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AUTOMERIZATION OF NAPHTHALENE - A CORRECTION[1]

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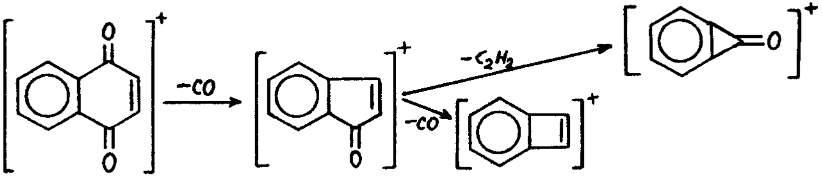
Previous communications[3] described the degenerate isomerization (automerization) of naphthalene-1-^{14}C under the influence of aluminium chloride; degradation of naphthalene *via* 1-nitro- and 1-amino-naphthalene to phthalic acid and hence by a Schmidt reaction to carbon dioxide and anthranilic acid indicated (for the naphthalene treated with water-promoted aluminium chloride in benzene at 60° for 2 hrs) scrambling of the label to all ten carbon atoms in naphthalene. This result was interpreted by various mechanisms, [3b,c] and was quoted in research papers[4] and in current awareness reports.[5]

In order to be able to study the kinetics of this process and the effects of the solvent, catalyst and temperature, a simpler method was required which could dispense with chemical degradations. Recourse was therefore had to naphthalene-1-^{13}C whose isotopic scrambling could be followed (i) without degradation by means of n.m.r. (studied by ^{13}C-satellites in the proton spectrum at 100 MHz), or (ii) after one single oxidation to 1,4-naphthoquinone, by mass spectrometry[6] as shown in Table 1.

Surprisingly, as shown by both methods, we have been unable to confirm with ^{13}C the results obtained previously with ^{14}C: if automerixation takes place, it amounts to less than 4% of the theoretical yield. Therefore, although on rechecking the results of radioactivity measurements with phthalic acids from previous degradations these were found to be reproducible, the previously reported data[3] appear to be doubtful, seemingly owing to possible contamination with radioactive trace impurities. Though the activities of naphthalene-1-^{14}C and its degradation products (starting from commercially available naphthalene-1-^{14}C from the Radiochemical Centre, Amersham, diluted 80 times with pure naphthalene) had been measured in parallel for products treated and untreated with aluminium chloride, all intermediates of the parallel runs being purified by recrystallization and/or adsorption or ion exchange chromatography, the sensitivity of the radioactive label is a pitfall from which labelling with stable isotopes is free.

Table 1. Mass-spectrometric degradation of positive radical-ions derived from 1,4-naphthoquinone



Formula		$C_{10}H_6O_2^{+\cdot}$	$C_9H_6O^{+\cdot}$	$C_8H_6^{+\cdot}$	$C_7H_4O^{+\cdot}$
α-Carbon atoms		4	3	2	3
^{13}C % retention	Untreated	100	77.4	48.8 - 49.4	74.9
	Treated[a]	100	73.1 - 74.2	49.1 - 49.8	75.6 - 76.2
	Treated[b]	100	-	50.7	77.1 - 77.5
	Treated[c]	100	-	49.1	75.6

[a] $AlCl_3 + H_2O$ molar ratio 1:1; [b] $AlCl_3 + H_2O$ molar ratio 1:0.2; [c] $AlCl_3$+ HCl.

Naphthalene-1-^{13}C, m.p. 78 - 79°, was prepared[7] and found by mass apectrometry at 9 eV to contain 54.1% labelled product and to be free from impurities. Amounts of 0.4 g naphthalene-1-^{13}C in 2.5 ml benzene were treated at 60° for 2 hrs with 0.4 g aluminium chloride (commercial, sublimed, or exposed to atmospheric moisture, and checked by analysing the $AlCl_3$ content in the catalyst employed). After chilling and hydrolysing, the naphthalene was extracted with ether and purified by steam distillation, yield 67 - 75 mg, m.p. 77 - 78°. Proton magnetic resonance in CCl_4 solution failed to show migration of the label from the α-position. Oxidation of the product left (63 mg) after distillation of the carbon tetrachloride, by chromic anhydride in acetic acid - water at 50° for 40 min, afforded naphthoquinone m.p. 120°, yield 29 mg. This was purified by g. l. c. on silicone/chromosorb at 150°. The mass spectral data (cf.[6,7]) presented in Table 1 (recalculated for a labelled compound content of 100% after correcting for naturally occuring ^{13}C) are proportional not to the total numbers of carbon atoms in the fragment ions (as would have been the case if complete automerization had taken place) but to the numbers of initial α-carbon atoms retained in the ion, indicating absence of automerisation.

Heating the reaction product after hydrolysis to 300° and then isolating purified naphthalene-^{13}C did not change the n. m. r. or mass spectra. Bubbling dry hydrogen chloride through the naphthalene - $AlCl_3$ - benzene mixture (experiment c in Table 1) or using sublimed aluminium chloride produced only slight modifications of the spectra, which cannot be safely attributed to an automerization (in any case less than 4%).

Similar negative results have been independently obtained with naphthalene-1-^{13}C using n. m. r. and e. s. r. techniques by H.A. Staab and M. Haenel[8], whom we thank for communicating their unpublished results.

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