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HETEROCYCLIC ANALOGS OF PLEIADIENE

XXIII.* REDOX DISPROPORTIONATION OF N-SUBSTITUTED ACEPERIMIDONES. UNUSUALLY FACILE REDUCTION OF THE C=O GROUP

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UDC 547.856.7:542.941.8:543.422.25.4

In the reaction of chloranil with N-monosubstituted aceperimidones, in addition to dehydrogenation of the CH_2CH_2 bridge, the C=O group is unexpectedly reduced, and 1-alkylaceperimidylenes are obtained. N,N'-Disubstituted aceperimidones form disubstituted aceperimidylenones under the same conditions.

Continuing our research on the synthesis of aceperimidylene derivatives, we subjected various aceperimidones to the action of chloranil. It was found that the corresponding aceperimidylenones (IIb-d) are formed in 57-70% yields on brief heating of N,N'-disubstituted aceperimidones with an equimolar amount of chloranil in benzene. Their structure was proved by their PMR spectra, in which a singlet related to the CH=CH bridge appears at 7.05 ppm in place of the signals of a CH_2CH_2 bridge at 3.16 ppm that are characteristic for the starting compounds. The UV spectra of the aceperimidylenones contain an intense longwave band at 380-385 nm, whereas this band is found at 320-330 nm in the spectra of aceperimidones. The aceperimidylenones are

TABLE 1. Synthesized Compounds

Compound	mp, °C (solvent)	$\nu_{C=O}$, cm^{-1} (mineral oil)	λ_{max}, nm (log ε)	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
Ia	313—314 (butanol)	1690		$C_{13}H_{10}N_2O$	74,4	5,2	13,1	74,3	4,8	13,3	70
Ic	219—220 (n-propanol)	1670	325	$C_{27}H_{22}N_2O$	83,0	5,3	6,8	83,0	5,7	7,2	60
Id	180—181 (butanol)	1670	333	$C_{21}H_{18}N_2O$	79,7	5,3	8,9	80,2	5,8	8,9	40
IIb	172—173 (heptane)	1660	385 (3,96)	$C_{15}H_{12}N_2O$	76,3	5,1	12,2	76,3	5,1	11,9	70
IIc	169—170 (aqueous acetone)	1660	385 (4.08)	$C_{27}H_{20}N_2O$	83,5	5,6	6,9	83,5	5,2	7,2	80
IId	148—149 (aqueous alcohol)	1660	380 (4,06)	$C_{21}H_{16}N_2O$	80,9	5,1	9,2	80,7	5,2	8,9	80
IIIb	261—262 (xylene)	1670		$C_{15}H_{14}N_2O$	75,8	6,2	12,3	75.6	6,0	11,8	65
IVa	275—276 (butanol)	1677		$C_{14}H_{10}N_2O$	75,4	5,0	12,7	75,7	4,6	12,6	15

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*See [1] for communication XXII.

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 545-547, April, 1976. Original article submitted April 29, 1975.

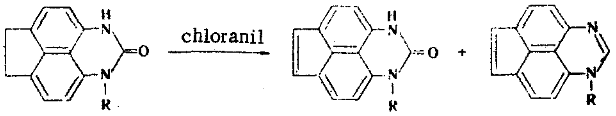
characteristically yellow. In contrast to aceperimidones, they fluoresce intensely on irradiation with UV light, and this is conveniently used for chromatographic identification. A characteristic triplet, all of the peaks of which are extremely intense, is present in the IR spectra of IIb-d at 1520-1690 cm^{-1}. We assigned the highest-frequency band of this triplet to the C=O stretching vibrations (Table 1).

Ia-d IIa-d

I, II a $R^1=R^2=H$; b $R^1=R^2=CH_3$; c $R^1=R^2=C_6H_5CH_2$; d $R^1=CH_3$, $R^2=C_6H_5CH_2$

We obtained unexpected results in the dehydrogenation of N-mono-substituted aceperimidones (III). In this case we were able to isolate only a small amount of the corresponding aceperimidylenone (IVa). The chief reaction product was found to be an N-substituted aceperimidylene (Va, b), which was identical with respect to all of its properties to the N-methyl- and N-ethylaceperimidylene that we previously obtained by another method [1].

Thus in the reaction of the oxidizing agent chloranil, along with oxidative transformation, one observes a reductive process, and the amide C=O group, the difficulties involved in the reduction of which are widely known, undergoes reduction.



IIIa, b IVa, b Va, b

III-V a $R=CH_3$; b $R=C_2H_5$

Formally speaking, the transformation consists in transfer of two hydrogen atoms from the CH_2CH_2 bridge to the C=O group with splitting out of a water molecule. This transfer process is evidently realized by chloranil, which is initially reduced to tetrachlorohydroquinone; the latter, on reduction of the C=O group, is again oxidized to chloranil. In fact, N-methylaceperimidylene is formed when tetrachlorohydroquinone is heated with 1-methylaceperimidylenone, although the reaction does not proceed as smoothly as in the reaction of chloranil with IIIa, b. A more detailed study of this reaction should be the subject of a special investigation.

EXPERIMENTAL METHOD

The UV spectra were recorded with an SF-4A spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were measured with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The properties of the synthesized compounds are presented in Table 1.

Aceperimidone (Ia). A mixture of 5.14 g (0.02 mole) of 4,5-di-aminoacenaphthene hydrochloride and 2.4 g (0.04 mole) of urea was fused at 220-240° for 40 min, after which the fused material was triturated and treated with water to give 4.0 g of crude aceperimidone, which was crystallized from acetic acid or ethyl acetate to give 2.8 g (70%) of a colorless crystalline substance with mp 313-314°.

N-Methylaceperimidone (IIIa). This compound was obtained by the method in [2].

N-Ethylaceperimidone (IIIb). A mixture of 1.1 g (5 mmole) of 1-ethylaceperimidine and 1.2 g (20 mmole) of powdered potassium hydroxide (100%) was heated in a Kjeldahl flask to 175° and maintained at this temperature for 1 h. It was then cooled, and the fused material was treated with 5% HCl solution until it was acidic with respect to Congo red. The resulting brown precipitate was removed by filtration, washed with water, and dried to give 0.7 g (59%) of a light-brown product. Crystallization from xylene gave yellow crystals with mp 261-262°.

Symmetrical Dialkylaceperimidones (Ib, c). A 0.01-mole sample of aceperimidone Ia was dissolved in 70 ml of ethanol, 0.1 mole of alkali and 0.1 mole of alkyl halide were added, and the mixture was refluxed for 3 h. It was then cooled, and the resulting precipitate was removed by filtration. The solvent was removed from the solution by distillation, and the residue was treated with 20 ml of chloroform. The chloroform extract was chromatographed with a column filled with Al_2O_3 (elution with diethyl ether). The first fraction was collected and worked up to give Ib, c as colorless crystals. Compound Ib was previously obtained by the method in [3].

1-Methyl-3-benzylaceperimidone (Id). A 0.22-g (1 mmole) sample of IIIa was dissolved by heating in alcohol while nitrogen was bubbled through the solution continuously. A solution of 0.22 g (3 mmole) of potassium hydroxide in 5 ml of alcohol was added, and the mixture was allowed to stand for 20 min. A 0.24-ml (2 mmole) sample of benzyl chloride was added, and the mixture was refluxed for 3 h. The product was isolated as in the case of Ib, c to give colorless or slightly yellowish crystals with mp 181-182° (from butanol) in 40% yield.

N,N'-Dialkylaceperimidylenones (IIb-d). A mixture of 0.1 mole of Ib-d and 0.11 mole of chloranil was dissolved in 50 ml of absolute benzene, and the solution was heated at 60° for 10 min. It was then cooled and chromatographed with a column filled with Al_2O_3 [elution with benzene–ether (1 : 1)]. The second fraction was collected.

Reaction of Chloranil with 1-Methylaceperimidone. A solution of 0.22 g (1 mmole) of IIIa and 0.24 g (1 mmole) of chloranil in 10 ml of absolute chlorobenzene was refluxed for 30 min, after which it was cooled and chromatographed with a column filled with Al_2O_3 (elution with chloroform). The second fraction was collected, and the solvent was removed to give 0.12 g (57%) of Va with mp 179-180° (from CCl_4), in agreement with the melting point in [1]. The IR spectrum of product Va was identical to the spectrum of a genuine sample. Elution with alcohol gave 0.033 g (15%) of 1-methylaceperimidylenone (third zone) IVa with mp 275-276° (from butanol).

Reaction of Chloranil with 1-Ethylaceperimidone (IIIb). A mixture of 0.1 g (0.5 mmole) of IIIb and 0.12 g (0.5 mmole) of chloranil in 5 ml of absolute benzene was refluxed for 10 min, after which the solvent was evaporated, and the residue was heated with 10% NaOH solution. It was then washed with water, dried, and dissolved in 10 ml of chloroform. The chloroform solution was chromatographed with a column filled with Al_2O_3 [elution with chloroform–petroleum ether (1 : 1)] to give 0.06 g (60%) of Vb (previously obtained by the method in [1]) with mp 118-119° (from isooctane). The IR spectrum of the product was identical to the IR spectrum of a genuine sample. Compound IVb was not isolated.

Reaction of Tetrachlorohydroquinone with 1-Methylaceperimidylenone (IVa). A mixture of 0.1 g (0.49 mmole) of IVa and 0.12 g (0.49 mmole) of tetrachlorohydroquinone in 10 ml of absolute chlorobenzene was refluxed for 3 h, after which it was cooled and chromatographed with a column filled with Al_2O_3 (elution with chloroform) to give 0.02 g (20%) of Va, which, according to the IR spectral data, was identical to an original sample.

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