voltage of 3.5 kV, and an ion-source temperature of 230-250°C. The substances were introduced into the mass spectrometer through a direct admission system at 40-100°C. The purity of the compounds was monitored by thin-layer chromatography. The synthesis of the compounds was published in [5-7].

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HETEROCYCLIC ANALOGS OF PLEIADIENE.

XXXIV.* RECYCLIZATION REACTIONS OF 1,3-DIALKYL-SUBSTITUTED PERIMIDONES, THIOPERIMIDONES, AND 2,3-DIHYDROPERIMIDINES. NEW TYPE OF PHENALENONES WITH CONDENSED HETEROCYCLIC RINGS

I. V. Borovlev and A. F. Pozharskii

UDC 547.856.7

The corresponding phenalenones are formed immediately in the reaction of 1,3-dialkyl-substituted perimidones, thioperimidones, and 2,3-dihydroperimidines with propiolic acids and β-keto acid esters in polyphosphoric acid (PPA) at 40-75°C. Acylation of the perimidone and 2,3-dihydroperimidine derivatives with cinnamic and acrylic acids in PPA occurs in the 6 position and is accompanied by recyclization with the formation of a dihydrophenalenone ring. Acylation of 1,3-dialkylperimidones with aliphatic acids in PPA leads to 6,7-diacyl derivatives, by crotonization of which the corresponding phenalenones were also synthesized. The properties of the compounds are discussed.

We recently observed [2] that 1,3,8-trimethyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (Va), which is evidently the first phenalenone with a condensed heterocyclic ring, is formed along with 6-acetyl-1,3-dimethylperimidone (IIa) in the acylation of 1,3-dimethylperimidone (Ia) with acetic acid in polyphosphoric acid (PPA). In view of the known theoretical significance of phenalenones and their occurrence in nature [3-5], we made a more detailed study of this reaction and also worked out other methods (including methods that were heretofore unknown in the chemistry of phenalenones) for recyclization that lead to the formation of compounds of the V type. It should emphasized that 1,3-dialkylperimidones are extremely convenient compounds for the study of recyclization reactions, since the peri positions in them are uniquely accessible to electrophilic attack. This is explained by the fact that the 4 and 9 positions are blocked by N-alkyl groups [2, 6, 7], whereas the 5 and 8

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*See [1] for communication XXXIII.

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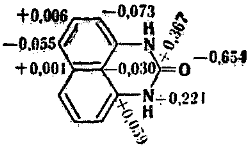
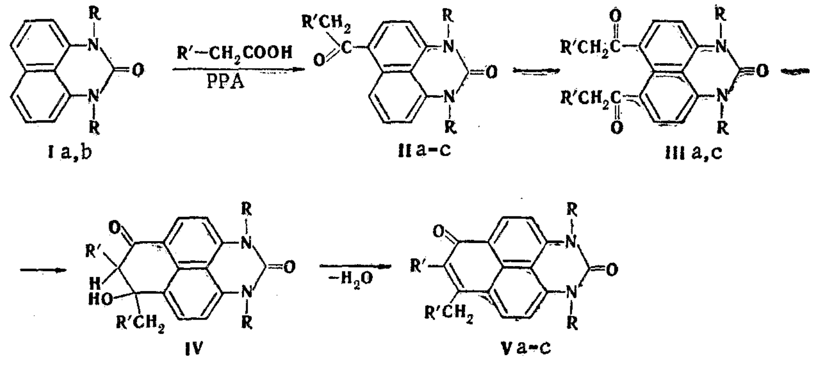
positions have an effective π charge of virtually zero because of the alternation of the charges in this system:



Acylation of Ia takes place at 50-55°C, and an increase in the amount of acetic acid from 1.2 moles to 2.5 moles (with respect to Ia) leads to a decrease in the yield of monoacetyl derivative IIa from 60% to 40%, whereas the yield of phenalenone Va increases by only 5% (from 30% to 35%). Somewhat lower yields of monoacetyl derivative IIb and phenalenone Vb (46 and 24%, respectively) were obtained in the acetylation of 1,3-diethylperimidone (Ib) with 1.5 moles of CH_3COOH. When propionic acid was used as the acylating agent, the yield of phenalenone Vc increased appreciably. Thus Vc was obtained in 37 and 75% yields, respectively, with 1.5 and 2.5 moles of CH_3CH_2COOH, whereas IIc was obtained in 55 and 3% yields. The structures of II and V were proved by means of the IR and PMR spectra, the features of which have been previously discussed [2, 6] (see also the Experimental section).

We established that phenalenones V are formed as a result of crotonic condensation of the intermediately formed 6,7-diacyl-1,3-dialkylperimidones (III), as in the case of 1,8-diacetylnaphthalene [8]. We were initially unable to isolate III, since they undergo conversion to phenalenones on the aluminum oxide used for the chromatographic separation of II and V. In fact, the crude product obtained when the reaction mixture is poured into water contains almost no phenalenone but rather consists of mono- and diacyl derivatives II and III. Their separation was based on the somewhat lower solubility of the latter in hot alcohol. Thus we obtained 6,7-diacetyl (IIIa) and 6,7-dipropionyl (IIIc) derivatives of 1,3-dimethylperimidone in 20 and 50% yields, respectively. Because of the loss of III during isolation, their actual yields can be judged from the amounts of phenalenones formed in the reaction. When α-methylene groups are absent in the acyl grouping (for example, in the case of benzoylation), the possibility of crotonization of the diacyl derivatives is excluded, and they are separated from the monoacylation products by chromatography.

The recyclization of III also proceeds readily when they are refluxed in piperidine. When we carried out the recyclization of IIIc in the presence of a catalytic amount of piperidine, we were also able to isolate an unstable intermediate product of aldol condensation (IV), the IR spectrum of which (in chloroform) contains a ν_{OH} band at 3610 cm^{-1}. Compound IV was converted quantitatively to Vc by brief heating in trifluoroacetic acid. Compound IV also does not have a characteristic melting point but changes color from yellow to orange when it is heated and melts at 302-303°C, i.e., at the melting point of Vc.

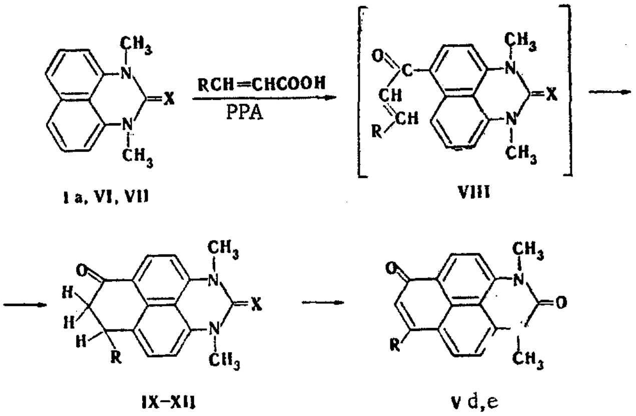


Ia $R=CH_3$; b $R=C_2H_5$; IIa, IIIa, Va $R=CH_3$, $R'=H$; IIb, Vb $R=C_2H_5$, $R'=H$;

IIc, IIIc, IVc, Vc $R=R'=CH_3$

In contrast to 1,3-dialkylperimidones, 1,3-dimethyl-2,3-dihydroperimidine (VI) and 1,3-dimethylthioperimidone (VII) do not form recyclization products under the same conditions; this is undoubtedly due to their lower activity in the acylation reaction [2] and the difficulty involved in the formation of 6,7-diacyl derivatives. The latter may be judged from the following fact: Whereas Ia reacts with 1.5 moles of benzoic acid in PPA for 5 h to give 6-benzoyl (43%) and 6,7-dibenzoyl (48%) derivatives, VI under the same conditions give monobenzoyl (54%) and dibenzoyl (3%) derivatives, and thione VII does not give diacylation products at all.

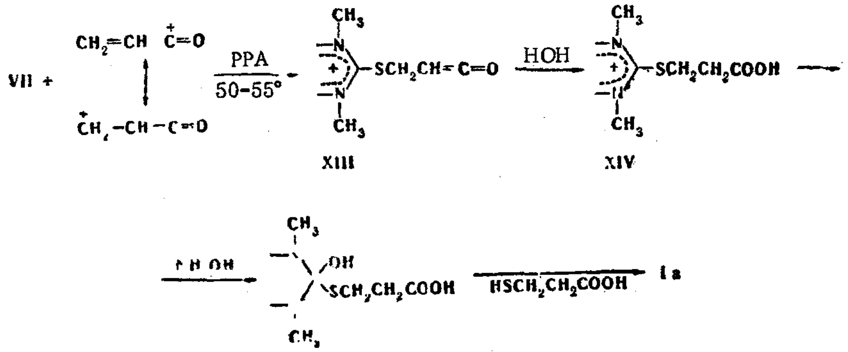
In the case of the acylation of perimidones and 2,3-dihydroperimidines with α,β-unsaturated carboxylic acids (for example, cinnamic and acrylic acids) the intermediately formed monoacyl derivatives VII undergo recyclization under the influence of PPA directly during the reaction. Compounds IX-XII, which contain a dihydrophenalenone ring, are formed in 48-73% yields in this reaction. As a rule, the reaction proceeds at 40-55°C. However, in the preparation of XII under these conditions a mixture of XII with another compound with a very close chromatographic mobility is formed. This other compound is evidently the corresponding cinnamoyl derivative VIII, since XII becomes the only reaction product when the temperature is raised. Attempts to acylate Ia with crotonic acid in PPA were unsuccessful because of resinification of the mixture.



Ia $X=O$; VI $X=H_2$; VII $X=S$; Vd $R=H$; e $R=C_6H_5$; IX $X=O$, $R=H$;
X $X=O$, $R=C_6H_5$; XI $X=H_2$, $R=H$; XII $X=H_2$, $R=C_6H_5$

When X is heated to 150-160°C in PPA, it undergoes dehydrogenation to give phenalenone Ve in 65% yield. Dehydrogenation also occurs when X is simply heated to 250°C (the product is obtained in 50% yield). Compound Ve can be obtained from Ia in one step by acylating Ia with cinnamic acid in PPA at 130-135°C. Compound IX is not inclined to undergo thermal dehydrogenation, but it is smoothly dehydrogenated by chloranil to give patent phenalenone Vd in 81% yield. An attempt to accomplish the oxidative dehydrogenation of XI and XII led to a complex mixture of substances that could not be separated into individual components.

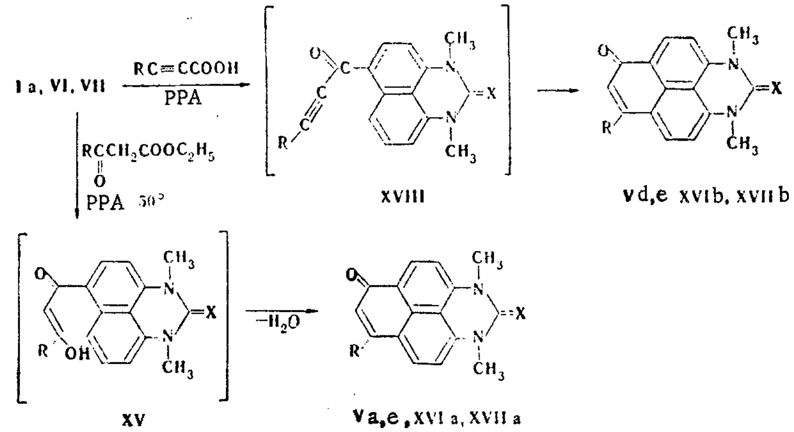
The result of the reaction of 1,3-dimethylthioperimidone VII with acrylic acid was somewhat unexpected. The only product of the reaction in PPA at 50-55°C was 1,3-dimethylperimidone (Ia) in 81% yield. This transformation evidently proceeds in conformity with the following scheme:



In the first step the ambident acryloyl cation present in the mixture alkylates VII at the sulfur atom with its "softer" (in accordance with the soft and hard acid and base principle) terminal C atom. The resulting cation (XIII) does not undergo acylation of the naphthalene ring under these conditions but is converted to salt XIV, which is readily soluble in water, when the mixture is decomposed with water. When the mixture is neutralized with ammonia, the salt undergoes nucleophilic attack by the OH^- ion to give Ia. By way of confirmation of this scheme, we were able to isolate XIV from the reaction mixture in the form of the perchlorate and prove its structure by means of elementary analysis and the IR and PMR spectra (see the Experimental section). 1,3-Dimethylperimidone precipitated immediately when the perchlorate of XIV was treated with ammonium hydroxide. Compound Ia is formed even when the salt of XIV is refluxed in water; this constitutes evidence for the greater electrophilicity of this cation as compared with the 1,3-dimethylperimidinium cation, which does not react with water [9].

Thus, in contrast to naphthalene derivatives [10, 11], the cyclization of the cinnamoyl- and acryloyl-substituted 1,3-dimethylperimidones and 1,3-dimethyl-2,3-dihydroperimidines (VIII) proceeds exclusively in the peri position. We were unable to detect o-cyclization products.

There is no mention in the literature of the use of β-keto acid esters and propiolic acid esters for the synthesis of phenalenones. Using acetoacetic and benzoylacetic esters, as well as phenylpropiolic and propiolic acids, in PPA we developed two new one-step methods for the synthesis of phenalenones that proceed in accordance with the following scheme:



Va X=O, R=CH_3; d X=O, R=H; e X=O, R=C_6H_5; XVIa X=H_2, R=CH_3; b X=H_2, R=C_6H_5; XVIIa X=S, R=CH_3; b X=S, R=C_6H_5

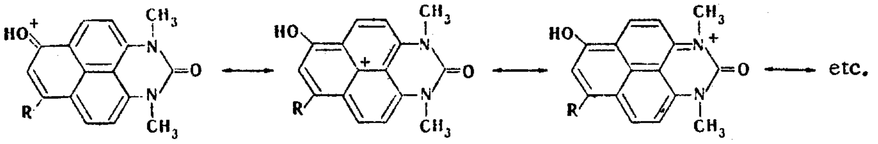
Thus phenalenones Va, XVIa, and XVIIa are formed in 83, 57, and 12% yields, respectively, in the reaction of 1,3-dimethyl derivatives of perimidone, 2,3-dihydroperimidine, and thioperimidone with acetoacetic ester in PPA at 50-55°C. Phenalenone Ve is formed in 58% yield in the reaction of Ia with benzoylacetic ester. The reaction evidently proceeds through a step involving the formation of monoacylation product XV, which cannot be isolated because of its high activity in a PPA medium. Perimidine itself does not react with acetoacetic ester in PPA at 50-55°C, and acetoacetic ester decomposes at higher temperatures.

The acylation of Ia, VI, and VII with phenylpropiolic acid at 40-75°C leads to the formation of phenalenones Ve, XVIb, and XVIIb in 72, 50, and 14% yields, respectively, i.e., in this case also the yields of phenalenones decrease on passing from Ia to VI and VII; this is in agreement with the above-noted decrease in the reactivities in the given order during acylation. Phenalenone Vd was obtained in only 13% yield in the reaction of Ia with propiolic acid at 50°C. In addition to Vd, a considerable amount of resin and a number of substances that could not be isolated in the individual state are formed in this reaction. We were also unable to isolate the intermediately formed monoacyl derivatives XVIII.

Thus an advantage of the methods of acylation by means of propiolic acids and β-keto acid esters is the fact that they make it possible to obtain phenalenones not only from perimidines but also from 2,3-dihydroperimidines and thioperimidones.

Of the compounds that we synthesized, 1,3-dialkyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrenes (Va-e), which in addition, are the most easily obtained compounds, are of the greatest interest. Phenalenones V are orange-yellow, high-melting substances that are moderately soluble in organic solvents. Their visible spectra contains two absorption maxima with approximately identical intensities at 460 and 485 nm. Dilute solutions of phenalenones Va-e have intense yellow-green luminescence with a maximum at 502-518 nm and a quantum yield of 0.56-0.72 [12]. For comparison we note that, as in the case of 4(9)- and 6(7)-acylperimidines, the luminescence quantum yield of 6-acetyl-1,3-dimethylperimidone (IIa) is only 0.2-0.3.

The IR spectra of phenalenones V are characterized by the presence of two absorption bands of carbonyl groups at 1670-1675 and 1629-1635 cm^{-1}, of which the latter is affiliated with the phenalenone ring (see the data for phenalenone itself [13]). Like phenalenone itself [4], the phenalenones that we obtained form stable hydrochlorides XIX with the positive charge delocalized not only in the phenalenone ring but also in the heteroring when dry HCl is bubbled into solutions in xylene (perimidones do not form salts with acids [9]):



XIX

EXPERIMENTAL

The calculation of the perimidone molecule by the Hückel MO method was accomplished with the Streitwiesser parameters. The IR spectra of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with an SF-4A spectrophotometer. The PMR spectra of 0.4-0.5-mole/liter solutions of the compounds were recorded with a Tesla BS 487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. Activity IV-V aluminum oxide (Brockmann scale) was used for chromatography.

Benzoylation of 1,3-Dimethylperimidone. A mixture of 1.06 g (5 mmole) of Ia, 0.92 g (7.5 mmole) of benzoic acid, and 10 g of PPA was stirred at 75-80°C for 5 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The yellow-green precipitate was removed by filtration, washed with water, and dried. The dry product was dissolved in the minimum amount of chloroform, and the solution was chromatographed with a column filled with aluminum oxide (~500 g) with elution by chloroform–benzene (1:1). Evaporation of the solvent from the first fraction gave a yellow oil, which crystallized rapidly when it was triturated with petroleum ether to give 0.68 g (43%) of 1,3-dimethyl-6-benzoylperimidone. Recrystallization from benzene–alcohol gave yellow-green crystals with mp 198-199°C. Found: C 76.2; H 5.5; N 9.0%. $C_{20}H_{16}N_2O_2$. Calculated: C 75.9; H 5.1; N 8.9%.

Workup of the second fraction yielded 1.02 g (48%) of pale yellow crystals of 1,3-dimethyl-6,7-dibenzoylperimidone with mp 273-274°C (from xylene). PMR spectrum (CF_3COO): 3.85 (6H, s, $N-CH_3$), 7.3-7.89 (10H, m, C_6H_5), 8.0 (2H, d, J = 10 Hz, 4,9-H), and 8.9 ppm (2H, d, J = 10 Hz, 5,8-H). Found: C 77.3; H 4.9; N 6.6%. $C_{27}H_{20}N_2O_3$. Calculated: C 77.1; H 4.8; N 6.7%.

Benzoylation of 1,3-Dimethyl-2,3-dihydroperimidine. A mixture of 1 g (5 mmole) of VI, 1 g (8.2 mmole) of benzoic acid, and 10 g of PPA was stirred at 70-75°C for 5 h, after which it was poured into water, and the aqueous mixture was neutralized. The dark-green precipitate was removed by filtration, washed with water, dried, and chromatographed with a column filled with 350 g of aluminum oxide (elution with chloroform). Two closely located yellow-green zones were eluted. Workup of the first zone gave 0.82 g (54%) of apple-green crystals of 1,3-dimethyl-6-benzoyl-2,3-dihydroperimidine with mp 125°C (from alcohol). Found: C 79.0; H 5.8; N 9.5%. $C_{20}H_{18}N_2O$. Calculated: C 79.4; H 6.0; N 9.3%. Workup of the second zone gave 0.07 g (3%) of pale-yellow crystals of 1,3-dimethyl-6,7-dibenzoyl-2,3-dihydroperimidine with mp 256-257°C (from xylene). Found: C 79.5; H 5.9; N 6.2%. $C_{27}H_{22}N_2O_2$. Calculated: C 79.8; H 5.5; N 6.6%.

Acylation of 1,3-Dimethylperimidone with Acetic Acid. The following method was a substantial modification of the method presented in [2]. A mixture of 1.06 g (5 mmole) of Ia, 0.7 ml (12.5 mmole) of acetic acid, and 15 g of PPA was stirred at 50-55°C for 6 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The green precipitate was removed by filtration, washed with water, and dried. The dry product was refluxed for 1 h with 12 ml of piperidine, during which an orange precipitate formed. The mixture was cooled and diluted to give five times its original volume with water, and the precipitate was removed by filtration, washed with water, and dried. Chromatographic separation on aluminum oxide by the method in [2] gave 0.51 g (40%) of 1,3-dimethyl-6-acetylperimidone (IIa) and 0.48 g (35%) of phenalenone Va, the constants of which are described in [2].

1,3-Dimethyl-6,7-diacetylperimidone (IIIa). The experiment was carried out as in the preceding case; however, the crude product was not heated with piperidine but rather was refluxed for 2-3 min in 25 ml of ethanol. The mixture was filtered, and the solid on the filter was washed with 5 ml of boiling alcohol and dried to give 0.3 g (20%) of light-yellow crystals of IIIa with mp 254-255°C (from toluene). Found: C 68.5; H 5.3; N 9.1%. $C_{17}H_{16}N_2O_3$. Calculated: C 68.9; H 5.4; N 9.4%.

Acylation of 1,3-Diethylperimidone with Acetic Acid. A mixture of 0.72 g (3 mmole) of 1,3-diethylperimidone, 0.26 ml (4.5 mmole) of acetic acid, and 7 g of PPA was stirred at 60-65°C for 3 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The dark-green precipitate was removed by filtration, washed with water, and dried. the dry product was dissolved in chloroform, and the solution was chromatographed with a column filled with 200 g of Al_2O_3. The first fraction was eluted with chloroform—benzene (1:1), and the second fraction was eluted with chloroform. Workup of the first fraction gave 0.39 g (46%) of pale-yellow crystals of 1,3-diethyl-6-acetylperimidone (IIb) with mp 135-136°C (from hexane). Found: C 72.0; H 6.2; N 10.1%. $C_{17}H_{18}N_2O_2$. Calculated: C 72.3; H 6.4; N 10.0%.

Workup of the second fraction gave 0.22 g (24%) of brown crystals of 1,3-diethyl-8-methyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (Vb) with mp 226-228°C (from benzene—hexane). IR spectrum ($CHCl_3$): ν_{CO} 1632 and 1671 cm^{-1}. Found: C 74.1; H 6.3; N 9.3%. $C_{19}H_{18}N_2O_2$. Calculated: C 74.5; H 5.9; N 9.1%.

Acylation of 1,3-Dimethylperimidone with Propionic Acid. A) A mixture of 0.64 g (3 mmole) of 1,3-dimethylperimidone, 0.33 ml (4.5 mmole) of propionic acid, and 7 g of PPA was stirred at 55-60°C for 3 h, after which it was poured into water, and the aqueous mixture was made alkaline with ammonia. The yellow precipitate was removed by filtration, washed with water, and dried. The dry product was dissolved in chloroform, and the solution was chromatographed with a column filled with 200 g of Al_2O_3. The first zone was eluted with chloroform—petroleum ether (1:1), and the second fraction was eluted with chloroform. Workup of the first fraction gave 0.45 g (55%) of yellow-green crystals of 1,3-dimethyl-6-propionylperimidone (IIc) with mp 206-207°C (from alcohol—benzene). Found: C 71.4; H 5.6; N 10.4%. $C_{16}H_{16}N_2O_2$. Calculated: C 71.4; H 6.0; N 10.4%.

Workup of the second fraction gave 0.35 g (37%) of yellow-orange crystals of 1,3,7-trimethyl-8-ethyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (Vc) (the product of aldol condensation of 1,3-dimethyl-6,7-dipropionylperimidone was often an impurity, and this hindered isolation of Vc) with mp 303-305°C (from xylene). IR spectrum ($CHCl_3$): ν_{CO} 1629 and 1671 cm^{-1}. PMR spectrum (CF_3COOH): 1.02 (3H, t, CH_3), 2.25 (3H, s, CH_3), 3.13 (2H, q, CH_2), 3.75 (6H, s, N—CH_3), 7.51 (1H, d, J = 9.2 Hz, 10-H), 7.53 (1H, d, J = 9.4 Hz, 4-H), 8.83 (1H, d, J = 9.2 Hz, 9-H), and 9.05 (1H, d, J = 9.4 Hz, 5-H). Found: C 74.8; H 5.9; N 9.0%. $C_{19}H_{18}N_2O_2$. Calculated: C 74.5; H 5.9; N 9.1%.

B) A mixture of 1.06 g (5 mmole) of 1,3-dimethylperimidone, 0.93 ml (12.5 mmole) of propionic acid, and 15 g of PPA was stirred at 55-60°C for 6 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The yellow-green precipitate was removed by filtration, washed with water, and dried. The dry product was refluxed with 12 ml of piperidine for 1 h, after which the mixture was cooled and diluted to five times its original volume with water. The precipitate was separated by filtration, washed with water, dried, and chromatographically separated by the method in the preceding experiment to give 0.04 g (3%) of 1,3-dimethyl-6-propionylperimidone and 1.15 g (75%) of Vc.

1,3-Dimethyl-6,7-dipropionylperimidone (IIIc). The experiment was carried out as in the preceding experiment (method B); however, the crude product was not heated with piperidine but rather was treated twice with 20 ml of boiling alcohol. The undissolved IIIc was dried to give 0.8 (50%) of light-yellow crystals with mp 217-218°C (from benzene). PMR spectrum ($CDCl_3$): 1.15 (6H, t, CH_3), 2.91 (4H, q, CH_2), 3.28 (6H, s, N—CH_3), 6.45 (2H, d, J = 8.6 Hz, 4,9-H), and 7.56 ppm (2H, d, J = 8.6 Hz, 5,8-H). Found: C 70.1; H 6.2; N 8.6%. $C_{19}H_{20}N_2O_3$. Calculated: C 70.4; H 6.2; N 8.6%.

Product of Aldol Condensation of 1,3-Dimethyl-6,7-dipropionylperimidone. A solution of 0.15 g of 1,3-dimethyl-6,7-dipropionylperimidone and 0.2 ml of piperidine in 10 ml of chloroform was refluxed for 2.5 h, after which it was allowed to stand overnight at room temperature. It was then chromatographed with a column filled with neutral activity V aluminum oxide (Brockmann scale); rapid elution with chloroform gave two zones. Workup of the first zone gave ~0.06 g (44%) of Vc, and workup of the second zone gave 0.08 g (53%) of 1,3,7-trimethyl-8-ethyl-8-hydroxy-2,6-dioxo-1,2,3,6,7,8-hexahydro-1,3-diazapyrene (IV). IR spectrum ($CHCl_3$): ν_{OH} 3610 cm^{-1}. Recrystallization from benzene—petroleum ether gave yellow crystals that did not have a characteristic melting point. When the crystals were heated, they gradually turned orange, and the compound melted at 302-303°C, i.e., at the melting point of Vc. According to the PMR data, the dehydration of IV proceeds readily and gives the product in quantitative yield when it is heated briefly in trifluoroacetic acid (until IV dissolved completely).

1,3-Dimethyl-2,6-dioxo-1,2,3,6,7,8-hexahydro-1,3-diazapyrene (IX). A mixture of 1.06 g (5 mmole) of 1,3-dimethylperimidone and 0.5 ml (7.5 mmole) of freshly distilled acrylic acid in 10 g of PPA was stirred at 50-55°C for 3 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The resinous precipitate was extracted with ten 5-ml portions of chloroform, and the extract was dried with sodium sulfate and chromatographed with a column filled with 300 g of Al_2O_3. The first yellow-green fraction was eluted with chloroform—petroleum ether (1:1). Evaporation of the solvent gave 0.64 g (48%) of pure IX as yellow-green crystals with mp 215-216°C (from alcohol). Found: C 71.9; H 5.6; N 10.8%. $C_{16}H_{14}N_2O_2$. Calculated: C 72.2; H 5.3; N 10.5%.

1,3-Dimethyl-6-oxo-1,2,3,6,7,8-hexahydro-1,3-diazapyrene (XI). A 0.5-ml (7.5 mmole) sample of acrylic acid was added to 1 g (5 mmole) of 1,3-dimethyl-2,3-dihydroperimidine in 10 g of PPA, and the mixture was stirred at 40-45°C for 4.5 h. It was then poured into water, and the aqueous mixture was neutralized. The dark-green precipitate was removed by filtration, washed with water, dried, and purified by chromatography on aluminum oxide (the first lemon-yellow fraction was eluted with chloroform) to give 0.66 g (52%) of shiny yellow-green plates of XI with mp 153-154°C (from alcohol). IR spectrum ($CHCl_3$): ν_{CO} 1640 cm^{-1}. PMR spectrum ($CDCl_3$): 2.6-3.4 (10H, m, N—CH_3 and CH_2), 4.1 (2H, s, CH_2), 6.38 (1H, d, J = 8 Hz, 10-H), 6.42 (1H, d, J = 8.5 Hz, 4-H), 7.18 (1H, d, J = 8 Hz, 9-H), and 8.1 ppm (1H, d, J = 8.5 Hz, 5-H). Found: C 76.0; H 6.0; N 11.3%. $C_{16}H_{16}N_2O$. Calculated: C 76.2; H 6.4; N 10.5%.

1,3-Dimethyl-8-phenyl-2,6-dioxo-1,2,3,6,7,8-hexahydro-1,3-diazapyrene (X). The reaction of 1.06 g (5 mmole) of 1,3-dimethylperimidone, 1.1 g (7.5 mmole) of cinnamic acid, and 10 g of PPA at 45-50°C for 4 h and subsequent isolation and chromatographic purification gave 1.24 g (73%) of X [the first fraction, which was eluted with chloroform—petroleum ether (1:1)] as bright-yellow crystals (from toluene). The product did not have a characteristic melting point because of dehydrogenation when it was heated. Found: C 77.6; H 5.6; N 8.0%. $C_{22}H_{18}N_2O_2$. Calculated: C 77.2; H 5.3; N 8.2%.

1,3-Dimethyl-8-phenyl-6-oxo-1,2,3,6,7,8-hexahydro-1,3-diazapyrene (XII). A mixture of 1 g (5 mmole) of 1,3-dimethyl-2,3-dihydroperimidine, 1.1 g (7.5 mmole) of cinnamic acid, and 10 g of PPA was heated with stirring in the course of 10 min to 105-110°C, after which it was maintained at this temperature for 45 min. Workup and chromatographic purification of the first yellow fraction (elution with chloroform) gave 1.2 g (73%) of XII as a clear yellowish oil that crystallized rapidly when it was triturated successively with diethyl ether and petroleum ether. The yellow crystals had mp 143-144°C (from benzene—petroleum ether). Found: C 80.2; H 5.8; N 8.2%. $C_{22}H_{20}N_2O$. Calculated: C 80.5; H 6.1; N 8.5%.

Attempted Acylation of 1,3-Dimethylperimidone with Crotonic Acid. A mixture of 1.06 g (5 mmole) of 1,3-dimethylperimidone, 0.65 g (7.5 mmole) of freshly distilled crotonic acid, and 10 g of PPA was subjected to the following conditions: 1) heating at 50-55°C for 2 h; 2) heating at 45-50°C for 2 h; 3) maintenance at room temperature for 2 days. However, workup of the reaction mixture in each case gave a large amount of dark-green resin, from which we were unable to isolate any individual compound.

Reaction of 1,3-Dimethylthioperimidone with Acrylic Acid in PPA. A mixture of 1.14 g (5 mmole) of 1,3-dimethylthioperimidone, 0.5 ml (7.5 mmole) of acrylic acid, and 10 g of PPA was stirred at 50-55°C for 7 h, after which it was poured into water, and the aqueous mixture was filtered to remove the insoluble impurities. Depending on the synthetic purposes, the resulting clear reddish solution was either neutralized with ammonia to pH 9-10 or treated with 40 ml of 30% perchloric acid. In the first case a white precipitate of 1,3-dimethylperimidone formed immediately and was removed by filtration, washed with water, and dried to give 0.86 g (81%) of product. In the second case the oily precipitate that formed crystallized immediately when it was allowed to stand and when it was triturated. The resulting 1,3-dimethyl-2-(β-carboxyethylthioxy)perimidinium perchlorate (XIV) was removed by filtration, washed with water, and dried to give red-brown crystals with mp 176-180°C. IR spectrum (mineral oil): ν_{CO} 1730 and ν_{OH} 3100-3300 cm^{-1}. PMR spectrum (CF_3COOH): 2.6 (2H, t, CH_2), 3.1 (2H, t, CH_2), 3.55 (6H, s, N–CH_3), 6.5 (2H, d, 4,9-H), and 7.0 ppm (4H, m, 5-8-H). Found: N 6.5%. $C_{16}H_{17}N_2O_6 \cdot SCl$. Calculated: N 7.0%.

1,3,8-Trimethyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (Va). A 1.06-g (5 mmole) sample of 1,3-dimethylperimidone and 0.95 g (7.5 mmole) of acetoacetic ester were added to 10 g of PPA, and the mixture was stirred at 50-55°C for 3 h, after which it was poured into water. The aqueous mixture was neutralized with ammonia, and the precipitate was removed by filtration, washed with water, and dried. Purification was achieved by chromatography (elution of the yellow-green zone with chloroform) to give 1.16 g (83%) of Va. UV spectrum, λ_{max} (log ε): 256 (4.37), 280 (4.04), 358 (3.58), 458 (4.34), and 483 nm (4.37).

XIX Hydrochloride (R = CH_3). This compound was formed by passing dry hydrogen chloride into a hot xylene solution of Va. The brown crystals had mp 278-280°C (dec.). IR spectrum (mineral oil): ν_{CO} 1680 and 1704 cm^{-1}. Found: C 64.4; H 4.9; Cl 11.3; N 9.5%. $C_{17}H_{51}ClN_2O_2$. Calculated: C 64.8; H 4.8; Cl 11.3; N 9.0%.

1,3,8-Trimethyl-6-oxo-1,2,3,6-tetrahydro-1,3-diazapyrene (XVIa). A mixture of 1.0 g (5 mmole) of freshly prepared 1,3-dimethyl-2,3-dihydroperimidine and 0.95 g (7.5 mmole) of acetoacetic ester in 10 g of PPA was stirred at 50-55°C for 3 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The resinous red precipitate and the aqueous layer were extracted with three 50-ml portions of chloroform, and the extract was dried with sodium sulfate. The chloroform was removed by evaporation to a volume of 30-35 ml, and the concentrate was chromatographed with elution of the orange zone with chloroform to give 0.75 g (57%) of orange-red crystals of XVIa with mp 252-254°C (from alcohol). IR spectrum ($CHCl_3$): ν_{CO} 1634 cm^{-1}. PMR spectrum (CF_3COOH): 2.25 (3H, s, CH_3), 2.85 (6H, s, N–CH_3), 4.65 (2H, s, CH_2), 6.48 (3H, m, 4, 7, 10-H), 7.85 (1H, d, J = 9.3 Hz, 9-H), and 8.1 ppm (1H, d, J = 9.5 Hz, 5-H). Found: C 77.0; H 6.0; N 10.7%. $C_{17}H_{16}N_2O$. Calculated: C 77.25; H 6.1; N 10.6%.

1,3,8-Trimethyl-6-oxo-2-thioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (XVIIa). A mixture of 1.14 g (5 mmole) of 1,3-dimethylthioperimidone, 0.95 ml (7.5 mmole) of acetoacetic ester, and 10 g of PPA was stirred at 50-55°C for 12 h, after which it was poured into water, and the aqueous mixture was neutralized. The light-brown precipitate was separated by filtration, washed with water, and dried. Purification was carried out by chromatography with collection of the first and second fractions (elution with chloroform). Workup of the first fraction gave ~0.7 g of impure starting compound. Workup of the second fraction gave 0.17 g (12%) of dark-yellow crystals of XVIIa with mp 303-304°C (from xylene). IR spectrum ($CHCl_3$): ν_{CO} 1648 cm^{-1}. Found: N 9.3%. $C_{17}H_{14}N_2OS$. Calculated: N 9.5%.

1,3-Dimethyl-8-phenyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (Ve). A) A mixture of 1.06 g (5 mmole) of 1,3-dimethylperimidone, 0.95 g (6.5 mmole) of phenylpropiolic acid, and 10 g of PPA was stirred at 50-55°C for 2 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The red precipitate was removed by filtration, washed with water, and dried. The dry product was extracted with warm chloroform (a total of ~150 ml), after which the chloroform was removed from the extract by evaporation to a volume of 35-40 ml, and the concentrate was chromatographed with a column filled with 350-400 g of Al_2O_3; the first and second fractions were eluted with chloroform. The first fraction contained the starting compound and colored impurities (0.12-0.15 g). Workup of the second yellow-green fraction gave 1.22 g (72%) of yellow-orange crystals of Ve with mp 302-303°C (from xylene). IR spectrum ($CHCl_3$): ν_{CO} 1631 and 1673 cm^{-1}. Found: C 78.0; H 4.85; N 8.5%. $C_{22}H_{16}N_2O_2$. Calculated: C 77.6; H 4.7; N 8.2%.

B) Compound Ve [0.98 g (58%)] was obtained as a result of the reaction of 1.06 g (5 mmole) of 1,3-dimethylperimidone and 1.44 g (7.5 mmole) of benzoylacetic ester in 10 g of PPA at 60-65°C for 8 h and subsequent isolation and chromatographic purification (elution with chloroform).

C) Compound Ve [0.2 g (50%)] was obtained as a result of heating 0.4 g of 1,3-dimethyl-8-phenyl-2,6-dioxo-1,2,3,6,7,8-hexahydro-1,3-diazapyrene (X) at 250-255°C for 1 h. The product was purified by chromatography.

D) A solution of 0.4 g of X in 6 g of PPA was stirred at 150-160°C for 30 min, during which the color of the mixture changed from violet to blue. The usual workup and purification gave 0.26 g (65%) of Ve.

E) A mixture of 1.06 g (5 mmole) of 1,3-dimethylperimidone and 1.1 g (7.5 mmole) of cinnamic acid in 10 g of PPA was heated rapidly to 130-135°C, and vigorous stirring at this temperature was continued for 30 min. Workup and chromatographic purification gave 0.75 g (44%) of Ve.

Hydrochloride XIX ($R = C_6H_5$). This compound precipitated immediately when dry hydrogen chloride was bubbled through a hot xylene solution of Ve. The precipitate was separated by filtration, washed with petroleum ether, and dried to give brown crystals with mp 267-269°C (dec.). IR spectrum (mineral oil): ν_{CO} 1683 and 1700 cm^{-1}. Found: C 69.6; H 4.9; Cl 9.0; N 7.7%. $C_{22}H_{17}ClN_2O_2$. Calculated: C 70.0; H 4.9; Cl 9.4; N 7.4%.

1,3-Dimethyl-8-phenyl-6-oxo-1,2,3,6-tetrahydro-1,3-diazpyrene (XVIb). A mixture of 1 g (5 mmole) of freshly prepared 1,3-dimethyl-2,3-dihydroperimidine, 0.95 g (6.5 mmole) of phenylpropiolic acid, and 10 g of PPA was stirred at 40-45°C for 2 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The semicrystalline black precipitate was separated and dissolved in 40 ml of chloroform. The chloroform solution was dried with sodium sulfate and chromatographed; the orange zone was eluted with chloroform. The solvent was removed from the eluate by evaporation to give 0.82 g (50%) of red crystals of XVIb with mp 146-147°C (from aqueous alcohol). IR spectrum ($CHCl_3$): ν_{CO} 1641 cm^{-1}. Found: C 80.6; H 5.8; N 8.3%. $C_{22}H_{18}N_2O$. Calculated: C 80.95; H 5.6; N 8.6%.

1,3-Dimethyl-8-phenyl-6-oxo-2-thioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (XVIIb). A mixture of 1.14 g (5 mmole) of 1,3-dimethylthioperimidone, 0.95 g (6.5 mmole) of phenylpropiolic acid, and 10 g of PPA was stirred at 50-55°C for 2 h, after which the temperature was raised to 70-75°C, and the mixture was maintained at this temperature for 3 h. The workup of the mixture and purification of the product were accomplished as in the preceding experiments. Workup of the first fraction gave ~0.6 g of very impure starting compound. Workup of the second yellow-green fraction gave 0.25 g (14%) of brown crystals of XVIIb with mp 243-245°C (from xylene) during slow heating; the compound shrank markedly at 205-215°C. IR spectrum ($CHCl_3$): ν_{CO} 1644 cm^{-1}. Found: N 8.9%. $C_{22}H_{16}N_2OS$. Calculated: N 9.0%.

1,3-Dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (Vd). A) A mixture of 1.06 g (5 mmole) of 1,3-dimethylperimidone, 0.46 g (6.5 mmole) of propiolic acid, and 10 g of PPA was stirred at 48-53°C for 3 h, after which it was poured into water, and the aqueous mixture was neutralized with ammonia. The black semicrystalline precipitate was separated and extracted with three 20-ml portions of boiling chloroform, and the extract was dried. The separation and purification were carried out by chromatography with collection of the fraction with intense yellow-green fluorescence (the fractions preceding it contained a complex mixture of substances, from which we were unable to isolate any individual compound). The chloroform was removed by evaporation to give 0.17 g (13%) of brown crystals of Vd with mp 300-301°C (from xylene—alcohol). IR spectrum: ($CHCl_3$): ν_{CO} 1634 and 1675 cm^{-1}. PMR spectrum (CF_3COOH): 3.76 (6H, s, $N-CH_3$), 7.3 (1H, d, J = 9.2 Hz, 7-H), 7.45 (1H, d, J = 8.7 Hz, 10-H), 7.58 (1H, d, J = 9.0 Hz, 4-H), 8.3 (1H, d, J = 9.2 Hz, 8-H), 8.47 (1H, d, J = 8.7 Hz, 9-H), and 9.06 ppm (1H, d, J = 9.0 Hz, $_5$-H). Found: C 72.3; H 5.0; N 10.3%. $C_{16}H_{12}N_2O_2$. Calculated: C 72.7; H 4.6; N 10.6%.

B) A 0.54-g (2.2 mmole) sample of chloranil was added to a solution of 0.53 g (2 mmole) of 1,3-dimethyl-2,6-dioxo-1,2,3,6,7,8-hexahydro-1,3-diazapyrene (IX) in 15 ml of absolute toluene, and the mixture was refluxed for 4 h. The toluene was removed by evaporation, and the residue was treated with a hot 10% KOH solution to remove the tetrachloroquinone. The precipitate was removed by filtration and washed on the filter with potassium hydroxide solution until the filtrate was faintly pink. It was then washed with water until the wash waters were neutral, after which it was washed with benzene (30 ml) and dried to give 0.42 g (81%) of almost pure Vd.

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