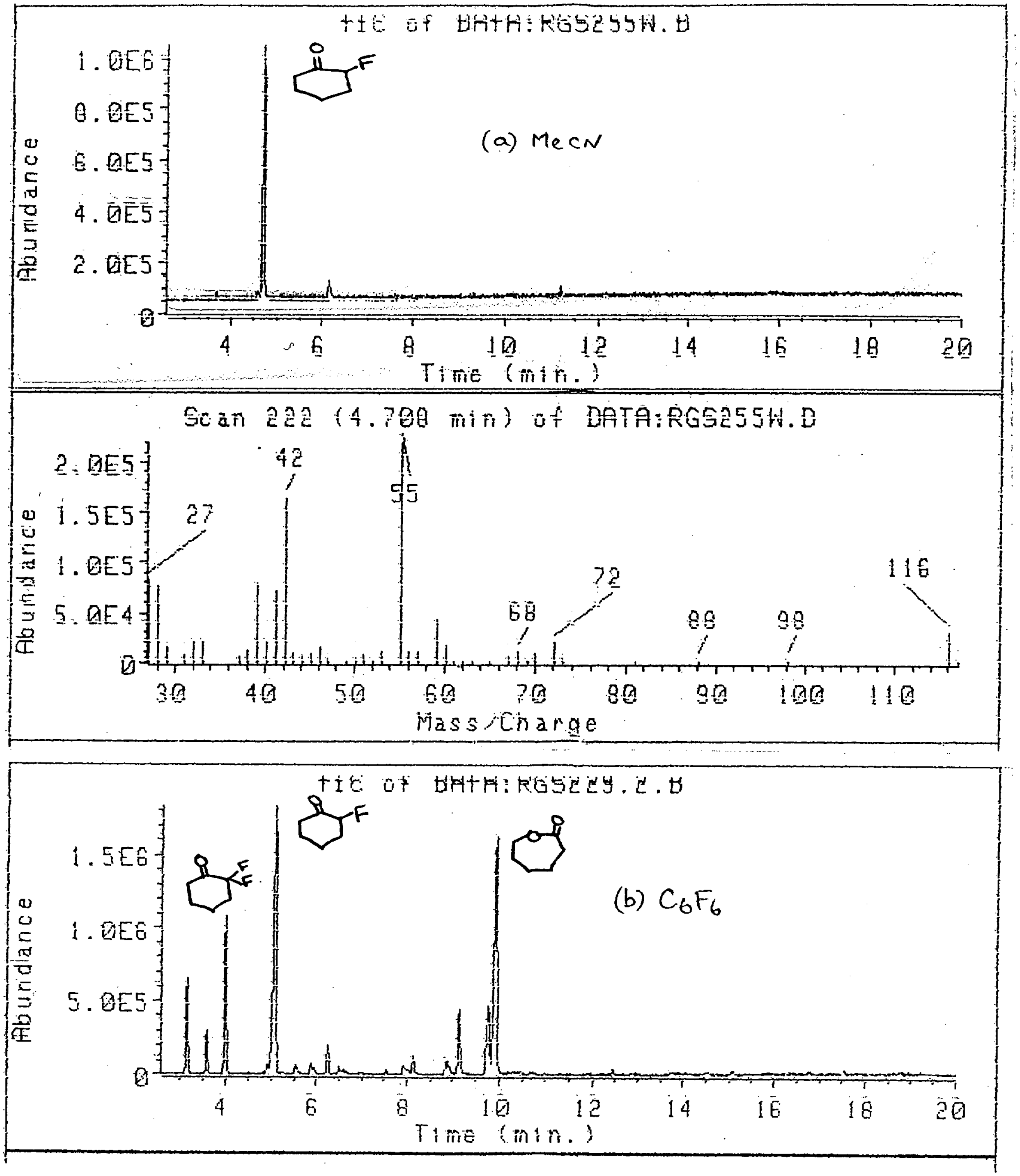
Reactions of TMS enol ethers with XeF_2.

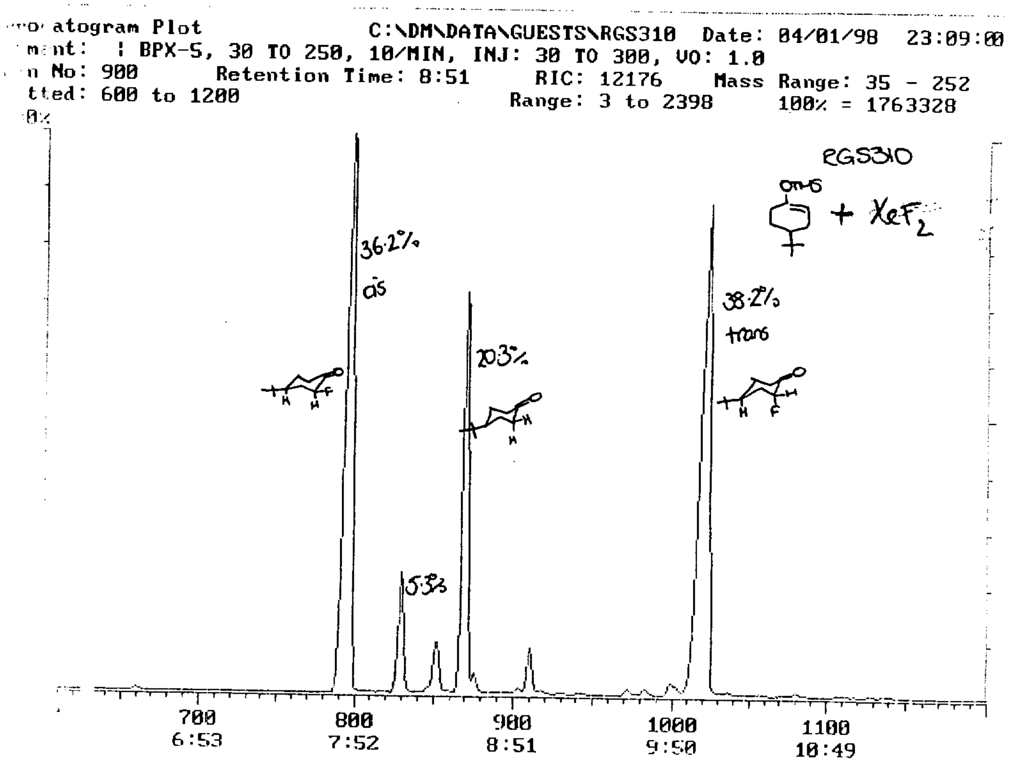
Enol ether of cyclohexanone. To a stirred solution of 1-trimethylsilyloxycyclohexene (254 mg) in acetonitrile (10 ml) in a 25 ml Pyrex flask was added xenon difluoride (500 mg) quickly and in one portion. The reaction was stirred at room temperature (1 h) in the glove box atmosphere of dry nitrogen. After this time the reaction mixture was removed from the glove box and the solvent removed by evaporation to give a colourless oil. This product was purified by Kugelrohr distillation and identified as 2-fluorocyclohexanone (156 mg, 92%), bp 150 °C at 30 mmHg (lit. bp 56-58 °C at 3.8 mmHg). ν_{max}/cm^{-1} 2920, 2891, 1756, 1455, 1101, 1015; δ_H ($CHCl_3$) 1.5-2.1 (m, 6H, CH_2), 2.25-2.45 (m, 2H, CH_2), 2.45-2.60 (m, 2H, CH_2), 4.87 (1H, dm, $J_{H,F}$ 48 Hz, CHF); δ_C 22.6 (d, $J_{C,F}$ 10 Hz, CH_2), 34.0 (d, $J_{C,F}$ 18 Hz, CH_2CHF), 40.0 (s, CH_2), 92.5 (d, $J_{C,F}$ 190 Hz, CHF) and 205.8 (q, CO); δ_F -188.7 (dm, $J_{F,H}$ 48 Hz); *m/z* Observed for $M^{\cdot+}$: 116.0637.C_6H_9FO requires 116.0637.

Using the same procedure and identical reaction conditions, the other TMS enol ethers were reacted with xenon difluoride.

Enol ether of norcamphor. The following work-up procedure was used to isolate the amide **14**. After reaction of xenon difluoride with the TMS enol ether of norcamphor, in the manner described above, the crude reaction product was obtained as an orange oil. This product mixture was separated using chromatatron chromatography (silica gel) using first ethyl acetate/ petroleum ether (bp 40-60 °C) as eluent. The proportion of ethyl acetate was gradually increased and the plate was finally eluted with methanol to give a colourless solid (R_f 0.2). This was recrystallised from ethyl acetate and identified as the amide **14** (110 mg, 29%), colourless needles, mp 159-160 °C (from ethyl acetate). (Found C, 64.80, H, 8.04, N, 8.28. $C_9H_{13}NO_2$ requires C, 64.67, H, 7.78, N, 8.38%); ν_{max}/cm^{-1} 3268, 2969, 1755, 1651, 1556, 1376, 1304, 1136, 1085; δ_H ($CHCl_3$) 5.58 (br.s, 1H, NH), 3.7 (m, 1H, $C\underline{H}NH$), 2.7 (1H, CH), 2.6 (1H, CH), 2.0 (s, 3H, CH_3), 1.4-1.9 (m, 6H); δ_C 22.6 (s, CH_2), 22.65 (s, CH_3), 25.7 (s, CH_2), 34.5 (s, CH_2), 40.7 (s, CH), 48.4 (s, CH), 58.9 (s, CH), 107.8 (q) and 216.1 (q); *m/z* $M^{\cdot+}$ 167[Observed for $M^{\cdot+}$: 167.0945.$C_9H_{13}NO_2$ requires 167.0946].



Showing the difference in the composition of the reaction mixtures when the TMS enol ether of cyclohexanone is treated with XeF_2 in a Pyrex flask in (a) MeCN solution and (b) C_6F_6 solution.



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o atogram Plot                C:\DM\DATA\GUESTS\RGS310  Date: 04/01/98  23:09:00
ment:   ! BPX-5, 30 TO 250, 10/MIN, INJ: 30 TO 300, VO: 1.0
n No: 900      Retention Time: 8:51     RIC: 12176    Mass Range: 35 - 252
tted: 600 to 1200                         Range: 3 to 2398     100% = 1763328
0%
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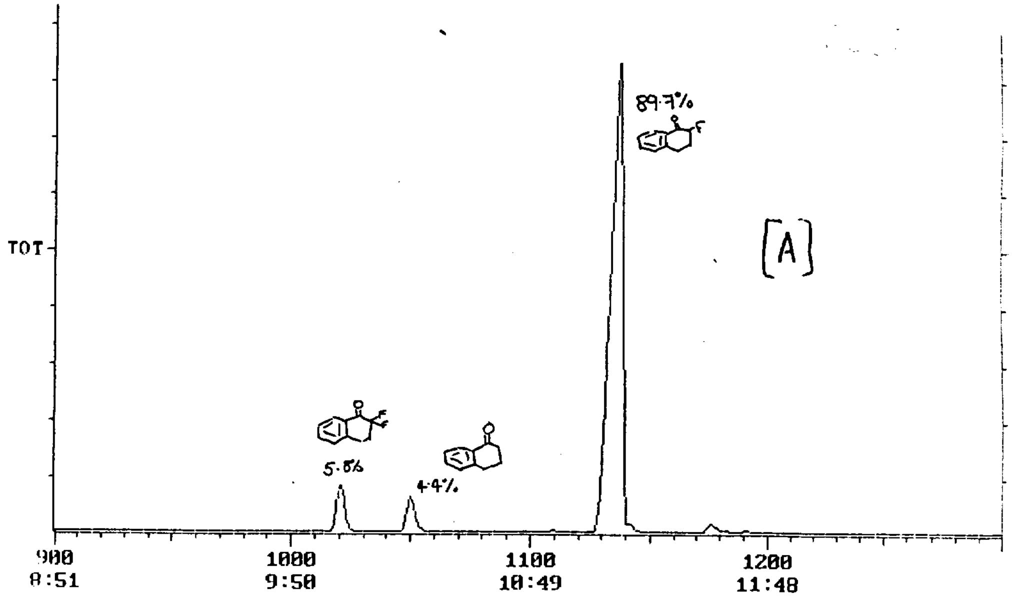
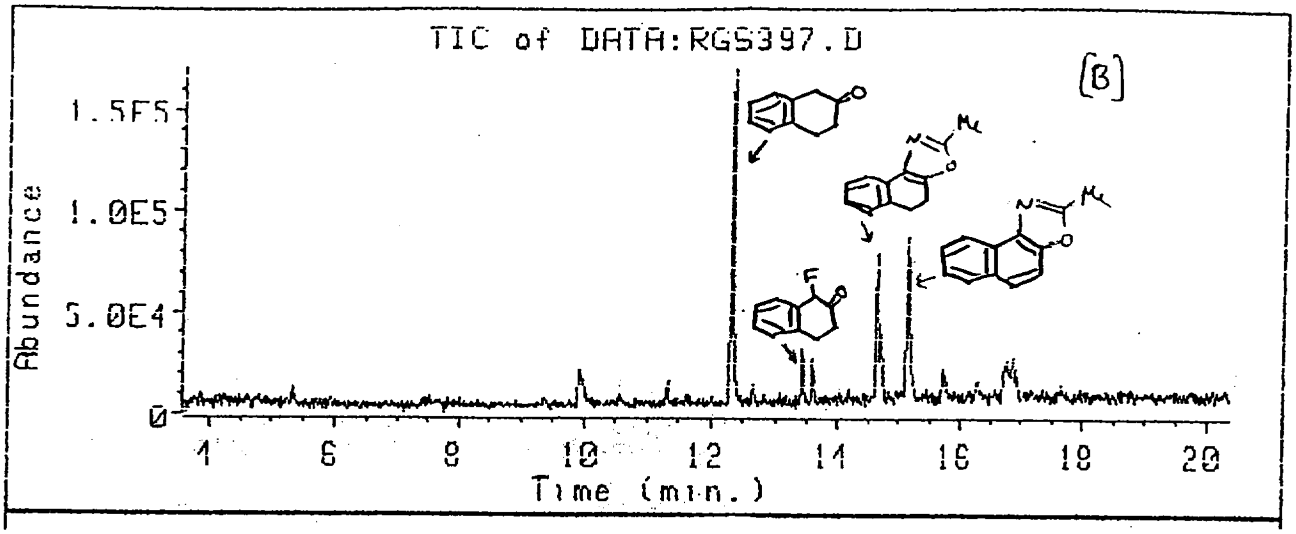
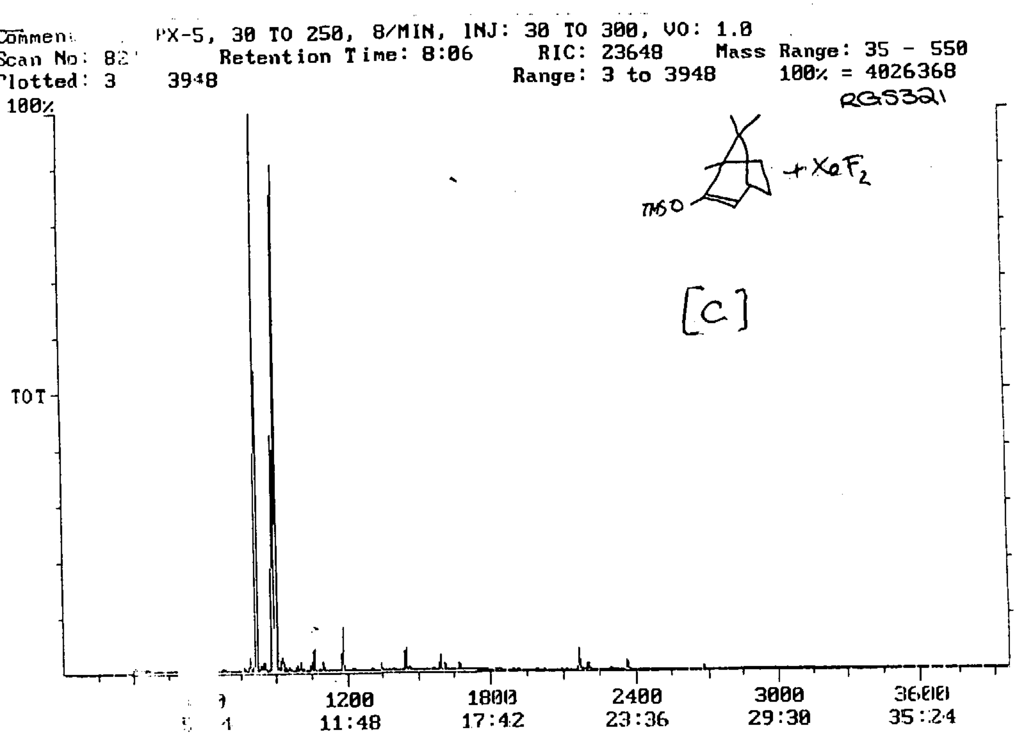
Showing the composition of the reaction mixture when the TMS enol ether of 4-tBu-cyclohexanone is treated with XeF$_2$ in MeCN. In contrast to the TMS enol ether of cyclohexanone (previous sheet), the formation of 20% of the ketone should be noted.

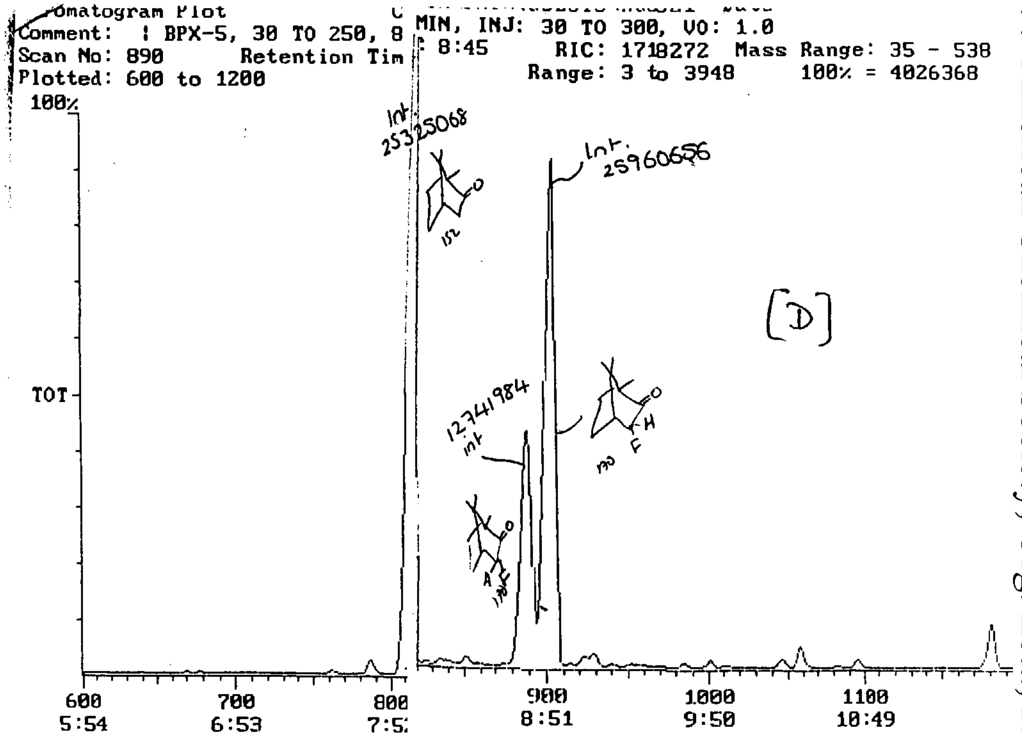


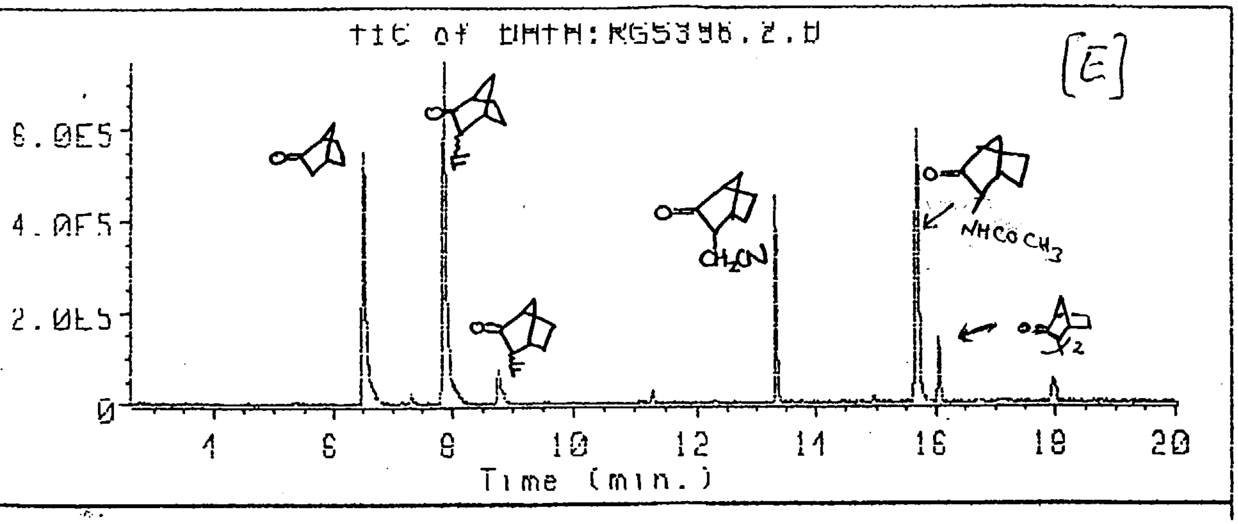


Comparison of the GCs of the reaction mixtures from:
(i) 1-tetralone TMS enol ether [A];
(ii) 2-tetralone TMS enol ether [B].

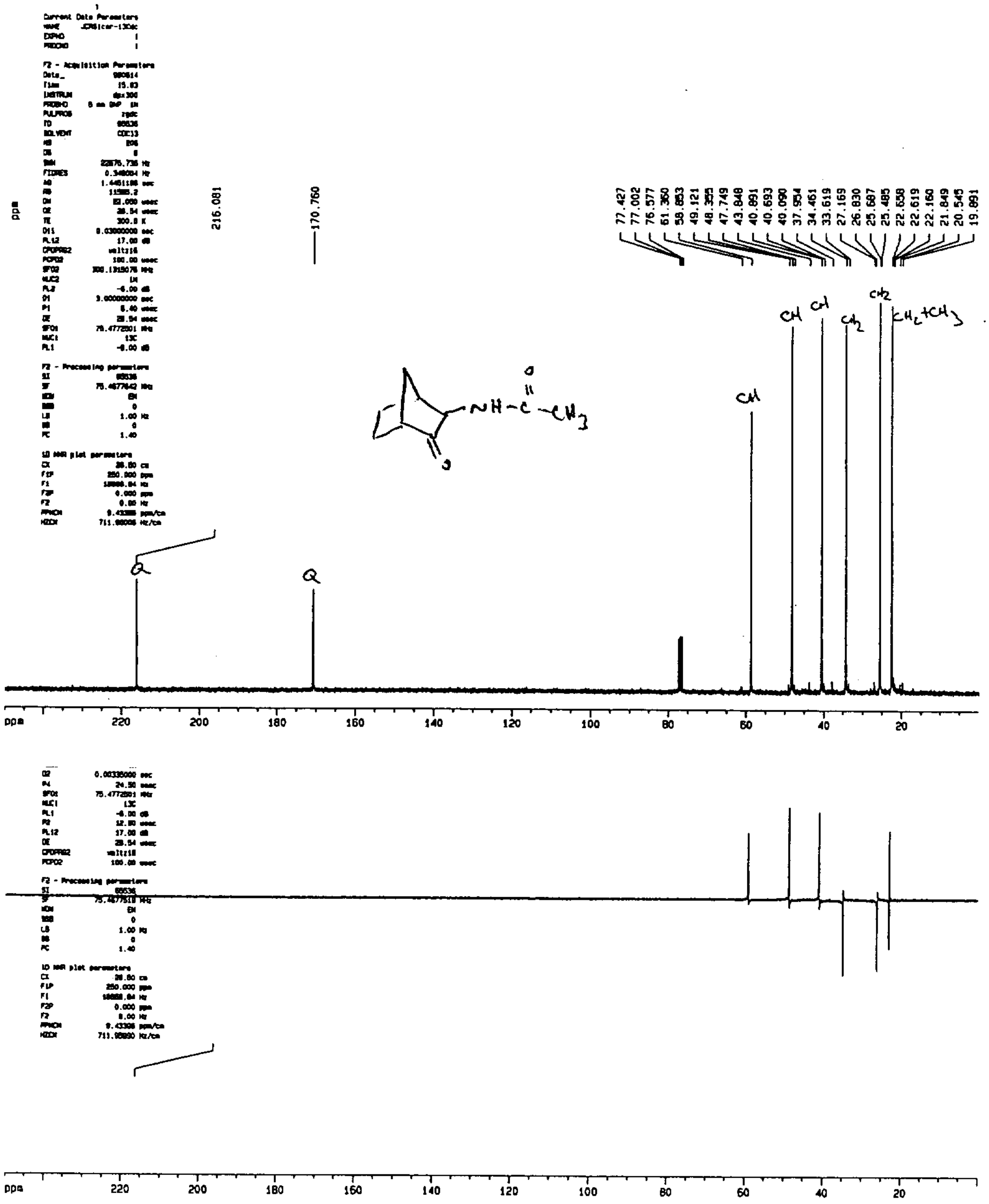
The chromatograph shows the absence of solvent derived products in the 1-tetralone reaction and, in contrast, the presence of solvent derived products in the 2-tetralone reaction and a low yield of the fluoro-product.



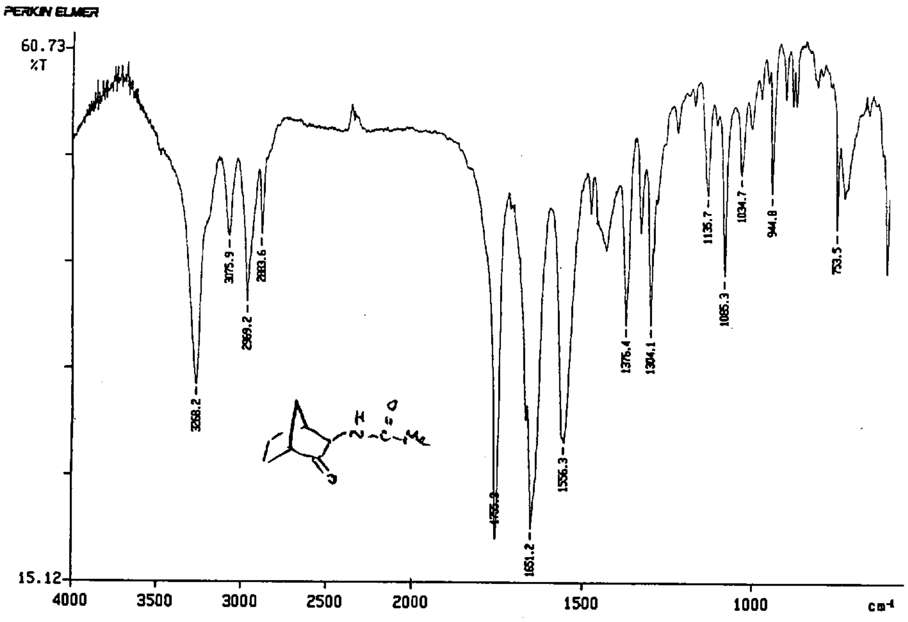


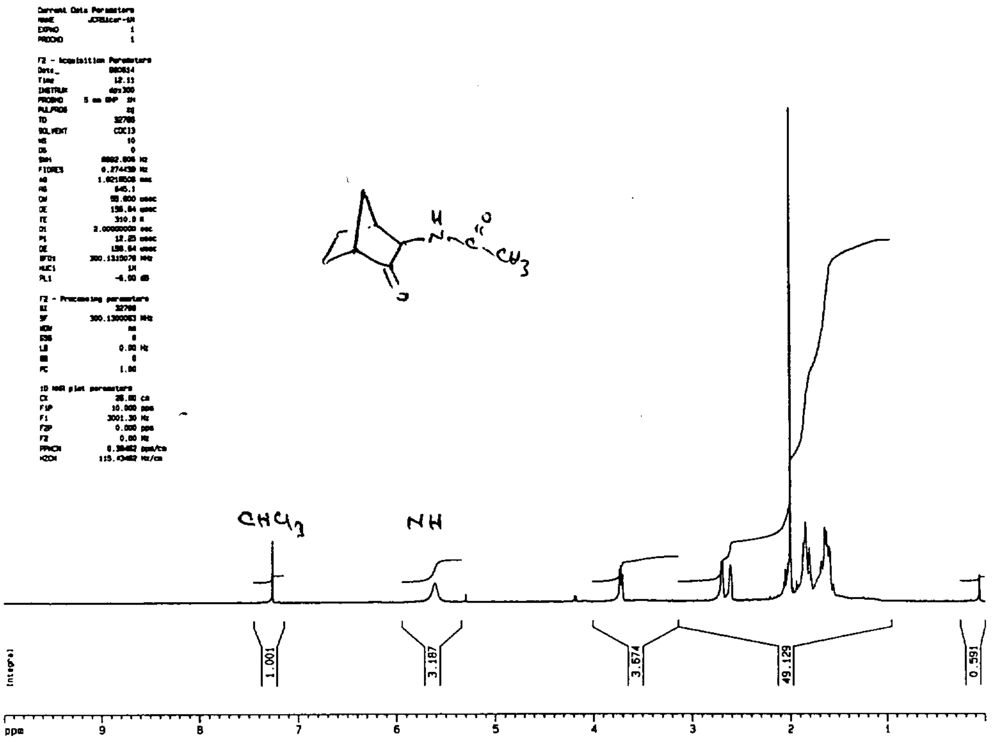


Comparison of the GCs of the reaction mixtures from:
(i) camphor TMS enol ether [C and D];
(ii) norcamphor TMS enol ether [E].
The chromatographs show the absence of solvent derived product in the camphor reaction and the presence of solvent/radical derived products in the norcamphor reaction.



Showing the ^{13}C NMR spectra of compound **14**.





Showing theIR and ^{1}H NMR spectra of compound **14**.