usually three) columns, and by comparing the fragmentation pattern in the mass spectrum. In the gas chromatograph–mass spectrometer combination, a Varian Aerograph, Model 204-2, was connected by a low volume heated line, fed through an effluent stream splitter, to the helium concentrator of a Perkin-Elmer-Hitachi RMU 6-D.

Synthesis of α,α,α-Trideuterio-*o*-xylene. A solution of 2.65 g (0.0175 mole) of methyl *o*-toluate and 0.6 g of lithium aluminum deuteride (Metal Hydrides) in 10 ml of ethyl ether was stirred at reflux for 12 hr. Work-up with aqueous acid gave 2.14 g (0.0172 mole) of a white solid, mp 31–33° (lit.[18] *o*-methylbenzyl alcohol mp 34°). The crude dideuterio alcohol (1 g) was added to 20 ml of cold, freshly distilled thionyl chloride, and the solution was slowly warmed to the boiling point and refluxed until gas evolution ceased. Excess thionyl chloride was removed on a rotary evaporator, and small portions of pentane were added and removed under vacuum to flush out the remaining traces of thionyl chloride. The resulting clear oil was dissolved in 20 ml of dry tetrahydrofuran and stirred at reflux under nitrogen with 0.26 g of lithium aluminum deuteride. The reaction mixture was acidified, and the product *o*-xylene was extracted into a known volume of pentane. Comparison of the gas chromatogram of this solution with a standard mixture indicated that 0.76 g of the deuterated *o*-xylene was present (theory, 0.88 g). The *o*-xylene was isolated by preparative gas chromatography to ensure purity of the sample. Analysis by mass spectroscopy at reduced ionization voltage showed the *o*-xylene to be 98% d_3 and 2% d_2, with no detectable amounts of d_1 or d_0.

Acknowledgments. The support of this research by the National Science Foundation (GP-3496) is gratefully acknowledged. The mass spectrometer used in this investigation was purchased under a National Science Foundation Research Instrument Grant. Mr. John S. Wishnok and Mr. Charles I. Barta participated in the development of the oxygen lamp and in measuring its spectral output.

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[18] "Handbook of Chemistry and Physics," 32nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1950, p 806.

Photochemistry of Sodium 9-Anthroate in Aqueous Solution[1]

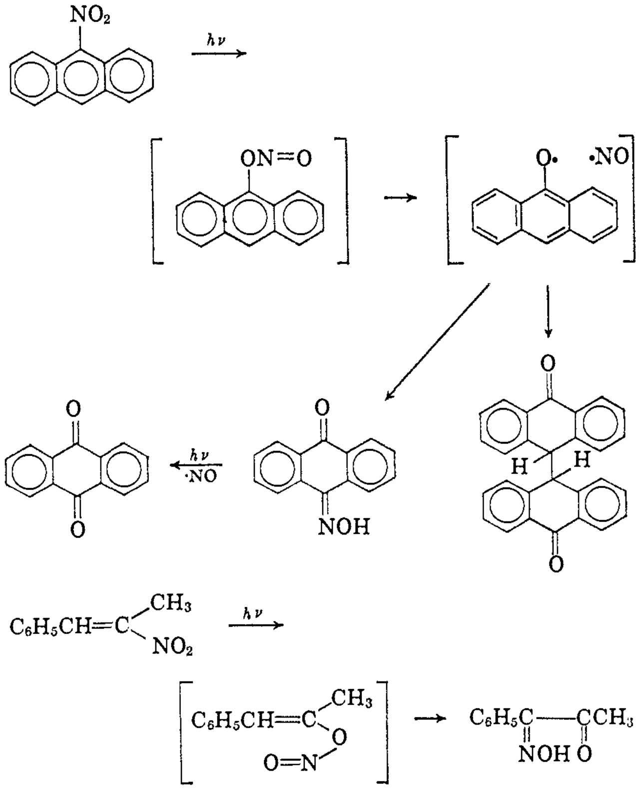
Anne W. Bradshaw and O. L. Chapman

Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. Received November 5, 1966

Abstract: The photochemistry of sodium 9-anthroate in aqueous solution has been investigated. Earlier reports that irradiation of sodium 9-anthroate in the presence of air gives photodimer and anthraquinone have been confirmed, and carbon monoxide, 10,10′-bianthrone, and anthracene have also been isolated. In degassed solutions sodium 9-anthroate gives anthrol anion and carbon monoxide. Air oxidation of the anthrol anion is responsible for formation of anthraquinone and 10,10′-bianthrone. The photochemical isomerization of sodium 9-anthroate to anthrol anion is considered to be analogous to the photoisomerization of 9-nitroanthracene.

Recent investigations of vinyl[2,3] and aryl[2,4] nitro compounds have uncovered photochemical rearrangements in which the nitro group isomerizes to a nitrite ester which then gives rise to products.

Irradiation (λ <410 mμ) of 9-nitroanthracene gives, for example, 10,10′-bianthrone as the major product and lesser amounts of anthraquinone and anthraquinone monooxime,[2,5] while β-methyl-β-nitrostyrene gives 1-phenyl-1-oximino-2-propanone.[2,3]



As one aspect of our investigation of these rearrangements, we have considered whether the carboxylate anion which is isoelectronic with the nitro group might show related rearrangements. Both the nitro group and the carboxylate group are capable of n → π* and π → π* transitions. Sodium 9-anthroate was selected for initial study because of its relationship to 9-nitroanthracene. Weigert and Ludwig have reported[6] that irradiation of aqueous solutions of sodium 9-anthroate which were open to air gave a precipitate (anthraquinone)

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[1] Photochemical Transformations, part XVIII. Portions of this report were abstracted from the M.S. thesis of A. W. Bradshaw, Iowa State University of Science and Technology, 1966.

[2] O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *Pure Appl. Chem.*, **9**, 585 (1964).

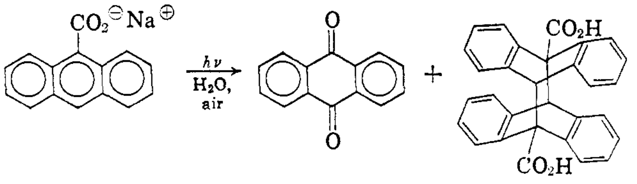
[3] O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Commun.*, 101 (1966).

[4] O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Am. Chem. Soc.*, **88**, 5550 (1966).

[5] F. D. Greene, *Bull. Soc. Chim. France*, 1356 (1960).

[6] F. Weigert and L. Ludwig, *Ber.*, **47**, 898 (1914).

and upon acidification the photodimer. Subsequent studies[7] have shown that the photodimer has the head-to-tail structure. Dufraisse and Mathieu have shown that irradiation of disodium anthracene-9,10-dicarboxylate in solutions exposed to air also gives anthraquinone.[8] It has been assumed generally that the formation of anthraquinone in these irradiations involved the 9,10-epidioxide in each case.



Results

The results of our initial irradiations of sodium 9-anthroate are given in Table I. The formation of photodimer and anthraquinone was confirmed, and 10,10′-bianthrone and anthracene were observed as minor products. Flushing the solution with purified nitrogen[9] during the irradiation (which should remove almost all oxygen from the solution) had little effect on product composition. A change in concentration of sodium 9-anthroate from 0.040 to 0.0045 *M* reduced the yield of dimer slightly but did not affect the yields of the other products significantly. Use of light of wavelength 290–360 mμ gave substantially lower yields of photodimer than were obtained when the full output of lamp above 290 mμ was used.[10] Irradiation of carefully degassed aqueous solutions of sodium 9-anthroate in sealed ampoules permitted isolation and characterization of carbon monoxide. Monitoring the irradiation of the degassed solutions in sealed ampoules by ultraviolet absorption spectroscopy revealed the presence of an intermediate with an absorption maximum at about 453 mμ. This absorption is characteristic of 9-anthrol anion (Figure 1).

Table I. Irradiation of Sodium 9-Anthroate

Conditions	% pure compound isolated Starting material	Dimer of 9-anthroic acid	Anthraquinone	Anthracene	10,10′-Bianthrone
5-hr irradiation in water in a Pyrex vessel open to the atmosphere; concn, 0.040 *M*	58	25	3	...	...
5-hr irradiation in water in a Pyrex vessel with nitrogen flush; concn, 0.040 *M*	33	39	4	...	...
20-hr irradiation in water in a Pyrex vessel with nitrogen flush; concn, 0.0045 *M*	42	31	9	4	2
19.5-hr irradiation in water in a Pyrex vessel using λ 290–360 mμ and nitrogen flush, concn, 0.0033 *M*	54	11	11	3	7

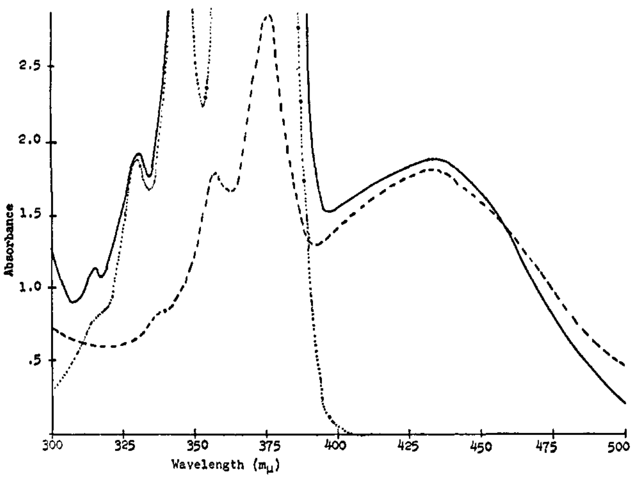


Figure 1. Ultraviolet spectra of anthrol anion, - - - -; sodium 9-anthroate, ... ; and the aqueous solution of sodium 9-anthroate after irradiation and before exposure to atmospheric oxygen, ———.

Irradiation (290–360 mμ) of the disodium salt of the photodimer in degassed solution in a sealed tube gave sodium 9-anthroate and the anthrol anion. The formation of dimer is thus photochemically reversible when light is absorbed by the dimer. Formation of anthrol anion presumably is a secondary process based on sodium 9-anthroate which has a greater molar extinction coefficient in this region than the dimer.

Discussion

The photochemical conversions of sodium 9-anthroate are summarized in Chart I. Formation of the photodimer is reversible, and this reversibility is presumably responsible for the wavelength dependence of dimer yield. Decarboxylation of sodium 9-anthroate is mildly surprising, but other photochemical decarboxylations are known.[11] In any event, decarboxylation is a minor process. The most interesting reaction is the photochemical conversion of 9-anthroate anion to anthrol anion. The anthrol anion is known to react rapidly with oxygen giving both anthraquinone and 10,10′-bianthrone.[12] In the absence of oxygen only anthrol anion is formed, but when oxygen is admitted during work-up it is oxidized to the observed products. The nature of the excitation (n,π^* or π,π^*) in sodium 9-anthroate and the multiplicity of the reactive state are not known.

The formation of the anthrol anion can be described in much the same fashion as the nitro to nitrite rearrangements. It is assumed for the sake of discussion

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[7] D. E. Applequist, T. L. Brown, J. P. Keiman, and S. T. Young, *Chem. Ind.* (London), 850 (1959).

[8] C. Dufraisse and J. Mathieu, *Bull. Soc. Chim. France*, **14**, 307, (1947).

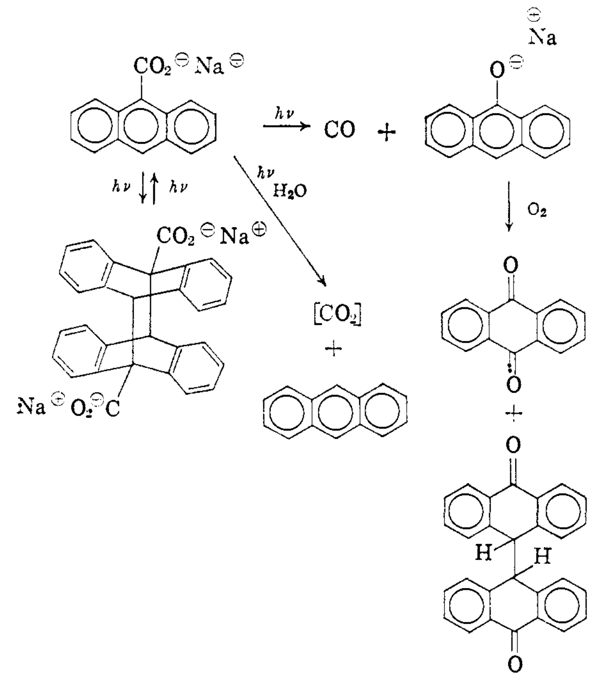
[9] Rigorous degassing by freeze–thaw cycles was not practical for synthesis scale work. Nitrogen flushing during the irradiation should keep the solutions almost oxygen free. In rigorously degassed solutions oxidation occurred during work-up, and this is presumed to be the case in the solutions flushed with nitrogen.

[10] This wavelength dependence is analogous to that reported by Greene for 9-nitroanthracene.[5]

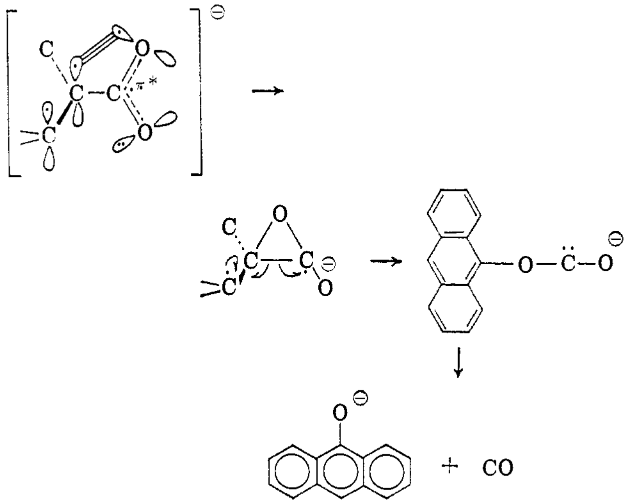
[11] J. D. Margerum, *J. Am. Chem. Soc.*, **87**, 3772 (1965).

[12] H. L. J. Backstrom and H. A. Beatty, *J. Phys. Chem.*, **35**, 2530 (1931).

Chart I



that the excitation responsible for this reaction is localized in the carboxylate group and is n,π^*. The plane of the carboxylate group will be nearly at right angles to the plane of the aromatic rings because of the *peri* hydrogens.



The out-of-plane carboxylate group has the half-vacant nonbonding orbital properly aligned for interaction with the π system of the aromatic rings.[13] The anthrol anion formed by loss of carbon monoxide is stable (in the absence of oxygen), in contrast to the 9-anthryloxy radical which is formed when nitric oxide is lost from the corresponding nitrite.

Experimental Section

Irradiation of Sodium 9-Anthroate Open to the Atmosphere. A water solution of sodium 9-anthroate was made by dissolving 9-anthroic acid (4.0 g, 0.018 mole) in water (450 ml) to which sodium hydroxide (18.0 ml of 1.00 *M*, 0.018 mole) had been added. The solution (0.040 *M*, pH 9.5) was filtered into a 500-ml capacity Pyrex immersion well. The solution, open to the atmosphere, was irradiated for 5 hr with a Hanovia Type A, medium-pressure, mercury arc lamp. The solution was filtered. The solid (56 mg, 1.4% of the sample weight, mp 234–237°) was dissolved in hot benzene and chromatographed on 40 g of silica gel giving anthraquinone (0.04 g, 1.1%, mp 255–262°). The filtrate from the irradiation was continuously extracted with ether giving anthraquinone (0.07 g, 1.8% yield). The total yield of anthraquinone was 2.9%.

The water solution was acidified with 1.5 ml of concentrated hydrochloric acid and continuously extracted with ether. White crystals formed in the yellow ether solution. Filtration yielded the photodimer of 9-anthroic acid (0.99 g, 25% yield, mp 216–220°, infrared 5.88 μ).

Anal. Calcd for $C_{30}H_{20}O_4$: C, 81.07; H, 4.54. Found: C, 80.98; H, 4.63.

The acid dimer was converted to the methyl ester (mp 222–223°, lit.[7] 226–227°) by addition of the acid chloride to methanol. The mass spectrum of the methyl ester showed *m/e* 472 (0.5% of base) for the parent ion and *m/e* 236 (93.5% of base) for symmetrical cleavage of the dimer.

Evaporation of the ether solution gave crude 9-anthroic acid (2.3 g, 58%) which was identified by infrared comparison.

Irradiation of Sodium 9-Anthroate with a Nitrogen Flush. A water solution of sodium 9-anthroate was made from 9-anthroic acid (4.0 g, 0.018 mole) and sodium hydroxide (18 ml of 1.00 *M*, 0.018 mole) and enough water to make a total volume of 450 ml. The solution (0.040 *M*, pH 9) was filtered into a 500-ml capacity Pyrex well. Nitrogen was passed through the solution for 1 hr. The yellow solution was irradiated for 5 hr with a Hanovia Type A, medium-pressure, mercury arc lamp with a continuous flow of purified nitrogen. The solution was filtered. The solid (120 mg, 3.0% of the sample weight) was chromatographed on 50 g of silica gel giving anthraquinone (0.10 g, 2.7%, mp 232–238°, identified by infrared comparison with an authentic sample). The mass spectrum of the product showed *m/e* 208 for the parent ion, *m/e* 180 with a metastable ion at *m/e* 155.5 for the loss of carbon monoxide, and *m/e* 152 with a metastable ion at 128.2 for the second loss of carbon monoxide, in agreement with the mass spectrum of anthraquinone reported by Beynon.[14]

Continuous extraction of the filtrate with ether gave anthraquinone (0.03 g, 0.8%). The total yield of anthraquinone was 3.5%.

The water solution was acidified with 1.5 ml of concentrated hydrochloric acid and continuously extracted with ether. Filtration of the yellow ether solution gave the photodimer of 9-anthroic acid (1.5 g, 39% yield, mp 219–220°) which was identified by infrared comparison. Evaporation of the ether gave crude 9-anthroic acid (1.3 g, 33%).

Irradiation of Sodium 9-Anthroate at Lower Concentrations. The solution of sodium 9-anthroate was made from 9-anthroic acid (2.00 g, 0.009 mole), sodium hydroxide (20 ml of 0.50 *M*, 0.010 mole), and enough water to make the total volume 2 l. The solution (0.0045 *M*, pH 11) was filtered into a Pyrex immersion well, and purified nitrogen was passed through for 2 hr. The nitrogen was purified by passage through a trap, two bottles of Fieser's solution, two traps, 18 *M* sulfuric acid, a trap, and finally a drying tower. The solution was irradiated for 20 hr with a Hanovia Type A, medium-pressure, mercury arc lamp.

The solution was filtered. The solid (0.2 g, 16% of the sample weight) was chromatographed on 40 g of silica gel giving anthracene (0.06 g, 4%, 206–214°), anthraquinone (0.17 g, 9%, 225–235°, C=O, 5.97 μ), and 10,10'-bianthrone (0.04 g, 2%, mp 243–247°, C=O, 6.02 μ).

The filtrate from the irradiation was acidified with 1.5 ml of concentrated hydrochloric acid and continuously extracted with ether. Filtration of the yellow ether solution after concentration gave the photodimer of 9-anthroic acid (0.62 g, 31% yield, mp 215–219°). Evaporation of the ether solution gave 9-anthroic acid (0.84 g, 42% yield, mp 212–214°).

Irradiation of Sodium 9-Anthroate with a Filter Solution. The filter solution was made by dissolving nickel sulfate (690 g of $NiSO_4 \cdot 6H_2O$) and cobalt sulfate (220 g of $CoSO_4 \cdot 7H_2O$) in water (1 l.). This solution for a 0.8-cm path length transmits 90% of the light at 300 mμ and less than 2.0% of the light from 360 to 540 mμ.

The solution of sodium 9-anthroate was made from 9-anthroic acid (2.4 g, 0.0108 mole), sodium hydroxide (1.00 g, 0.025 mole), and

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[13] The description of the excited state given above is very crude. Actually, the two nonbonding p atomic orbitals combine to give symmetric (n_s) and antisymmetric (n_a) combinations. The p atomic orbital representation is used for convenience.

[14] J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

enough water to make a total volume of 3.2 l. The solution (0.00328 M, pH >11) was filtered into a Pyrex immersion well. Purified nitrogen was passed through for 1.5 hr.

The solution was irradiated for 19.5 hr with a Hanovia Type A, medium-pressure, mercury arc lamp, The highest temperature that the filter solution reached was 55°. The solution was filtered. The solid (0.28 g, 12% of the sample weight) was chromatographed on 45 g of silica gel giving anthracene (0.02 g, 1%, mp 196–203°), anthraquinone (0.15 g, 6.7%, mp 230–239°), and 10,10′-bianthrone (0.09 g, 4.2%, mp 253–256°).

The filtrate was continuously extracted with ether for 3 days. The solid (0.2 g) from the evaporation of the ether was chromatographed on 20 g of silica gel giving anthracene (0.03 g, 1.5%, mp 185–190°), anthraquinone (0.09 g, 4.0%, mp 232–243°), and crude 10,10′-bianthrone (0.05 g, 2.4%, mp 235–240°). The total yields of the three products were anthracene (2.5%), anthraquinone (11%), and 10,10′-bianthrone (6.6%).

The filtrate was acidified with 10 ml of concentrated hydrochloric acid and continuously extracted with ether for 3 days. The ether solution was evaporated to dryness. The solid was recrystallized from benzene. Filtration of the hot benzene solution gave the photodimer of 9-anthroic acid (0.25 g, 11%). Upon cooling, the benzene solution gave crystals of 9-anthroic acid (1.4 g, 54%).

Irradiation of Sodium 9-Anthroate in a Sealed Tube. The ampoule was made from a test tube (13 × 100 mm) and a standard taper inner joint (14/20). The ampoule was filled with 5 ml of sodium 9-anthroate (0.003 M) in water. The ampoule was frozen in a Dry Ice–trichloroethylene bath, evacuated to 0.025 mm, closed, and allowed to thaw. This process was repeated except before being thawed the second time it was sealed off. The ampoule was irradiated for 5 hr with a Hanovia Type A, medium-pressure, mercury arc lamp using the nickel sulfate–cobalt sulfate filter solution described above. The ultraviolet spectrum (Figure 1) of the solution shows the presence of the anthrol anion.

Irradiation of Sodium 9-Anthroate in a Sealed Tube to Identify Carbon Monoxide. 9-Anthroic acid (2.00 g, 0.009 mole) and 10% sodium hydroxide (50 ml) were diluted to 75 ml. The solution (0.12 M) was put in a heavy-walled, Pyrex, 100-ml capacity tube fitted with a vacuum stopcock. The tube was frozen, evacuated to 0.02 mm, closed, and thawed. This process was repeated four times. The tube was irradiated for 19 hr with a Hanovia Type A, medium-pressure, mercury arc lamp using the nickel sulfate–cobalt sulfate filter solution described above. After irradiation the product gases were expanded into an infrared gas cell. The infrared spectrum showed, in addition to the bands for the water present, a broad band at 4.7 μ (lit.[15] for carbon monoxide 4.67 μ).

The solution was filtered giving a solid (0.02 g) which by infrared comparison was shown to be a mixture of anthraquinone and 10,10′-bianthrone. No further attempt at separation was made.

Irradiation of the Disodium Salt of the Photodimer of 9-Anthroic Acid in a Sealed Tube. The dimer of 9-anthroic acid (0.222 g, 0.0005 mole) was dissolved in 10% sodium hydroxide (20 ml) and diluted to 25 ml (0.02 M). An ampoule containing 6 ml of the solution was prepared in the manner previously described and irradiated. The ultraviolet spectrum of the solution showed the presence of sodium 9-anthroate and the anthrol anion. Filtration of the solution gave water-insoluble compounds (0.006 g, 11% of starting material). The filtrate was acidified and continuously extracted with ether. Filtration of the ether solution gave dimer (0.038 g, 71% yield) and evaporation gave 9-anthroic acid (0.007 g, 13% yield).

Acknowledgment. Portions of this research were supported by a grant from the National Science Foundation (GP-6740).

(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

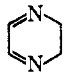
The Photorearrangement of 2,3-Dihydropyrazines

Peter Beak and John L. Miesel[1]

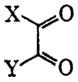
Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. *Received November 28, 1966*

Abstract: Six 2,3-dihydropyrazines have been found to rearrange to imidazoles upon photolysis. Data are presented in support of the proposal that the reaction proceeds through an irreversibly formed enediimine intermediate.

Formal comparison of the photolysis of the 2,3-dihydropyrazine system **1** with the photochemistry of the structurally related and extensively studied α-dicarbonyl systems **2** and six-membered cyclic dienes **3** could be of practical and theoretical interest.[2] Analogy with **2** suggests 1,4[3] and 1,2[4] additions, reduction,[5] oxidation,[4c,5] and radical formation[6] might occur upon photolysis of **1**. If **3** is allowed as an analogy, ring opening to a triunsaturated system,[7] ring closure to a bicyclo[2.2.0] system,[8] formation of a bicyclo[3.1.0] system,[7g,9] dimerization,[10] or aromatization[11] might



1



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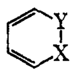

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(1) National Science Foundation Fellow, 1962–1964; University of Illinois Fellow, 1964–1965; Union Carbide Fellow, 1965–1966.

(2) The formal aspects of these comparisons must be emphasized. Different systems are involved and the details of the processes may be very different. *Cf.* J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 528–530.

(3) (a) A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 551 (1945); (b) R. Moore and W. Waters, *ibid.*, 238 (1953); (c) M. Rubin, *J. Org. Chem.*, **28**, 1949 (1963); (d) J. J. Bohning and K. Weiss, *J. Am. Chem. Soc.*, **88**, 2893 (1966), and references cited therein.

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(5) (a) W. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 118 (1962); (b) J. Meinwald and H. Klingle, *ibid.*, **88**, 2807 (1966); (c) P. W. Jolly and P. de Mayo, *Can. J. Chem.*, **42**, 170 (1964).

(6) Calvert and Pitts, ref 2, p 421.

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(8) (a) W. G. Dauben and G. J. Fonken, *ibid.*, **81**, 4060 (1959); (b) W. H. Schuller, R. N. Moore, J. E. Hawkins, and R. V. Lawrence, *J. Org. Chem.*, **27**, 1178 (1962); (c) H. Prinzbach and J. H. Hartenstein, *Angew. Chem. Intern. Ed. Engl.*, **2**, 471 (1963); (d) E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, **86**, 950 (1964); (e) W. G. Dauben and R. M. Coates, *ibid.*, **86**, 2490 (1964).

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