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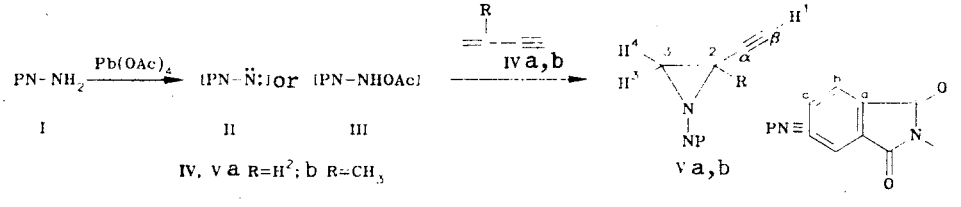
PHTHALIMIDOAZIRIDINYLATION OF THE SIMPLEST VINYLACETYLENES

M. A. Kuznetsov, V. V. Semenovskii, and V. A. Gindin

UDC 547.717'234.22'316.4:543.422.23

The oxidation of N-aminophthalimide with lead tetraacetate in the presence of butenyne and 2-methylbutenyne leads to the corresponding 1-phthalimido-2-ethynylaziridines in good yields.

In [1] we reported the chemoselective phthalimidoaziridinylation of a number of conjugated phenylbutenynes. The high reactivity of the double bond of these enynes with respect to phthalimidonitrene (II) [or to N-acetoxyaminophthalimide (III)*] may, in principle, be due to both the properties of strictly the enyne fragment and its additional conjugation with the phenyl group, which should lead to an increase in the energy of the highest occupied molecular orbital (HOMO) of the substrate and, consequently, its affinity for electrophilic nitrene II [3] (or N-acetoxy derivative III). Up until now, only two examples of the addition of phthalimidonitrene (II) to enynes that do not contain aromatic substituents have been known: the addition to 2,5,5-trimethyl-1-hexen-3-yne [4] (yield not specified) and to 1-(1-cyclopentenyl)-1-octyne [5], in which the yield of the adduct using a fivefold excess of the substrate was less then 40%. In this connection, we carried out the phthalimidoaziridinylation of the simplest vinylacetylenes, namely butenyne (IVa) and 2-methylbutenyne (IVb):



*The question of the nature of the intermediate in phthalimidoaziridinylation still remains open to debate [1, 2].

Leningrad State University, Leningrad 198904. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1176-1178, September, 1991. Original article submitted March 4, 1990.

TABLE 1. Characteristics of Va, b

Compound	Empirical formula	mp, °C	PMR spectrum, δ, ppm (J, Hz)	^{13}C NMR spectrum, ppm	Yield, %
Va*	$C_{12}H_8N_2O_2$	145	syn-Invertomer: 2,09 (d, J=2,0 H^1); 2,72 (d, d, J=7,0; J=2,5, H^3); 3,06 (d, d, d, J=7,0; J=5,5; J=2,2, H^2); 3,25 (d d, J=5,5; J=2,5, H^4) anti-Invertomer: 2,25 (d, J=2,0, H^1); 2,63 (d, d, J=5,5, J=2,0, H^4); 2,73 (d d, J=7,8; J=2,0, H^3); 3,00 (d d d, J=7,8; J=5,5; J=2,0, H^2)	syn-Invertomer: 30,51 ($C_{(2)}$); 37,12 ($C_{(3)}$); 73,44 (C_β); 77,79 (C_α); 122,95 (C_b); 130,02 (C_a); 133,96 (C_c); 165,19 (C=O) anti-Invertomer: 30,92 ($C_{(2)}$); 38,60 ($C_{(3)}$), 70,96 (C_β); 79,42 (C_α); 123,09 (C_b); 129,87 (C_a); 134,12 (C_c); 164,51 (C=O)	76
Vb**	$C_{13}H_{10}N_2O_2$	141,5	syn-Invertomer: 1,62 (s, CH_3); 2,12 (s H^1); 2,57 (d J=2,6, H^3); 3,28 (d, J=2,6, H^4); 7,66and7,74 (m, phthalimide protons anti-Invertomer: 1,48 (s, CH_3); 2,26 (s, H^1); 2,81 (d, J=2,6, H^4); 2,96 (d J=2,6, H^3)	syn-Invertomer: 22,17(CH_3); 37,90 ($C_{(2)}$); 44,20 ($C_{(3)}$); 72,36 (C_β); 80,99 (C_α); 122,78 (C_b); 130,08 (C_a); 133,78 (C_c); 164,93 (C=O) anti-Invertomer: 18,02 (CH_3); 36,27 ($C_{(2)}$); 43,50 ($C_{(3)}$); 69,02 (C_β); 83,36 (C_α); 122,96 (C_b); 134,00 (C_c); 165,33 (C=O)	67

*The phthalimide protons of the two invertomers give a common multiplet at 7.65-7.82 ppm. The ratio of the syn and anti forms is ≈ 3:7.

**The signals of the phthalimide protons at 7.7 ppm are covered by multiplets of the principal invertomer. The syn:anti ratio is ≈ 93:7. The weak signal of the C_a atom of the anti-invertomer is evidently lost in the noise.

The usual method [1] — the addition of lead tetraacetate to a suspension of N-aminophthalimide (I), potassium carbonate, and a small excess amount of enyne IV in CH_2Cl_2 — gives the corresponding 1-phthalimido-2-ethynylaziridines Va, b in satisfactory yields (40-45%), which, although they are lower than for phenylbutenynes (60-90% [1]) but appreciably surpass the yields of 1-N-(hetaryl)aziridines from the simplest olefins and dienes with a terminal double bond [6-8]. Thus one may assert that even the simplest enynes are quite active in phthalimido-aziridinylation and that, consequently, the high reactivity is a property of strictly the enyne fragment.

An improved method, which is normally used for unreactive substrates [9] (the addition of a dry mixture of lead tetraacetate and N-aminophthalimide to a solution of the enyne), makes it possible to increase the preparative yields of aziridines V by a factor of more than 1.5, evidently due to suppression of the side formation of the phthalimide [10]. As in the case of phenylbutenynes [1], we did not detect products involving reaction at the triple bond of enynes IVa, b.

The N-phthalimidoaziridines Va, b obtained are yellowish crystalline substances that melt without decomposition and can be stored for long periods at room temperature without visible changes. They have satisfactory elementary analyses, and their structures are confirmed completely by the ^1H and ^{13}C spectra, the assignment of the signals in which was done in analogy with the assignment previously realized for the corresponding 2-(phenylethynyl)- and 2-phenyl-3-ethynyl-substituted aziridines [1].

Compounds Va, b exist in solution in chloroform at room temperature in the form of an equilibrium mixture of invertomers with syn and anti orientations of the phthalimido and ethynyl groups, which is displayed in the NMR spectra by the presence of two sets of signals, which are partially superimposed. For aziridine Va the percentage of the syn invertomer is $\approx$ 30%, which indicates the extremely small difference in the energies of steric interaction of the phthalimide fragment with the hydrogen atom and the linear ethynyl group. In Vb the presence of a bulky methyl substituent markedly shifts the position of the equilibrium to favor the syn invertomer (syn:anti = 93:7). A comparison of the NMR spectra of 2-ethynylaziridines Va, b and their 2-(phenylethynyl)-substituted analogs [1] shows that the introduction of an addition aryl grouping into the triple bond has virtually no effect on the ratio of the invertomers nor on the ^1H and ^{13}C chemical shifts (CS) of the phthalimide residue. However, it is curious that the coupling of the rather remote (from one another) phenyl and phthalimido groupings is, nevertheless, manifested in additional shielding of the ortho protons of the phenyl substituent in the syn invertomers of 2-phenylethynyl-1-phthalimidoaziridines [1].

EXPERIMENTAL

The ^1H NMR (200 MHz) and ^{13}C (50.3 MHz) spectra of solutions of the compounds in $CDCl_3$ were recorded with a Bruker AC-200 spectrometer with tetramethylsilane (TMS) as the internal standard. The analyses for C, H, and N content were achieved by means of a Hewlett—Packard HP 185B spectrometer.

Butenyne IVa was obtained by distillation of 2-methyl-5-hexen-3-yn-2-ol over KOH, while 2-methylbutenyne (IVb) was obtained by dehydration of 2-methyl-3-butyn-2-ol by the method in [11].

1-Phthalimidodoaziridines (Va, b). A dry mixture of 3.24 g (20 mmole) of N-aminophthalimide (I) [12] and 9.74 g (22 mmole)d of lead tetraacetate was added in small portions with cooling (to −20°C) in the course of 10 min with stirring to a suspension of 8.28 g (60 mmole) of potassium carbonate in a mixture of 5.2 g (100 mmole) of enyne IVa or 1.6 g (25 mmole) of enyne IVb with CH_2Cl_2, after which the mixture was stirred for another 20-30 min at −20°C and then for 1 h at room temperature. It was then filtered through as a layer (2-3 cm) of silica gel, and the residue was washed with CH_2Cl_2 until the filtrate was colorless. The filtrate was evaporated in vacuo, and the solid residue was recrystallized from hexane—ethyl acetate. The mother liquor was evaporated, and the residue was again recrystallized from the same mixture to give, according to the TLC and NMR spectral data, aziridines Va (3.21 g) and Vb (3.03 g) (Table 1).

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AZIRIDINYL KETONES AND THEIR CYCLIC ANILS. 11.* FLUORINE-CONTAINING PHOTOCHROMES

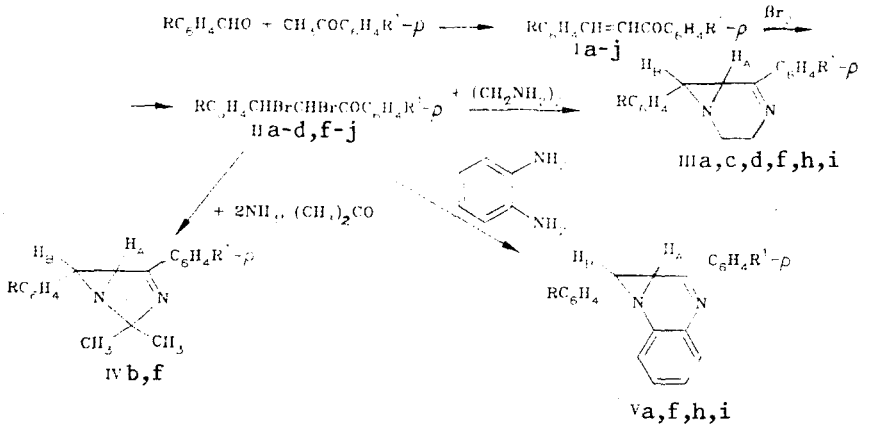
V. D. Orlov, N. P. Vorob'eva, A. A. Tishchenko, O. M. Pikalev, V. I. Popov, and L. M. Yagupol'skii

UDC 547.717:541.65.67

Chalcones with fluorine-containing groups were converted to α,β-dibromides and then to cyclic aziridinyl anils. The introduction of an electron-acceptor trifluoromethylsulfonyl group leads to a significant, although smaller as compared with the nitro group, bathochromic shift of the minimum of the reflection spectrum. Fluorine-containing substituents decrease appreciably the dark-decolorization time of the aziridinyl anils.

The photochromic properties of bicyclic compounds that contain an aziridine ring has been of interest to many researchers [1-3]. It has been noted [2] that a pronounced change in color (from light yellow to blue) occurs when there is an electron-acceptor p-nitrophenyl radical in the three-membered ring. It therefore seemed of interest to ascertain whether this is an effect of the manifestation of mesomeric activity of the nitro group or is characteristic for any strong electron acceptors. With this in mind, we accomplished the synthesis of cyclic aziridinyl anils with various fluorine-containing substituents and studied their structures and properties. We simultaneously studied the effect of these substituents on some spectral properties of intermediate compounds — chalcones and their dibromides.

The synthesis of III-V proceeds via the scheme



I—V a R=2-F, b R=4-F, c R=2-CF_3, d R=2-$SCHF_2$, e R=2-SO_2CHF_2, f R=4-SO_2CF_3, a-f R=H; g-i R=4-NO_2, g R^1=SO_2F, h R^1=SO_2CHF_2, i R^1=$SO_2C_3F_7$; j R=H, R^1=SO_2F

Crotonic condensation is realized in the case of acidic catalysis (in a mixture of glacial acetic acid and three to five drops of concentrated H_2SO_4). The progress of the reaction was monitored by TLC. o-Substituted benzaldehydes undergo this reaction with difficulty. To attain the yields of unsaturated ketones Ic-e indicated in Table 1 one must increase the H_2SO_4 concentration and the reaction time. For example, Id was obtained in a 13% solution of sulfuric acid in glacial acetic acid after 10 days at room temperature (heating caused resinification).

*See [1] for Communication 10.

A. M. Gor'kii Kharkov State University, Kharkov 310077. Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev 252156. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1179-1184, September, 1991. Original article submitted January 26, 1990.

 0009-3122/91/2709-0942$12.50