

SHORT
COMMUNICATIONS

Migration of Phthalimido Group in the Cycloheptatriene System*

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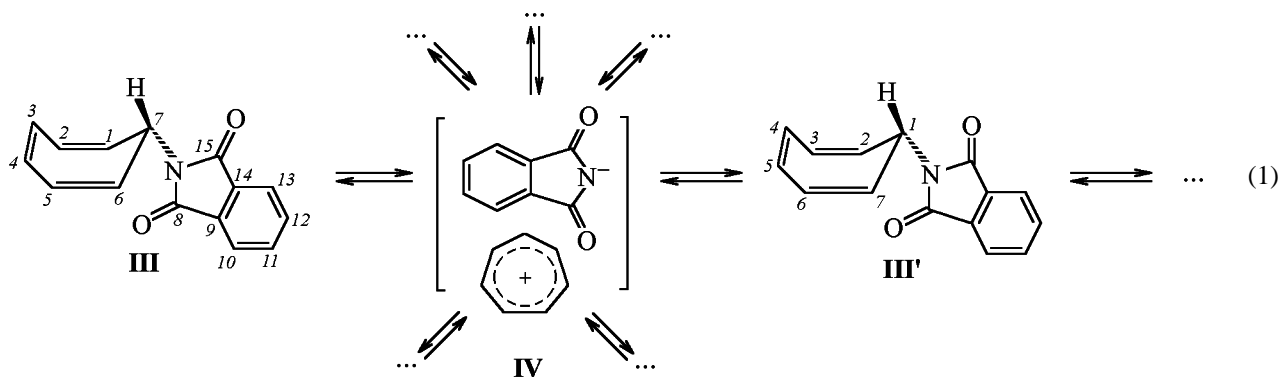
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Roundabout rearrangements of element-centered cycloheptatriene derivatives up till now have been subject only of occasional studies. Among them have been revealed migrations of iso(thio, seleno)cyanato [1, 2], azido [3], thio [4-6] groups and chlorine [7] in the cycloheptatriene ring. Aiming at investigation of new rearrangements of N-centered groups in the cycloheptatriene system we prepared *N*-cycloheptatrienylphthalimide and studied its fluctional behavior.

Tropylium tetrafluoroborate (**I**) reacted with sodium phthalimide (**II**) in acetonitrile to furnish *N*-(cyclohepta-1,3,5-trien-7-yl)phthalimide (**III**) whose composition and structure were confirmed by elemental analysis and IR, ^1H , and ^{13}C NMR spectra. The boat configuration of compound **III** with the phthalimido group in a quasiequatorial position follows from the values of the coupling constants $^3J(\text{H}^1\text{H}^7)$ 5.10 Hz and $^4J(\text{H}^2\text{H}^7)$ 1.66 Hz in the ^1H NMR spectrum. These values of constants considerably differ from those for $\text{C}_7\text{H}_7\text{SnPh}_3$ derivative

where the quasiaxial position of the triphenyltin group was proved by X-ray diffraction analysis [8]. In the ^1H NMR spectra of compound **III** registered at 80 and 300 MHz in deuterio-nitrobenzene at heating the solution to 140°C a synchronous reversible broadening was observed that at 200°C (^1H NMR spectrum at 80 MHz) resulted in the coalescence of the indicator signals belonging to the cycloheptatrienyl protons H^7 , H^1 , H^6 , H^2 , H^5 and H^3 , H^4 . A similar synchronous broadening in this temperature range was also observed for the signals of ^{13}C nuclei in the corresponding positions of the seven-membered ring in the course of recording dynamic ^{13}C NMR spectrum of compound **III** solution.

This spectral behavior testifies to the occurrence of roundabout rearrangements of the phthalimido group along the perimeter of the cycloheptatriene ring that proceed by dissociation-recombination mechanism with intermediate formation of a tight ion pair: tropylium cation-phthalimide anion (**IV**) (Scheme 1).



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The dissociation-recombination as prevailing mechanism operating in migration of the phthalimido group is also confirmed by the 2D ^1H EXSY NMR spectrum of compound **III** that reveals the presence of exchange cross-peaks between all pairs of signals from the seven-membered ring at 150°C . The rate of the observed dynamic process is independent of solution concentration in the concentration range c 0.007–0.2 mol l^{-1} . From the analysis of peak form of the proton and carbon signals of the heptatriene ring were estimated the activation parameters of degenerate migration of the phthalimido group around the perimeter of the cycloheptatriene ring, as follows: $\text{C}_6\text{D}_5\text{NO}_2$, $\Delta G_{180^\circ\text{C}}^\ddagger$ 24.8 kcal mol^{-1} , $k_{180^\circ\text{C}}$ 9.4 s^{-1} .

N-(Cyclohepta-1,3,5-trien-7-yl)phthalimide (III).

To a solution of tropylium tetrafluoroborate (**I**) (0.890 g, 5 mmol) in 20 ml of anhydrous acetonitrile at 20°C was added dropwise while stirring 5 mmol (0.845 g) of sodium phthalimide (**II**) in 20 ml of anhydrous acetonitrile. The mixture was boiled at stirring for 15 min. The separated precipitate of NaBF_4 was filtered off and washed with CH_3CN (2×10 ml). The solvent was removed in a vacuum. The residue was twice recrystallized from acetonitrile. Yield of compound **III** 1.08 g (91%), colorless crystals, mp $175\text{--}176^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1760, 1710 (C=O), 1620, 1600 (C=C), 1150, 1100, 1070, 980. ^1H NMR spectrum (300 MHz), δ , ppm: 4.48 t.t (1H, $^3J_{1,7}$ 5.10, $^4J_{2,7}$ 1.66 Hz, H 7), 5.53 m (2H, $^3J_{1,2}$ 9.01, $^4J_{1,3}$ 0.68 Hz, H 1,6), 5.96 m (2H, $^3J_{2,3}$ 3.66 Hz, H 2,5), 6.44 m (2H, H 3,5), 6.93–7.47 m (4H, H arom). ^{13}C NMR spectrum (75.47 MHz), δ , ppm: 50.31 (C 7), 123.14 (C 1,6), 123.71 (C 2,5), 124.08 (C 3,4), 131.50 (C 10,13), 132.51 (C 9,14), 133.64 (C 11,12). Mass spectrum, m/z (I_{rel} , %): 237 (66.9) [$\text{C}_7\text{H}_7\text{N}(\text{CO})_2\text{C}_6\text{H}_4=\text{M}$] $^+$, 219 (90.6) [$\text{M}-\text{H}_2\text{O}$] $^+$, 208 (34.6) [$\text{M}-\text{HCO}$] $^+$, 180 (21.0) [$\text{M}-\text{MeNCO}$] $^+$,

130 (100), [$\text{C}_7\text{H}_6\text{N}$] $^+$, 91 (24.1) [C_7H_7] $^+$, 90 (22.5) [C_7H_6] $^+$, 78 (28) [C_6H_6] $^+$, 77 (47.5) [C_6H_5] $^+$, 76 (88.7) [C_6H_4] $^+$. Found, %: C 75.88; H 4.58; N 5.98. $\text{C}_{15}\text{H}_{11}\text{NO}_2$. Calculated, %: C 75.93; H 4.67; N 5.90.

IR spectra were recorded on spectrophotometer Specord 75IR from mulls in mineral oil. ^1H NMR spectra were registered on spectrometers Bruker AM and Tesla BS-487C at operating frequencies 300 and 80 MHz respectively. ^{13}C NMR spectra were obtained on spectrometer Bruker AM at operating frequency 75.47 MHz. Internal reference TMS, concentration of compounds in solution 0.2 mol l^{-1} . Mass spectra were measured on HP 5995 instrument with direct admission of the sample into an ion source, EI, 70 eV, 60°C .

REFERENCES

1. Fiegel, M., Kessler, H., and Walter, A., *Chem. Ber.*, 1978, vol. 111, N 8, pp. 2947–2959.
2. Kessler, H., *Chimia*, 1973, vol. 27, no. 8, p. 444.
3. Fiegel, M. and Kessler, H., *J. Am. Chem. Soc.*, 1979, vol. 101, no. 8, pp. 1943–1950.
4. Dushenko, G.A., Mikhailov, I.E., Zschunke, A., Hakam, N., Mugge, C., and Minkin, V.I., *Mendeleev Commun.*, 1995, pp. 133–134.
5. Dushenko, G.A., Mikhailov, I.E., Zschunke, A., Hakam, N., Mugge, C., and Minkin, V.I., *Mendeleev Commun.*, 1997, pp. 50–51.
6. Minkin, V.I., Mikhailov, I.E., Dushenko, G.A., Kompan, O.E., and Zhunke, A., *Izv. Akad. Nauk, Ser. Khim.*, 1998, no. 5, pp. 913–923.
7. Fiegel, M. and Kessler, H., *Angew. Chem.*, 1977, vol. 89, no. 4, pp. 266–267.
8. Mahh, B.E., Taylor, B.F., Taylor, A., and Wood, R., *J. Organomet. Chem.*, 1978, vol. 162, pp. 137–144.