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PHOTOLYSIS AND THERMOLYSIS OF N-NITROSO-N-CYCLOPROPYL-SULFONAMIDES AND -CARBOXAMIDES. THE N-CYCLOPROPYLAMIDYL RADICAL.

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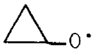
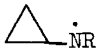
The stabilizing interaction between a cyclopropyl group and a developing free radical centre adjacent to this moiety is well-established, although the exact origin of this effect is still under discussion (1). Examples include the formation of cyclopropylcarbinyl radicals, I, and of cyclopropoxy radicals, II. The former type of radicals gives usually a mixture of cyclic and non-cyclic products, i.e. the cyclopropyl ring is not necessarily broken (2). On the other hand formation of the cyclopropoxy radical always seems to lead exclusively to cleavage of the three-membered ring, possibly by a concerted multiple bond cleavage reaction (3).

I

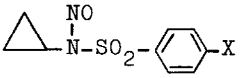


II

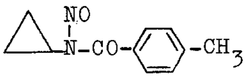


III,R = $ArSO_2$ or ArCO

In the present communication we wish to report the photolytical and thermal decomposition reactions of the N-nitroso-N-cyclopropyl-sulfonamides IV and of the -carboxamide V (4) which are potential precursors of the hitherto unknown nitrogen analogue III of the carbon and oxygen radicals I and II. Generally, photolysis of N-nitrosamides will be initiated by N-N bond rupture (5), in

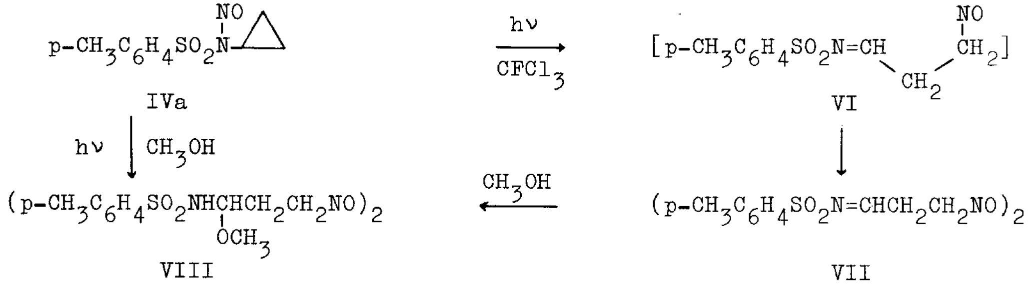


IVa (X = CH_3); IVb (X = NO_2)



V

our case leading to the formation of the N-cyclopropylamidyl radicals III. Accordingly, photolysis (6) of IVa in $CFCl_3$ at -60° for 1.5 hrs gives the rather unstable trans nitroso alkane dimer* VII in 95% yield (PMR ($CDCl_3$): δ 2.43 (s, 3H), 3.00 (m, 2H), 4.45 (t, 2H), 7.24-7.85 (m, 4H), 8.58 (t, 1H) ppm; IR ($CHCl_3$): 1620, 1320, 1150 cm^{-1}; UV (dioxane): λ_m 288 nm (ε 9400)). PMR analysis of the crude reaction mixture revealed that no product was formed containing an intact cyclopropyl ring.



The photolysis of IVa was also carried out in CH_3OH as the solvent at -60° for 1.5 hrs. The product was the trans nitroso alkane dimer VIII which may be formed by addition of the solvent to the N=C bond of the initially formed product VII (VIII; 62% yield; m.p. 125-128° (dec.); PMR (CD_3NO_2): δ 2.12 (m, 2H), 2.45 (s, 3H), 3.18 (s, 3H), 4.20 (t, 2H), 4.68 (m, 1H), 6.22 (d, 1H), 7.32-7.86 (m, 4H) ppm; IR (KBr): 3370, 1330, 1160 cm^{-1}; UV (dioxane): λ_m 288 nm (ε 7700)). The rapid addition of CH_3OH could be demonstrated by the conversion of VII

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* During photolysis a strong 15 line ESR spectrum was observed which may be ascribed to the nitroxide $(p\text{-}CH_3C_6H_4SO_2N{=}CHCH_2CH_2)_2NO^{\cdot}$ (a_N = 13.2, a_H = 11.2 (4H) gauss) formed by photolysis of the intermediate monomeric nitroso alkane VI. ESR spectra obtained at various temperatures between +20 and -80° showed a strong linewidth-alternation effect as expected for this type of nitroxides (7).

into VIII upon treatment with CH_3OH at room temperature*. Again, after photolysis no product with an intact cyclopropyl ring could be detected.

Similar photolytical reactions were observed for the N-nitroso-N-cyclopropylcarboxamide V. Photolysis of V in methanol at -20° for 2 hrs gives the trans nitroso alkane dimer $(p\text{-}CH_3C_6H_4CONHCH(OCH_3)CH_2CH_2NO)_2$ in 50% yield (PMR ($CDCl_3$): δ 2.33 (s, 3H), ca. 2.30 (t, 2H), 3.31 (s, 3H), 4.41 (t, 3H), 5.45 (m, 1H), 7.11-7.81 (m, 4H) ppm; IR ($CHCl_3$): 3390, 1645, 1280 cm^{-1}; UV (ethanol): sh. at 275 nm (ϵ 5800)).

These experiments indicate that photolysis of IVa and V both in an inert solvent ($CFCl_3$) and in a solvent capable of hydrogen donation (CH_3OH) leads exclusively to cyclopropyl ring opened products in a facile rearrangement reaction. In both cases homolysis of the N-N bond and ring opening (either concerted or in a two step process) would give an intermediate $RN{=}CHCH_2CH_2^{\bullet}$ radical, which recombines** efficiently with NO to give the observed reaction products. Substituting methyl for cyclopropyl in the N-nitrosamides changes the reaction path. Photolysis of N-nitroso-N-methylacetamide in methanol gives by denitrosation N-methylacetamide in high yield (5). Irradiation of N-nitroso-N-methyltosylamide with sunlight is known to give denitrosation to N-methyltosylamide (8). We have found that photolysis of this nitrosamide in CH_3OH at -60° for 4 hrs affords a mixture of products with tosylamide (9) as the major component in about 40% yield.

The thermal reactions of the N-nitroso-N-cyclopropylamides have also been investigated. During the last decades, extensive evidence has been accumulated that thermolysis of N-nitroso-N-alkylsulfonamides (10) and -carboxamides (11) usually proceeds via a diazo ester intermediate. We have found that thermolysis (under nitrogen in the dark) of IVa ($X = CH_3$) and IVb ($X = NO_2$) in methanol at 20° for 20 hrs gives the parent N-cyclopropylsulfonamide in 77 and 90% yield respectively. Apparently denitrosation occurs more readily than rearrangement, as has also been observed for especially N-nitroso-N-alkylsul-

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* Further methanolysis or hydrolysis of VIII provides tosylamide.

** NO migration might be an intramolecular process.

fonamides with higher alkyl groups (12). It is interesting to note that the carbonyl analogue V does show the rearrangement to diazo ester under comparable conditions. Thermolysis in CH_3OH for 20 hrs at 20°or for 15 min. at 65° affords p-methylbenzoic acid (92 and 96% respectively). In benzene as the solvent (15 min. at 80°) a mixture is obtained of p-methylbenzoic acid (36%), cyclopropyl p-methylbenzoate (36%) and allyl p-methylbenzoate (28%).
Further studies are in progress and will be reported in due time.

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