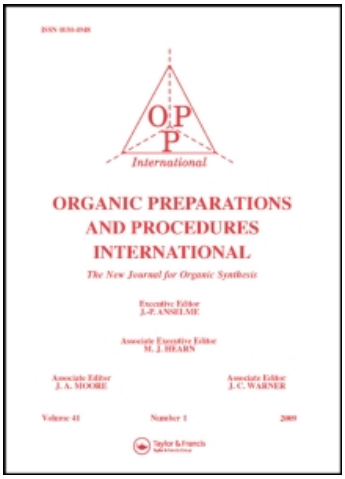

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B. Stanovnik[a]; M. Tisler[a]
[a] Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

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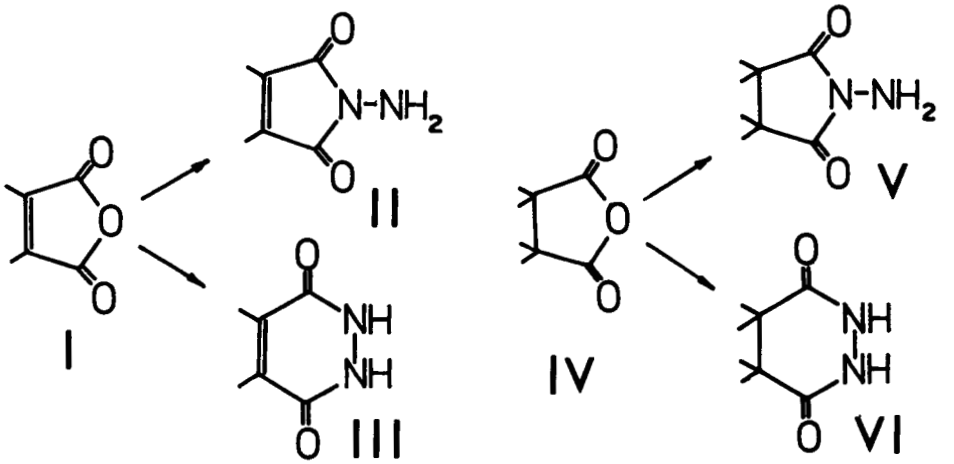
STRUCTURAL ASSIGNMENT OF CYCLIC PRODUCTS FROM 1,2-DICARBOXYLIC ANHYDRIDES AND HYDRAZINE. S,S-DIMETHYL SULFOXIMIDES

B. Stanovnik and M. Tisler

Department of Chemistry, University of Ljubljana
Ljubljana, Yugoslavia

Anhydrides of cyclic 1,2-dicarboxylic acids can, in principle, react with hydrazine to give besides the linear hydrazides either the cyclic N-aminoimides (II, V) or derivatives of maleic hydrazide (III, VI). It is well known that maleic anhydride or phthalic anhydride is converted with hydrazine into the corresponding cyclic hydrazide (III).[1,2] However, N-aminophthalimide is formed first and thereafter is



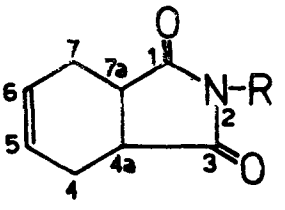
transformed into phthalhydrazide. There are also some exceptions and 3,6-diphenylphthalic anhydride is reported to give exclusively the N-aminophthalimide derivative.[3] Heterocyclic dicarboxylic anhydrides - e.g., quinolinic anhydride - also form cyclic hydrazides.[4] The course of the reaction seems to be in many cases influenced by electronic, steric and/or solvent effects. However, the initially formed N-aminomaleimides (II) are easily rearranged into cyclic hydrazides (VI) in the presence of an acid, base or upon heating.[1]

Anhydrides of cyclic systems which do not contain a double bond (IV) give preferentially the N-amino derivatives (V), rather than the corresponding cyclic hydrazides (VI). Moreover, with hydrazine succinic anhydride does not form a cyclic hydrazide which can be obtained only by reduction of maleic hydrazide.[7]

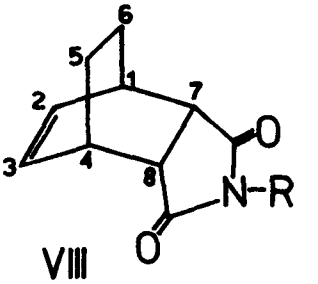
Recently, the mode of formation of maleimides, isomaleimides and pyridazinones has been investigated and some data were presented which may help to resolve discrepancies regarding the structures of these compounds. It is stated, that on the basis IR and/or NMR spectra, ferric chloride test and formation of acetoxy derivatives, it may be possible to differentiate between these types of simple compounds.[8]

We would like to show that N-aminoimides of more complex molecules can be easily distinguished from the corresponding isomeric cyclic hydrazides. Several cyclic anhydrides prepared by a Diels-Alder reaction, afforded N-aminoimides after treatment with hydrazine. The structure assignment of these products (VII-X, R = NH_2) is based upon the formation of N-

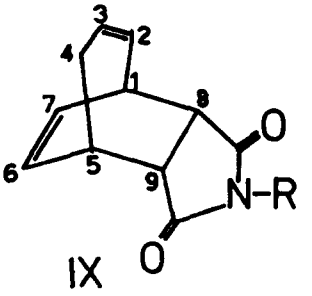
amino nitrenes with lead tetraacetate. If the reaction is run in dimethyl sulfoxide the N-amino nitrenes can be trapped as the corresponding S,S-dimethyl sulfoximedes.[9] All products which we have isolated from this reaction were found to be the corresponding S,S-dimethyl sulfoximides (VII-X, R = $-N{=}SOMe_2$).



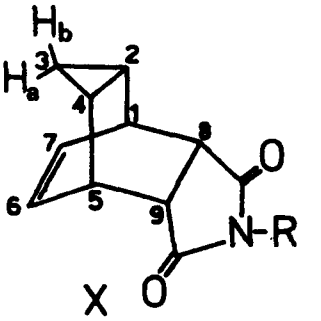
VII



VIII



IX



X

Since the cyclic hydrazides of the type III or VI do not form the corresponding sulfoximides, this reaction can be used for structure assignments of simple and complex molecules of the N-amino type.

EXPERIMENTAL[10]

Starting materials. - N-Amino-4-cyclohexene-1,2-dicarboxamide was prepared according to the published procedure.[5] The following anhydrides were prepared in a Diels-Alder reaction as described in the literature: bicyclo[2.2.2]oct-2-ene-7,

8-dicarboxylic anhydride[11] [NMR (DMSO-d_6): τ 3.82 (t,H_5H_6), 6.75 (t,H_7H_8), 7.0 (m,H_1H_4), 8.55 (broad m, 2- and 3-CH_2)]; bicyclo[3.2.2]nona-2,6-diene-8,9-dicarboxylic anhydride[12] and tricyclo[3.2.2.$0^{2,4}$]-non-6-ene-8,9-dicarboxylic anhydride[13] [NMR (DMSO-d_6) τ 6.60 (m,H_1H_5), 8.75 (m,H_2H_4), 9.65 (m,H_{3a}), 9.90 (m,H_{3b}), 4.1 (m,H_6H_7), 6.65 (m,H_8H_9)].

General procedure for the preparation of N-aminoimides. - An ethanolic (or DMF) solution of the anhydride was treated with hydrazine hydrate (10% excess) and heated under reflux for 15 min. The solvent was evaporated in vacuo and the product was separated. In this manner the following compounds were obtained.

N-Amino bicyclo[2.2.2]oct-2-ene-7,8-dicarboximide (VIII, R = NH_2), mp. 124-125° (from ethanol); mass spectrum: M^+=192; NMR (DMSO-d_6) τ 3.82 (dd,H_2H_3), 8.60 (broad m, 5- and 6-CH_2), 7.05 (m,$H_4H_7H_8$).

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N,14.58
Found: C, 62.36, H, 6.42; N,14.46

N-Amino bicyclo[3.2.2]nona-2,6-diene-8,9-dicarboximide (IX, R = NH_2), mp. 108-113° (from benzene and n-hexane); mass spectrum: M^+ = 204.

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92, N,13.72
Found: C, 64.50; H, 6.06; N,14.20

N-Amino tricyclo[3.3.3.$0^{2,4}$]non-6-ene-8,9-dicarboximide (X, R = NH_2), mp. 122-124° (from ethanol); mass spectrum: M^+ = 204; NMR (DMSO-d_6) τ 7.05 (m,H_1H_5), 8.9 (m,H_2H_4) 10.0 (m,H_{3a}),

9.8 (m,H_{3b}), 4.42 (m,H_6H_7), 6.85 (m,H_8H_9), 5.22 (broad, NH_2).

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N,13.72
Found: C, 64.45; H, 5.97; N,14.03

General procedure for the preparation of S,S-dimethyl sulfoximides. - The N-amino compound (0.01 mole) was dissolved in dry dimethyl sulfoxide (20 ml) and lead tetraacetate (4.43 g) was added in one portion. The mixture was heated at 80-100° for 5 min. and the solvent evaporated in vacuo. The residue was extracted with chloroform and the product, obtained after evaporation of the solvent, was purified by crystallization. In this manner the following compounds were prepared (yields 56-78%).

S,S-Dimethyl-N-(4-cyclohexene-1,2-dicarboximido)sulfoximide (VII, R = -N=$SOMe_2$), mp. 202-204° (from ethyl acetate); mass spectrum: M^+ = 242; NMR (DMSO-d_6) τ 4.05 (m,H_5H_6), 7.67 (m,4- and 7-CH_2), 6.87 (m,$H_{4a}H_{7a}$), 6.8 (s,$SOMe_2$).

Anal. Calcd. for $C_{10}H_{14}N_2O_3S$: C,49.58; H,5.83; N,11.57
Found: C,49.32; H,6.02; N,11.32

S,S-Dimethyl-N-(bicyclo[2.2.2]oct-2-ene-7,8-dicarboximido)sulfoximide (VIII, R = -N=$SOMe_2$), mp. 227-229° (washed with n-hexane); mass spectrum: M^+ = 268; NMR (DMSO-d_6) τ 3.95 (t,H_2H_3), 7.05 (m,H_1H_4), 7.15 (m,H_7H_8), 8.65 (broad m, 5- and 6-CH_2).

Anal. Calcd. for $C_{12}H_{16}N_2O_3S$: C,53.73; H,6.01; N,10.44
Found: C,53.66; H,6.10; N,10.56

S,S-Dimethyl-N-(bicyclo[3.2.2]nona-2,6-diene-8,9-dicarboximido)sulfoximide (IX, R = -N=$SOMe_2$), mp. 202-203° (from ethanol); mass spectrum: M^+ = 280; NMR (DMSO-d_6) τ 4.60 (m,H_3), 4.15 (m,H_2), 3.95 (m,H_6), 3.70 (m,H_7), 7.70 (m,4-CH_2), 7.1 (broad m, H_1H_5), 6.7 and 5.9 (dd, H_8 and H_9), 6.87 (s, $SOMe_2$).

Anal. Calcd. for $C_{13}H_{16}N_2O_3S$: C,55.71; H,5.75; N,10.00
Found: C,55.62; H,5.82; N,10.14

S,S-Dimethyl-N-(tricyclo[3.2.2.$0^{2,4}$]non-6-ene-8,9-dicarboximido)sulfoximide (X, R = -N=$SOMe_2$), mp. 217-218° (from ethanol); mass spectrum: M^+ = 280; NMR (in DMSO-d_6) τ 7.02 (m,H_1H_5), 8.9 (m,H_2H_4), 9.85 (m,H_{3a}), 10.0 (m,H_{3b}), 4.33 (m, H_6H_7), 6.85 (m,H_8H_9), 6.9 (s, $SOMe_2$).

Anal. Calcd. for $C_{13}H_{16}N_2O_3S$: C,55.71; H,5.75; N,10.00
Found: C,55.57; H,6.00; N,10.04

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