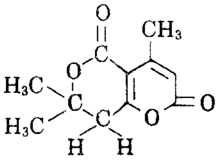
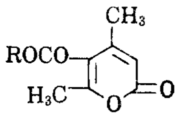
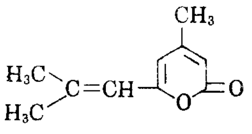
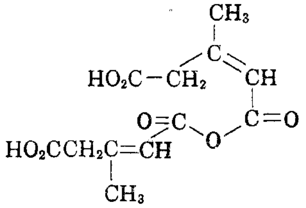
rect route to this pyrone which is of interest as a possible intermediate or inhibitor in the biosynthesis of cholesterol. This direct synthesis has been achieved to give 35% yield of the pyrone from the acid. The acid is first heated to 250° at atmospheric pressure for one hour and then, after addition of copper, to 300° for an additional hour during which time the pyrone distills from the reaction mixture.

The formation of the dimer can be accounted for assuming a condensation in the linear anhydride (IV) between a methylene group and anhydride carbonyl followed by lactonization and decarboxylation or by a self-acylation of the anhydride and its decarboxylated product followed by a rearrangement in which the intermediate is lactonized rather than decarboxylated as in previously observed[5] reactions of this type. There may be no fundamental difference in these two possibilities. In each the anhydride, or acid, carbonyl condenses at the methylene carbon as a means of providing the carbon—carbon bond required to form the 2-pyrone ring. Both have, however, been previously observed only as base-catalyzed reactions. The dimer has been obtained from the senecioyl chloride acylation of the anhydride which indicated the feasibility of the later reaction sequence.


I


II


III


IV

EXPERIMENTAL[6]

Preparation of the dimer (I). Fifty grams (0.35 mole) of β-methylglutaconic acid was placed in a 125-ml. Claisen flask with a receiver, an ebulator, and a thermometer. The pressure was reduced to 3 mm. The flask was heated to 185° over a 0.5-hr. period. The temperature was held constant until the pressure which suddenly rises to 60 mm. dropped to 10 mm. The temperature was then again raised slowly and the material distilling between 180 and 210° was collected. Upon recrystallization from methanol 15 g. of material, m.p. 154–155°, was obtained.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; sapon. equiv. 69.4; mol. wt. 208.4. Found: C, 63.36; H, 6.09; sapon. equiv., 69 (in ethylene glycol); mol. wt. 204 (Rast).

Conversion of dimer to phorone. One gram (0.0048 mole) of the dimer was dissolved in 20 ml. of 1N potassium hydroxide in ethylene glycol. The solution was heated slowly to 130° over a period of 30 min. and held at this temperature for 15 min. Ten ml. of water was added to the cooled solution. The acidified solution was extracted with ether. The ether extracts were washed with aqueous sodium carbonate, dried, and evaporated to give a residue. Distillation of this residue gave 0.2 g. of material which gave a positive ketone test. The infrared spectra of this product was identical with that of an authentic sample of phorone. The dinitrophenylhydrazone, m.p. 109°, was prepared and gave no depression in melting point when a mixed melting point was run with an authentic sample.

4-Methyl-6-(2′-methylpropenyl)-2-pyrone by pyrolysis of the dimer. A mixture of 5.0 g. (0.024 mole) of the high boiling fraction and 1.0 g. of copper powder was heated on a Wood's metal bath at 270–290° for 1.5 hr. After the initial heating period the temperature of the bath was gradually raised to 350°. There was collected as distillate 1.7 g. (43%) of 4-methyl-6-(2′-methylpropenyl)-2-pyrone. Refractionation gave a fraction b.p. 109°/1 mm., which was recrystallized from ether to give the pyrone, m.p. 45–46°. The infrared spectrum of the product was identical with that of an authentic sample of the pyrone prepared as previously described.

4-Methyl-6-(2′-methylpropenyl)-2-pyrone by pyrolysis of β-methylglutaconic acid. In a 25-ml. distilling flask was placed 15.0 g. (0.104 mole) of crude β-methylglutaconic acid. The flask was immersed in a Wood's metal bath previously heated to 250°. The crude acid melted and evolved carbon dioxide vigorously. A small amount of low boiling material was collected as distillate. After this initial reaction had subsided, the flask was heated for 1 hr. at 250° and then, after adding 1.0 g. of copper powder, at 300° for 1 hr. The temperature of the bath was then gradually raised to 360° during which time 3.1 g. (38%) of 4-methyl-6-(2′-methylpropenyl)-2-pyrone was collected. The infrared spectrum of the product was identical with that of an authentic sample of the pyrone prepared as previously described.

Acknowledgment. The authors wish to acknowledge partial support of this research through grants from the Damon Runyon Memorial Fund, National Science Foundation, Eastman Kodak Company, and United States Public Health Service.

Department of Chemistry
University of Louisville
Louisville 8, Ky.

---

[5] Richard H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, **74**, 3893 (1952).

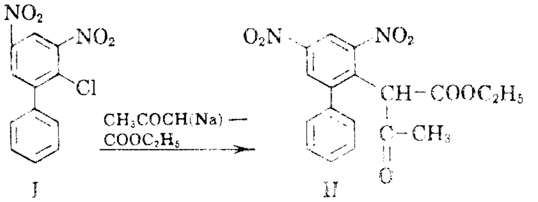
[6] Analyses by Micro Tech Laboratories, Skokie, Ill.

Some 1,3-Dinitrophenanthrene Derivatives

Charles K. Bradsher and Dorothy J. Beavers

Received April 22, 1957

In earlier experiments,[1] directed toward the synthesis of dinitrophenanthrene derivatives, it was found that 3,5-dinitro-2-chlorobiphenyl (I) with

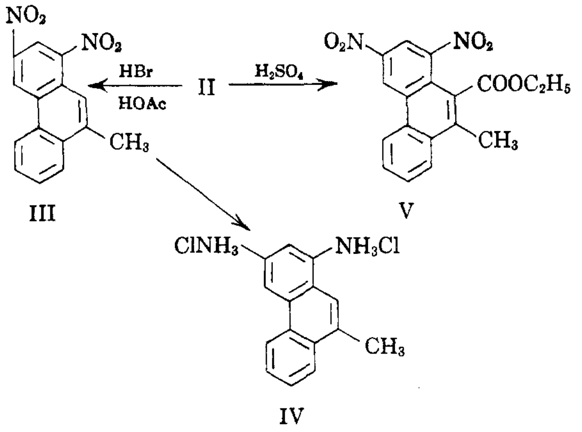


---

[1] C. K. Bradsher and S. T. Amore, *J. Am. Chem. Soc.*, **66**, 1283 (1944).

sodio-acetoacetic ester in ethanol merely underwent ethoxylation, while in inert solvents such as benzene, xylene, or dioxane, no reaction was apparent. Subsequently, Zaheer and Kacker[2] observed that, in ether the reaction (I–II) is very slow (2–3% yield after 58 hours)[3] but found that sodioacetoacetic ester and the halide (I) could be made to react more completely if heated *without solvent* at 100–110°. More recently Zaheer and Kacker[4] have published a warning that carrying out the reaction on a scale larger than five to six grams of the diphenyl compound may lead to explosion.

It has been our own experience that violent decomposition occurred frequently (two runs out of seven) even on a 5.5 g. scale. It has also been found that an easily controlled reaction, leading to cleaner products, can be obtained at a moderate temperature by use of a large excess of acetoacetic ester as the solvent. As had been anticipated,[1] the dinitrobiphenylyl ester (II) may be cyclized in a boiling hydrobromic–acetic acid medium, affording 1,3-dinitro-9-methylphenanthrene (III) in 54% yield. Reduction of the dinitrophenanthrene (III) yielded 1,3-diamino-9-methylphenanthrene, isolated as the dihydrochloride (IV).



The two nitro groups have a strong deactivating influence on all of the rings of the phenanthrene skeleton of III, as evidenced by its resistance to nitration.

Cyclization of the keto ester II in concentrated sulfuric acid appeared to occur without decarboxylation, yielding a mixture consisting chiefly of ethyl 1,3-dinitro-9-methyl-10-phenanthrenecarboxylate (V) contaminated with some of the free acid.

EXPERIMENTAL

Ethyl α-(3,5-dinitrobiphenylyl-2)acetoacetate (II). Sodium metal (0.25 g.) was allowed to react with 7 g. of dry ethyl acetoacetate and the mixture was heated for 15.5 hr. at 60° with 1.5 g. of 3,5-dinitro-2-chlorobiphenyl.[1] The mixture was dissolved in 3% sodium hydroxide solution, and the product was precipitated by acidification with nitric acid. Recrystallization from ethanol yielded 0.9 g. (45%) of yellow prisms, approximate m.p. 105–107.5°. The analytical sample was obtained by recrystallization from ethanol, m.p. 104–106° (lit.[4] m.p. 102–103°); λ_{max}[5] (log ε) 250 (4.34) and 327 mμ (broad, 3.30); λ_{min} 298 mμ (3.10).

Anal. Calcd. for $C_{18}H_{16}N_2O_7$: C, 58.06; H, 4.33. Found: C, 58.33; H, 4.41.

Essentially the same yield (42% of slightly less pure material, m.p. 100–107°) was obtained when the condensation was carried out as above except that the reaction was allowed to proceed for 12 days at 20°. Essentially the same results were obtained when 3,5-dinitro-2-bromobiphenyl[2] was allowed to react for 16 hr. at 60° (45%) or for one month at 20° (43.5%).

1,3-Dinitro-9-methylphenanthrene (III). One gram of the dinitrobiphenylylacetoacetic ester (II) was dissolved in 20 ml. of acetic acid, 12 ml. of 48% hydrobromic acid was added, and the mixture was refluxed for 8 hr. The product was collected and recrystallized from benzene affording 0.41 g. (54%) of a grey powder, m.p. 215–217°. An analytical sample obtained by recrystallization from ethanol consisted of yellow needles, m.p. 221–222.5°; λ_{max} (log ε) 239 (4.58), 307 (inflection, 383) 355 mμ (broad, 3.97); λ_{min} 301 mμ (3.69).

Anal. Calcd. for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57. Found: C, 63.76; H, 3.53.

Samples of the dinitromethylphenanthrene (III), crystallized from benzene, appeared to be solvated and could not be freed from benzene even by drying for 24 hr. at 80° (1 mm.).

A 0.5-gram sample of III was dissolved in glacial acetic acid (75 ml.) and heated with 10 ml. of fuming nitric acid at 90° for 1 hr. The starting material was recovered unchanged.

1,3-Diamino-9-methylphenanthrene dihydrochloride (IV). One-half gram of the dinitromethylphenanthrene (III) was suspended in 150 ml. of absolute ethanol, 0.1 g. of Adams' catalyst was added, and the mixture was hydrogenated with stirring at room temperature. After slightly more than the theoretical quantity of hydrogen had been absorbed, the solution was filtered and poured into water. The resulting mixture was extracted with ether four times, and the ethereal extract washed with water and then saturated with hydrogen chloride, affording a pale pink solid. Recrystallization from ethanol-concentrated hydrochloric acid yielded cream-colored prisms shrinking at 310° before decomposing at 315–317°.

Anal. Calcd. for $C_{15}H_{15}Cl_2N_2 \cdot {}^1/_2H_2O$: C, 59.41; H, 5.32. Found: C, 59.64; H, 5.58.

1,3-Dinitro-9-methyl-10-carbethoxyphenanthrene (V). (*a*) *By cyclization of the keto ester* II. Three grams of the keto ester II was dissolved in 125 ml. of concentrated sulfuric acid at room temperature, and the purple solution stirred occasionally during the course of 0.5 hr. The mixture was then poured on ice and the flocculent precipitate was collected, washed with water, and dried, yielding 2.63 g. of a tan solid. The solid was suspended in 200 ml. of a 15% ammonia solution and the mixture heated at 60° with stirring. Filtration of the red solution yielded a quantity of solid

---

[2] S. H. Zaheer and I. K. Kacker, *J. Indian Chem. Soc.*, **23**, 380 (1946).

[3] This very slow rate of reaction can best be attributed to steric factors. Zaheer and Kacker[2] have rejected the explanation of Bradsher and Amore[1] that steric hindrance about the activated halogen atom makes the size of the approaching anions of paramount importance. On the other hand they have offered no explanation for the fact that an ethanol solution of ethyl sodioacetoacetate with 2,4-dinitrochlorobenzene (unhindered) yields an acetoacetic ester derivative, while the same solution with 3,5-dinitro-2-chlorobiphenyl (hindered) yields the 2-ethoxy derivative.

[4] S. H. Zaheer and I. K. Kacker, *J. Indian Chem. Soc.*, **32**, 491 (1955).

[5] All spectra were determined in 95% ethanol using 1-cm. silica cells.

which was again suspended in 200 ml. of 15% ammonia solution and stirred overnight. Filtration yielded 1.76 g. of crude undissolved ester as a tan solid, m.p. 230–235°.

(*b*) *From the acid via the silver salt.* The ammonia extract obtained above (400 ml.) was added with stirring to a solution formed by dissolving 2 g. of silver nitrate in 40 ml. of concentrated ammonium hydroxide. The solution was heated in the steam bath for 2.5 hr. and then stirred overnight at room temperature. The chocolate powder was collected and dried; yield 0.56 g. The silver salt was suspended in 60 ml. of methanol containing 1 g. of ethyl iodide and the mixture refluxed for 4 hr. After removal of the silver iodide by filtration, the ester was isolated and recrystallized from ethanol, yielding 0.2 g. of long yellow needles, m.p. 230–234°. The analytical sample (procedure b) melted at 237–239°.

Anal. Calcd. for $C_{18}H_{14}N_2O_6$: C, 61.01; H, 3.98. Found: C, 61.11; H, 4.28.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, N. C.

Photodimerization of Acridizinium Salts

CHARLES K. BRADSHER, LEO E. BEAVERS,[1]
AND JAMES H. JONES

Received May 22, 1957

Crystalline acridizinium bromide monohydrate[2] (I) when exposed to irradiation by sunlight or from a sun lamp is converted to a higher melting, less soluble compound lacking the yellow color and the fluorescence characteristic of the starting material. The ultraviolet absorption spectrum of the new compound (Fig. 1) makes it clear that the irradiation has destroyed the conjugation characteristic of the acridizinium system. The possibility that photooxidation has taken place is easily eliminated by the observation that there is no change in weight during irradiation. Analysis indicates that the new product (II) has approximately the same composition as the starting material.

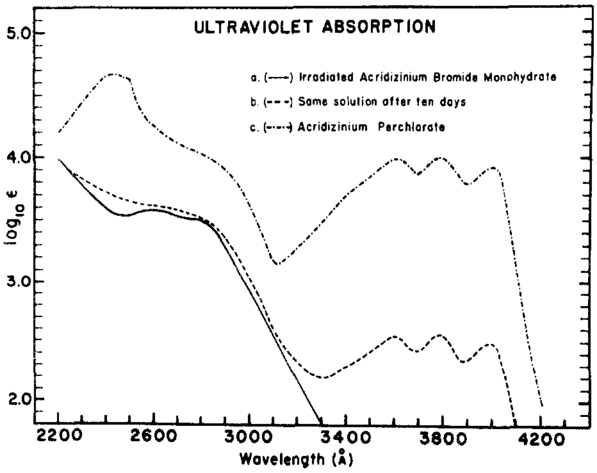
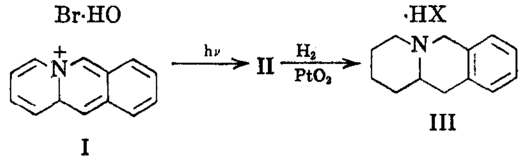


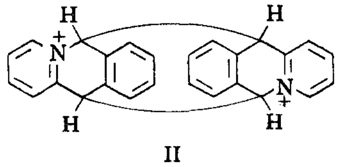
FIGURE 1.

The irradiation product is a salt and can be converted to a picrate and a perchlorate having the composition expected for the acridizinium analog. The bromide (II) was unaffected by refluxing for two hours in 48% hydrobromic acid and when heated at 100° with 6*N* nitric acid it was merely converted to the nitrate salt. When the bromide II was reduced catalytically in the presence of platinum oxide the only product identified was a salt of benzo[c]azabicyclo[4.4.0]decane (III).



An interesting observation was that a solution of the nonfluorescent irradiated bromide (II), in 95% ethanol, after standing at room temperature for ten days became faintly fluorescent. Spectroscopic examination of the solution showed a definite indication of the presence of a small quantity of the acridizinium ion. When the irradiation product (II) in 95% ethanol solution was refluxed for 18 hours it afforded acridizinium bromide in 82% yield. If this is a simple thermal dissociation it occurs more readily in solution since a sample of crystalline irradiated bromide II was unchanged after heating in a drying oven at 75° for 24 hours.

Analogy between the acridizinium ion and anthracene[3] suggested that the new product might be a photodimer. Anthracene[4] and many of its derivatives[5] dimerize when irradiated in *solution*, and the dimers are known to dissociate[5] on heating. Since the acridizinium ion is unsymmetrical, several isomeric forms of the meso-connected ion are theoretically possible. Structure II seems most likely[6] in that it permits maximum separation between the like charges.



II

Observations concerning boiling point elevation of ethanol solutions, although complicated by the

---

[1] Public Health Service Research Fellow of the National Institutes of Health, 1952–1954. This investigation was supported in part by a research grant (G-2364) of the National Science Foundation.

[2] C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **77**, 4812 (1955).

[3] A subsequent communication will describe another anthracene-type reaction of the acridizinium ion.

[4] J. Fritzsche, *J. Prakt. Chem.*, **101**, 333 (1867).

[5] F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **77**, 3852 (1955).

[6] It is possible that a detailed picture of the structure of II will be provided by the methods of x-ray crystallography. Professor J. M. Robertson has indicated his interest in the problem.