

SYNTHESIS AND REACTIONS OF METHYLESTERS OF 4-(3-R-SYDNONYL)-2,4-DIOXOBUTANOIC ACID WITH BROMINE AND p-TOLYL AZIDE

A. L. Fridman, E. G. Yufareva,
N. A. Kolobov, and S. S. Novikov

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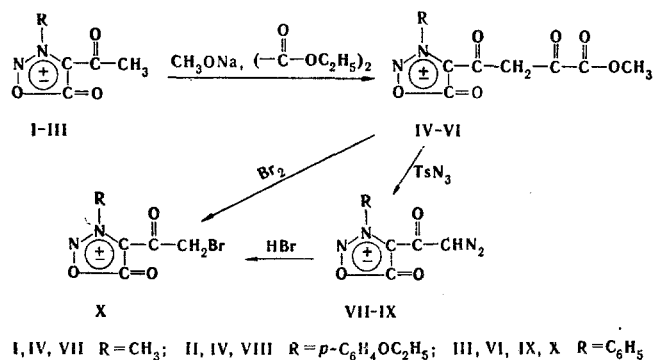
We have found that 3-R-4-acetylsydnone (I-III) react with diethyl oxalate in methanol in the presence of sodium methoxide to give methyl esters of 4-(3-R-sydnonyl)-2,4-dioxobutanoic acid (IV-VI). Cleavage of the carbon-carbon bond with splitting out of the oxalyl residue and the formation of 3-R-4-diazoacetylsydnone (VII-IX) was observed in the reaction of IV-VI with tosyl azide. Similarly, VI reacts with bromine to give 3-R-4-bromoacetylsydnone (X).

The IR spectra of esters IV-VI contain absorption bands at 1780-1790 cm^{-1} (carbonyl group of the sydnone ring), 1720-1760 and 1270-1300 cm^{-1} (ester group), and 1620-1630 cm^{-1} (broad band of a 2,4-diketo group). Multiplets of protons of the OCH_3 group are observed in the PMR spectra at 3.95 ppm. The diazo group in VII-IX absorbs at 2125-2140 cm^{-1} , the sydnone carbonyl group absorbs at 1775-1780 cm^{-1} , and the keto group absorbs at 1605-1620 cm^{-1} .

Methyl 4-(3-Methylsydnonyl)-2,4-dioxobutanoate (IV). A solution of 2.16 g of sodium methoxide in 14 ml of methanol was added at 10-15° to a mixture of 5.68 g (0.04 mole) of 3-methyl-4-acetylsydnone (I) and 5.84 g (0.04 mole) of diethyl oxalate. After 3 h, the precipitate was removed by filtration, washed with methanol, and treated with 150 ml of ether, 50 ml of water, and 20% sulfuric acid until the aqueous layer was strongly acidic. The ether layer was separated and washed to neutrality with water and 1% sodium bicarbonate solution. The ether was removed, and the residue was recrystallized from ethanol to give 3.12 g (55%) of IV with mp 114-116°. Esters V (mp 169-170°, 54% yield) and VI (mp 134-136°, 53% yield) were similarly obtained.

3-R-4-Diazoacetylsydnone (VII-IX). A 10% excess amount of triethylamine was added at no higher than 30° to an equimolar amount of esters IV-VI and tosyl azide in chloroform. After 1 h, the chloroform solution was washed with 3% KOH solution and water, the solvent was evaporated, and the residue was recrystallized from ethanol to give VII (mp 81-83°, 51% yield), VIII (mp 158-159°, 45% yield), and IX (mp 176-178°, 42% yield).

3-Phenyl-4-bromoacetylsydnone (X). A solution of 1.6 g (0.01 mole) of bromine in 5 ml of chloroform was added to a solution of 2.9 g (0.01 mole) of VI in 30 ml of chloroform. After



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the mixture had become colorless, the solvent was removed, and the residue was washed with ether and recrystallized from ethanol to give 1.8 g (63%) of X with mp 110-111°. An identical sample of X (according to the IR spectra) was also obtained in 60% yield by heating IX in excess hydrobromic acid.

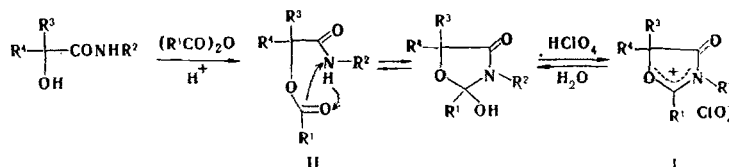
The results of elementary analysis of IV-IX for C, H, and N were in agreement with the calculated values.

SYNTHESIS OF 4(5H)-OXAZOLONIUM SALTS

G. N. Dorofeenko, V. D. Karpenko, and Yu. I. Ryabukhin

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We have established that representatives of a new class of compounds — 2-alkyl-4(5H)-oxazolonium salts (I) — are formed in the reaction of α -hydroxy carboxylic acid amides with aliphatic acid anhydrides in the presence of 70% perchloric acid.



The IR spectra of salts I contain a highly intense characteristic band of carbonyl absorption at 1830 cm^{-1} . This sort of anomalously high frequency indicates an increase in the multiplicity of the C=O bond because of a shift in the electron density from the carbonyl oxygen atom to the positively charged fragment of the molecule. The 70- cm^{-1} increase in this frequency in the spectra of I as compared, for example, with the spectra of 4H-1,3-benzoxazin-4-onium salts (1755-1766 cm^{-1}) is due to additional strengthening of the bond because of the strained character of the five-membered ring. The absorption bands at 1590 and 1515-1548 cm^{-1} are probably due to the skeletal vibrations of the oxazolonium cation (primarily those of the $\text{O}=\text{C}^+-\text{N}$ fragment). The signals of the 2-methyl groups, which appear in the PMR spectra of Ia-c,e at 2.4-2.5 ppm (CF_3COOH , 20°C, hexamethyldisiloxane), constitute evidence for localization of the positive charge on this fragment, viz., concentration of the partial charge of the cation on the meso carbon atom.

When salts I are treated with water, alcohol, or ammonia, the oxazolonium ring is opened to give α -acyloxy carboxylic acid amides (II) in quantitative yields. This method was used to obtain α -acetoxypyruvic acid anilide, with mp 121-122° (from aqueous alcohol) (the melting

TABLE 1

Compound	R ¹	R ²	R ³	R ⁴	mp, °C	Yield, %
Ia	CH ₃	H	CH ₃	H	85	98
Ib	CH ₃	C ₆ H ₅	CH ₃	H	135-137	90
Ic	CH ₃	C ₆ H ₅	CH ₃	CH ₃	174-176	66
Id	C ₃ H ₇	C ₆ H ₅	CH ₃	CH ₃	126-127,5	59
Ie	CH ₃	C ₆ H ₅	-(CH ₂) ₅ -		225	75

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344006. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 5, p. 702, May, 1977. Original article submitted August 24, 1976.

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