# DIENE SYNTHESIS WITH 2-PYRONES AND 2-PYRIDONES

## XIV.* 1,4-CYCLOADDUCTS OF 1-ALKYL-2-PYRIDONES WITH N-PHENYLMALEINIMIDE AND MALEINIMIDE

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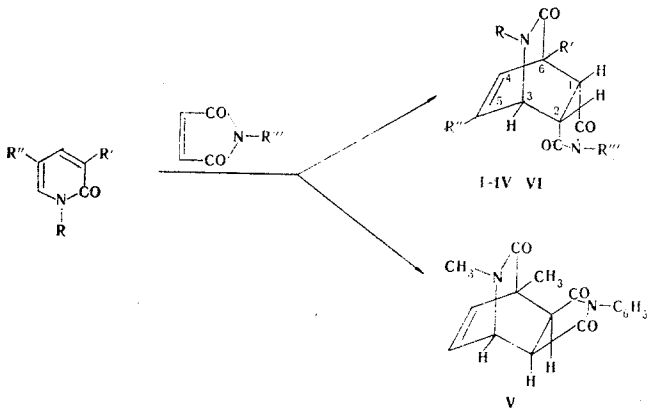
1-Alkyl-2-pyridones react with N-phenylmaleinimide and maleinimide stereoselectively via the scheme of the diene synthesis to give imides of 8-alkyl-8-azabicyclo[2.2.2]-4-octen-7-one-1,2-dioic acid. 3-Unsubstituted 2-pyridones form adducts with an endo configuration, whereas 1,3-dimethyl-2-pyridone gives an exo adduct under the same conditions. The endo- and exo-bridge adducts readily undergo retrograde diene disintegration on heating.

In the present research for the first time we have realized the diene synthesis for 1-alkyl-2-pyridones with N-phenylmaleinimide and maleinimide, 1,4-Cycloadducts, i.e., N-phenylimides I-V, and this imide (VI) of 8-alkyl-8-azabicyclo[2.2.2]-4-octen-7-one-1,2-dioic acid, were obtained in 30-80% yields when xylene solutions of the starting reagents were refluxed.



I-IV VI

V

I R=$C_3H_7$, R′=R″=H, R‴=$C_6H_5$; II R=*i*-$C_4H_9$, R′=R″=H, R‴=$C_6H_5$; III R=*i*-$C_5H_{11}$, R′=R″=H, R‴=$C_6H_5$; IV R=R″=$CH_3$, R′=H, R‴=$C_6H_5$; VI R=$C_3H_7$, R′=R″=R‴=H

The compositions of adducts I-VI were confirmed by elementary analysis and mass spectroscopy, and their structures were proved by their IR spectra (absorption of the lactam bridges CO at 1680-1690 $cm^{-1}$ and imide CO at 1715 and 1780 $cm^{-1}$) as well as by the PMR spectra (Fig. 1).

All of the investigated reactions proceed with one of the two possible stereoisomers, the configurations of which were established by PMR spectroscopy [1, 2]. On the basis of the close or completely identical $J_{1,6}$ and $J_{2,3}$ values (Table 2) of adducts I-IV and VI and the endo adducts of 2-pyridones [1-methyl-2-

* See [1] for communication XIII.

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TABLE 1. Imides of 8-Alkyl-8-azabicyclo[2.2.2]-4-octen-7-one-1,2-dioic Acid

| Compound | R | R′ | R″ | R‴ | Heating time, h | mp, °C | $R_f$ in $CHCl_3$ |
|---|---|---|---|---|---|---|---|
| I | $C_3H_7$ | H | H | $C_6H_5$ | 24 | 165 | 0,5 |
| II | $i$-$C_4H_9$ | H | H | $C_6H_5$ | 26 | 166—167 | 0,5 |
| III | $i$-$C_5H_{11}$ | H | H | $C_6H_5$ | 26 | 166—168 | 0,5 |
| IV | $CH_3$ | H | $CH_3$ | $C_6H_5$ | 30 | 175—176 | 0,5 |
| V | $CH_3$ | $CH_3$ | H | $C_6H_5$ | 30 | 226 | 0,5 |
| VI | $C_3H_7$ | H | H | H | 15 | 236—237 | 0,4 |

TABLE 1 (continued)

| Compound | Empirical formula | Found | | | Calculated | | | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | C, % | H, % | M* | C, % | H, % | M | |
| I | $C_{18}H_{18}N_2O_3$ | 69,5 | 5,9 | 310 | 69,6 | 5,9 | 310 | 80 |
| II | $C_{19}H_{20}N_2O_3$ | 70,5 | 6,3 | 324 | 70,4 | 6,2 | 324 | 58 |
| III | $C_{20}H_{22}N_2O_3$ | 71,0 | 6,7 | — | 70,9 | 6,6 | 338 | 53 |
| IV | $C_{17}H_{16}N_2O_3$ | 68,7 | 5,5 | 296 | 68,9 | 5,4 | 296 | 43 |
| V | $C_{17}H_{16}N_2O_3$ | 68,8 | 5,5 | 296 | 68,9 | 5,4 | 296 | 30 |
| VI | $C_{12}H_{14}N_2O_3$ | 61,4 | 6,1 | 234 | 61,5 | 6,0 | 234 | 56 |

*By mass spectrometry.

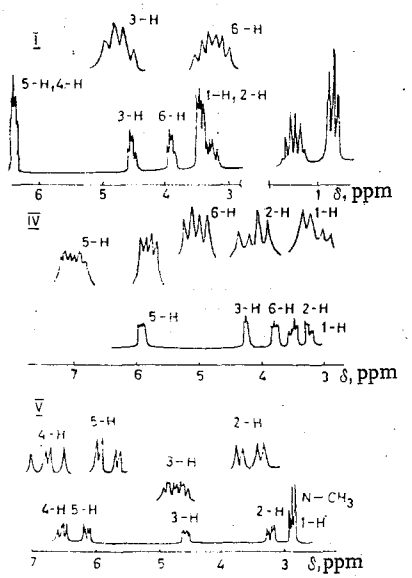


Fig. 1. PMR spectra of adducts I, IV, and V.

pyridone with maleic anhydride ($J_{1,6}$ = 3.5 Hz, $J_{2,3}$ = 4.0 Hz [3] and with N-phenylmaleinimide ($J_{1,6}$ = 4.4 Hz, $J_{2,3}$ = 4.6 Hz) [4], we assigned an endo configuration to adducts I-IV and VI. An exo configuration was assigned to adduct V, inasmuch as the $J_{2,3}$ constant for it differed from the corresponding constants for adducts I-IV and VI by 1.5 Hz (see Table 2 and Fig. 1) and was identical to the $J_{2,3}$ values of the exo adduct of 2-pyridone with N-phenylmaleinimide [1]. It should be noted that the same difference of 1.5 Hz was observed for the $J_{2,3}$ constants of the isomeric endo and exo adducts of 2-pyridone with N-phenylmaleinimide ($J_{2,3}$ = 4 and 2.5 Hz, respectively) [1].

The conclusion regarding the configuration of the adducts is confirmed by a comparison of the chemical shifts of the 1-H, 2-H, and 3-H protons of exo adduct V and isomeric endo adduct IV. The signals of the 1-H and 2-H protons are found at stronger field (2.83 and 3.39 ppm) for exo adduct V than for the endo adduct (IV, 3.37 and 3.49 ppm), whereas the signal of the 3-H proton of adduct V is found at weaker field than in the case of IV (4.56 and 4.28 ppm, respectively) (Table 2 and Fig. 1). This relationship is in agreement with the literature data [2, 5] for other bridged endo and exo adducts.

The investigated reactions of the diene synthesis of 1-alkyl-2-pyridones proceeded stereoselectively. 2-Pyridones without substituents at the ends of the conjugated system reacted with N-phenylmaleinimide and maleinimide in conformity with Alder's rule to give endo isomers, whereas 1,3-dimethyl-2-pyridone gave an exo adduct under these conditions.

In the case of the endo (I) and exo (V) adducts, the ability of bicyclic systems with an endo azocarbonyl bridge to undergo retrograde diene decomposition on heating above the melting point was demonstrated for the first time.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with IKS-22 and UR-20 spectrometers. The PMR spectra of $CHCl_3$ solutions (for adducts I-V) and pyridine solutions (for adduct VI) were recorded with a Varian-HA 100 spectrometer with hexamethyldisiloxane as the internal standard.

Imides (I-VI) of 8-Alkyl-8-azabicyclo[2.2.2]-4-octen-7-one-1,2-dioic Acids. These compounds were

TABLE 2. Parameters of the PMR Spectra of Adducts I-VI

| Compound | Position of the proton | δ, ppm | Multiplicity* | Spin–spin coupling constants, Hz | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $J_{1,6}$ | $J_{2,3}$ | $J_{5,6}$ | $J_{3,4}$ | $J_{1,2}$ |
| I | 1 | 3,35 | q | 4,5 | 4,0 | 5,8 | 6,5 | — |
| | 2 | 3,5 | q | | | | | |
| | 6 | 3,92 | m | | | | | |
| | 3 | 4,52 | m | | | | | |
| | 5 | 6,38 | m | | | | | |
| | 4 | | | | | | | |
| II | 1 | 3,35 | m | 4,5 | 4,0 | 6,5 | 6,0 | — |
| | 2 | | | | | | | |
| | 6 | 3,91 | m | | | | | |
| | 3 | 4,55 | m | | | | | |
| | 5 | 6,45 | m | | | | | |
| | 4 | | | | | | | |
| III | 1 | 3,10 | q | 4,0 | 4,0 | 6,0 | 6,5 | — |
| | 2 | 3,32 | q | | | | | |
| | 6 | 3,88 | m | | | | | |
| | 3 | 3,56 | m | | | | | |
| | 5 | 6,50 | m | | | | | |
| | 4 | | | | | | | |
| IV | 1 | 3,27 | q | 3,7 | 4,0 | 6,0 | — | 8,0 |
| | 2 | 3,49 | q | | | | | |
| | 6 | 3,86 | q | | | | | |
| | 3 | 4,28 | q | | | | | |
| | 5 | 5,84 | m | | | | | |
| V | 1 | 2.83 | q | — | 2,5 | — | 5,5 | 8,5 |
| | 2 | 3,39 | q | | | | | |
| | 3 | 4,56 | m | | | | | |
| | 5 | 6,12 | m | | | | | |
| | 4 | 6,54 | q | | | | | |
| VI | 1 | 3.55 | | 4,0 | 4,0 | 7,0 | 6,0 | — |
| | 2 | 3,55 | m | | | | | |
| | 6 | 4,10 | m | | | | | |
| | 3 | 4,77 | m | | | | | |
| | 5 | 6,33 | m | | | | | |
| | 4 | 6,7 | m | | | | | |

*Abbreviations: q is quartet and m is multiplet.

obtained by refluxing solutions of equimolecular amounts of 2-pyridones and the dienophile (maleinimide or N-phenylmaleinimide) (0.004 mole of each) in 8-10 ml of xylene. The mixture was cooled, and the xylene was removed by vacuum distillation. The compositions of the residues obtained were monitored by thin-layer chromotography (TLC), after which the residues were washed several times with ether to remove the starting compounds. Adducts I-III, V, and VI were purified by recrystallization from alcohol, whereas adduct IV was purified by column chromotography with $Al_2O_3$ (elution with chloroform) and by recrystallization from ethyl acetate. The individuality of the adducts obtained was monitored by TLC on $Al_2O_3$ ($CHCl_3$). The reaction times, physical constants, yields, and results of elementary analysis are presented in Table 2.

Thermolysis of Adducts I and V. A 0.2-g sample of endo-8-propyl-8-azabicyclo[2.2.2]-4-octen-7-one-1,2-dioic acid N-phenylimide (I) was heated in vacuo in a sublimation apparatus at 165-180° (7 mm). Yellow crystals of N-phenylmaleinimide sublimed in 10-15 min. The yield of product with mp 88-89° (from cyclohexane) was 0.1 g (91%); no melting-point depression was observed for a mixture of this product with an authentic sample. According to the TLC data and the IR spectrum, the oily residue was 1-propyl-2-pyridone. N-Phenylmaleinimide [0.05 g (84%)] and 0.04 g of 1,3-dimethyl-2-pyridone were similarly obtained by thermolysis of 0.1 g of exo-6,8-dimethyl-8-azabicyclo[2.2.2]-4-octen-7-one-1,2-dioic acid N-phenylimide (V) at 225-240° (6 mm).

## LITERATURE CITED


1. N. P. Shusherina, L. V. Betaneli, and A. U. Stepanyants, Dokl. Akad. Nauk SSSR, 213, 1107 (1973).
2. N. P. Shusherina, M. V. Gapeeva, A. U. Stepanyants, Yu. A. Knirel', and R. Ya. Levina, Zh. Organ. Khim., 8, 2426 (1971).
3. H. Tomisawa and H. Hongo, Chem. Pharm. Bull. Japan, 18, 925 (1970).
4. N. P. Shusherina and M. V. Gapeeva, Zh. Organ. Khim., 9, 848 (1973).
5. M. Cava and N. Pollack, J. Amer. Chem. Soc., 88, 4112 (1966).