1624-13-1; IV, 17926-98-6; V, 17926-99-7; VI, 18067-61-3; VII, 33780-58-4; norbornadiene, 121-46-0; tetracarbonylnickel, 13463-39-3.

Acknowledgment.—Authors P. W. Jennings and G. E. Voecks wish to thank Dr. William Waters for his help with the nmr work. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and Cities Service Oil Co. for support of this research.

(12) The complete X-ray data will be published in an appropriate journal.

The Photochemistry of 1-Keto-2-carbomethoxymethylenebenzocyclobutene

RICHARD J. SPANGLER* AND J. C. SUTTON[1]

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

Received November 12, 1971

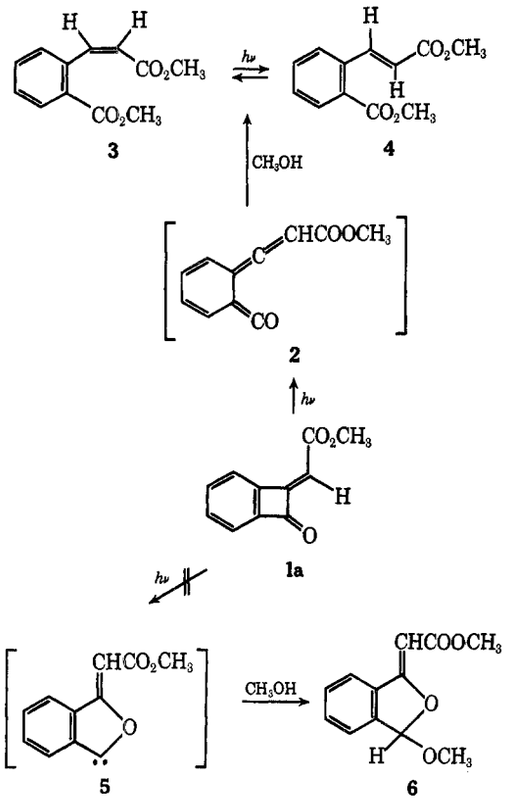
We wish to report our results on the photochemical decomposition of 1-keto-2-carbomethoxymethylenebenzocyclobutene (**1a**). This keto ester is of interest because of its relation to the recently studied 2-methylenecyclobutanones,[2] benzocyclobutenones,[3] and benzocyclobutadienequinone.[4]

Ultraviolet irradiation of a dilute methanol solution of **1a** gave, upon preparative tlc, a 15% yield of an 85:15 mixture of cis and trans methyl *o*-carbomethoxycinnamate (**3** and **4**, Scheme I), as the major reaction products. Several additional unidentified minor components were also obtained in a combined yield of 6%. The remainder of the material remained at the origin of the tlc plate as a brown gum. Esters **3** and **4** were separated by preparative gas chromatography.

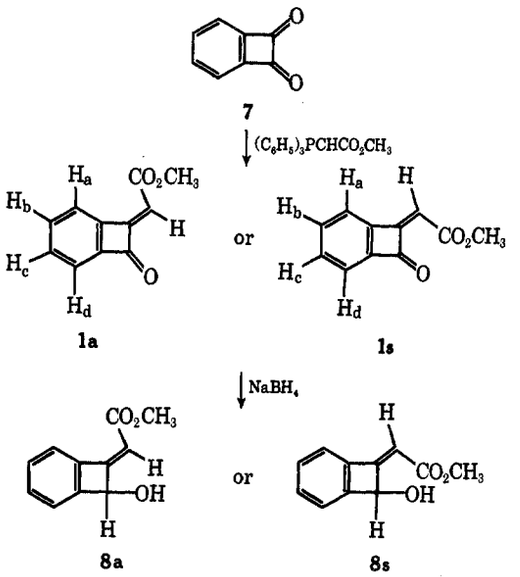
Methyl *o*-carbomethoxy-*cis*-cinnamate (**3**) showed the following spectral properties: nmr δ 3.51 (s, 3 H), 3.80

(1) NDEA Predoctoral Trainee, 1967–1970.
(2) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).
(3) M. P. Cava and R. J. Spangler, *ibid.*, **89**, 4550 (1967).
(4) H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **101**, 1457 (1968).

SCHEME I



SCHEME II



(s, 3 H), 5.99 (d, 1 H, J = 12 cps), 7.20–7.64 (m, 4 H), 7.92–8.08 (m, 1 H); decoupling at δ 5.99 collapsed two peaks at 7.47 and 7.59 to a single peak at 7.53; uv λ_{max} 216 nm (log ϵ 4.10), 284 (3.47); ir (KBr pellet) 2945, 1729, 1717, 1635, 1482, 1434, 1394, 1297, 1268, 1199, 1161, 1134, 1080, 821, 758, and 708 cm^{-1}; mass spectrum m/e (rel intensity) 220 (4), 205 (2), 189 (8), 173 (12), 161 (100), 146 (5), 145 (6), 130 (6), 129 (7), 118 (9). Methyl *o*-carbomethoxy-*trans*-cinnamate (**4**) showed these properties: nmr δ 3.78 (s, 3 H), 3.90 (s, 3 H), 6.27 (d, 1 H, J = 16 cps), 7.24–7.64 (m, 3 H), 7.82–8.03 (m, 1 H), 8.45 (d, 1 H, J = 16 cps); uv λ_{max} 224 nm (log ϵ 4.12), 271 (4.06); ir (KBr pellet) 2950, 1717, 1638, 1482, 1436, 1321, 1260, 1196, 1175, 1132, 1080, 977, 763, 719 cm^{-1}; mass spectrum identical with that of cis isomer **3**. These spectra are fully consistent with the assigned structures; furthermore trans diester **4** was identical with an authentic sample prepared by the method of Elvidge and Jones.[5] Irradiation of a solution of pure **4**[5] for 58 hr with a 350-nm light source smoothly yielded an 85:15 mixture of **3** and **4**, identical with the mixture of **3** and **4** obtained upon irradiation of **1a**. Keto ester **1a** was found to be stable toward refluxing methanol in the dark.

Thus, the major observable photodecomposition pathway of **1a** appears to be an initial ring opening to give the *o*-benzoquinone intermediate **2**. By analogy with the photochemistry of benzocyclobutadienequinone (**7**)[4] we feel that *o*-quinone **2** is a likely intermediate, although there is no direct proof for its existence. Ring opening is then followed by reaction of the intermediate **2** with the solvent, methanol, to give the methyl *o*-carbomethoxycinnamates (**3** and **4**). These in turn are in photoequilibrium with each other (Scheme I). Significantly, we did not detect any of the acetal **6**, the product to be expected if **1a** underwent a photochemical ring expansion to the oxacarbene **5** in a manner analogous to that of numerous cyclobutanones[2] and benzocyclobutadienequinone (**7**).[4]

Compound **1** was synthesized by the method of Cava and Pohl[6] from benzocyclobutadienequinone (**7**) and triphenylphosphinecarbomethoxymethylene (Scheme II). However, the stereochemistry about the double bond of **1** was not determined by these workers. The heretofore unreported nmr spectrum of **1** showed a singlet (3 H) at δ 3.86, a singlet (1 H) at 6.16, a multiplet (3 H) at 7.56–7.83, and a multiplet (1 H) at 8.26–8.38. This spectrum is consistent with the anti isomer **1a** and not the syn isomer **1s**, in that one of the aromatic protons is clearly deshielded relative to the remaining three. We attribute this deshielding to the proximity of H_a (Scheme II) to the ester carbonyl group. That this deshielding is not due to the proximity of H_d (Scheme II) to the ketone carbonyl is clear from examining the nmr spectra of other benzocyclobutenones. For example, the nmr spectrum of benzocyclobutenone itself consists of a broad aromatic multiplet centered at δ 7.33 in which the proton ortho to the carbonyl function is not deshielded relative to the other three aromatic protons. To further substantiate this conclusion, **1** was reduced with sodium borohydride to the alcohol **8** (Scheme II). The infrared spectrum of **8**, determined at several concentrations in carbon tetrachloride solution, showed no evidence of intramolecular hydrogen bonding. This behavior is to be expected from the anti isomer **8a** but not from the syn isomer **8s**. Thus we are confident that **1** is of anti stereochemistry, as depicted in **1a**.

Experimental Section

General.—A Rayonet photochemical reactor Model RPR-100 equipped with a 350-nm light source was used for irradiations. Ir spectra were determined with a Perkin-Elmer Model 621 spectrometer. Nmr spectra were determined with a Varian HA-100 or a Varian A-60 spectrometer. Uv spectra were determined in methanol solution with a Perkin-Elmer Model 202

(5) J. A. Elvidge and D. E. H. Jones, *J. Chem. Soc. C*, 2059 (1967).

(6) M. P. Cava and R. J. Pohl, *J. Amer. Chem. Soc.*, **82**, 5242 (1960).

spectrometer. Mass spectra were determined with a Hitachi Perkin-Elmer RMU 6E mass spectrometer at 70 eV. Carbon and hydrogen analyses were determined with a Perkin-Elmer Model 240 elemental analyzer at the University of Idaho.

Photolysis of 1-Keto-2-carbomethoxymethylenebenzocyclobutene[6] (1a) in Methanol Solution.—To a quartz vessel were added 139 mg (0.740 mmol) of 1-keto-2-carbomethoxymethylenebenzocyclobutene (**1a**) and 20 ml of methanol. The reaction vessel was then flushed with nitrogen and the system was closed. The solution was then irradiated at 350 nm and the reaction was monitored with gas chromatography. After 28 hr gc showed that the starting material had all reacted and the irradiation was stopped. The methanol was then removed by a rotary evaporator. The residue was dissolved in chloroform and streaked on an 8 in. × 8 in. × 1000 μ preparative thin layer plate of neutral alumina previously oven dried for 2 hr. The plate was developed with chloroform, and the main band (R_f 0.77) was removed from the plate and extracted with several portions of chloroform to give 24 mg (0.109 mmol, 15% yield) of cis and trans methyl *o*-carbomethoxycinnamate (**3** and **4**). Gas chromatography indicated that the cis:trans ratio was 85:15. Pure **3** and **4** were obtained by preparative gas chromatography using a 10 ft × 1/4 in. 5% SE-30 column at 195°.

In addition to the methyl *o*-carbomethoxycinnamates isolated, several minor bands were removed from the thin layer plate and extracted with chloroform. Solvent removal gave a total of 8 mg of material which was not characterized. The remainder of the material remained as a brown band at the origin of the thin layer plate and was also not characterized.

Photoisomerization of Methyl *o*-Carbomethoxy-*trans*-cinnamate(4).—To a quartz nmr tube was added 2 drops of methyl *o*-carbomethoxy-*trans*-cinnamate (**4**)[6] followed by several drops of deuteriochloroform with 1% tetramethylsilane. The reaction mixture was then put under a nitrogen atmosphere and sealed with an nmr cap. The mixture was then irradiated at 350 nm and the reaction was monitored with nmr. After 58 hr both nmr and gc analysis showed the solution contained a mixture of 85% cis cinnamate **3** and 15% trans cinnamate **4**.

Pure cis-cinnamate (**3**) was obtained by preparative gas chromatography using a 10 ft × 1/4 in. 5% SE-30 column at 195°. Reinjection of a small amount of the collected material indicated high (97+%) purity and that no isomerization to trans-cinnamate (**4**) had occurred on gc.

Thermal Reaction of 1-Keto-2-carbomethoxymethylenebenzocyclobutene (1a) with Methanol.—To a 10-ml flask equipped with reflux condenser, drying tube, magnetic stirrer, and heating mantle were added 25 mg of **1a** and 5 ml of methanol. Aluminum foil was wrapped around the reaction flask and condenser to prevent any light-induced reaction from occurring. The solution was then refluxed for 48 hr.

After solvent removal, gc analysis showed that the residue had a retention time identical with that of authentic 1-keto-2-carbomethoxymethylenebenzocyclobutene (**1a**). The nmr spectrum was also identical with that of authentic keto ester **1a** and, furthermore, no peaks corresponding to either cis or trans methyl *o*-carbomethoxycinnamate (**3** or **4**) were detected.

1-Hydroxy-2-carbomethoxymethylenebenzocyclobutene (8a).—To a 50-ml flask equipped with magnetic stirrer were added 150 mg (0.615 mmol) of 1-keto-2-carbomethoxymethylenebenzocyclobutene (**1a**) and 15 ml of methanol. The solution was stirred at room temperature until **1a** was dissolved and then 6 mg (0.63 meq) of sodium borohydride was added to the mixture with stirring. Stirring was continued for 0.5 hr. Dilution with water, extraction with chloroform, drying, and solvent removal gave 177 mg (0.615 mmol) of crude **8a** in a quantitative yield, as a thick, light yellow oil. Analysis by gc showed that the crude alcohol was 95+% pure and was contaminated with a slight amount of the keto ester starting material. Collection by gc using a 10 ft × 1/4 in. 10% SE-30 column at 183° gave **8a** as a light yellow viscous liquid (*Anal.* Calcd: C, 69.46; H, 5.30. Found: C, 69.65; H, 5.35%.): nmr δ 3.60 (s, 3 H), 4.10 (d, 1 H, J = 9 cps, shifted and collapsed to a singlet when H^+ was added), 5.36 (d, 1 H, J = 9 cps, collapsed to singlet when H^+ was added), 5.67 (s, 1 H), 7.16–7.38 (m, 3 H), 7.55–7.79 (m, 1 H); mass spectrum *m/e* (rel intensity) 190 (40), 175 (43), 158 (15), 131 (100), 130 (24), 103 (66), 102 (37), 77 (58), 51 (29). The ir spectrum determined from a 0.25 M solution of **8a** in carbon tetrachloride showed a broad (hydrogen bonded) hydroxyl absorption centered at 3450 cm^{-1} with a very small sharp band (nonhydrogen bonded) at 3590 cm^{-1}. In spectra determined at 0.025 and 0.0025 M, the broad band centered at 3450 cm^{-1} became much smaller and almost disappeared while the sharp band at 3590 cm^{-1} grew more intense upon dilution.

Registry No.—**1a**, 34288-39-6; **3**, 34288-40-9; **4**, 18454-56-3; **8a**, 34288-77-2.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

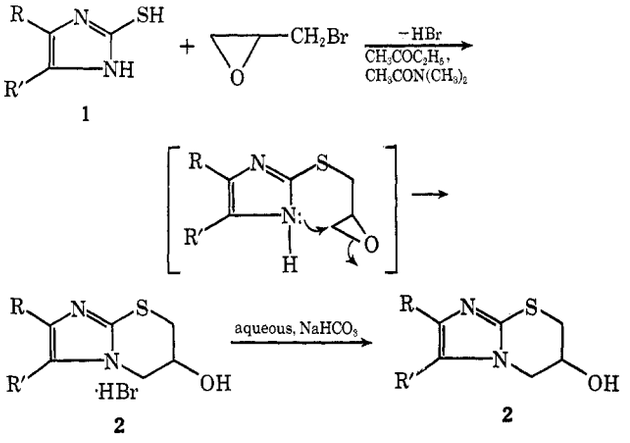
A New Synthesis of the 1,3-Thiazine Ring System

HOWARD ALPER* AND EDMUND C. H. KEUNG[1]

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

Received October 27, 1971

This note describes a simple synthesis of the 1,3-thiazine ring system, some derivatives of which have been shown to exhibit important physiological activity.[2] We became interested in these heterocycles while investigating the products obtained from the reaction of 2-mercaptobenzimidazole with α-halo ketones.[3] It seemed reasonable that treatment of this and related mercaptoazoles (**1**) with epoxy halides such as epibromohydrin would result in condensation followed by intramolecular cyclization to give the thiazine derivative **2** with the hydroxyl group on a ring carbon.



R = R′ = C_6H_5, H, C_4H_4, $C_2H_2N_2$

The hydroxyl functionality would be a handle for preparing numerous other potentially useful thiazines.

Treatment of 4,5-diphenyl-2-mercaptoimidazole[4a] (**1**, R = R′ = C_6H_5) with epibromohydrin in a mixture of 2-butanone and *N*,*N*-dimethylacetamide (10:1) at 85° for 2 hr gave the hydrobromide salt of **2** from which

(1) National Science Foundation Undergraduate Research Participant.

(2) For example, see R. M. Gesler and A. R. Surrey, *J. Pharmacol. Exp. Ther.*, **122**, 4 (1958); A. R. Surrey, W. G. Webb, and R. M. Gesler, *J. Amer. Chem. Soc.*, **80**, 3469 (1958); B. Loder, G. G. F. Newton, and E. P. Abraham, *Biochem. J.*, **79**, 408 (1961); J. C. Wilson, R. N. Downer, and H. E. Sheffer, *J. Heterocycl. Chem.*, **7**, 955 (1970).

(3) H. Alper, E. C. H. Keung, and (in part) R. A. Partis, *J. Org. Chem.*, **36**, 1352 (1971).

(4) (a) Aldrich Chemical Co., Milwaukee, Wis.; (b) Pfaltz and Bauer, Inc., New York, N. Y.