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STRUCTURE DETERMINATION OF 2-METHOXYTROPONE-CYCLOHEPTATRIENE ADDUCTS BY MASS SPECTROMETRY

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We have previously reported the formation of a cage molecule, pentacyclo[$7.5.0.0^{2,7}.0^{5,13}.0^{6,12}$]-tetradeca-3, 10-dien-8-one (I), and its 7-chloro derivative (II) by the reactions of cycloheptatriene with tropone and 2-chlorotropone, respectively (1). The structure of the chloro derivative (II) was also established by an X-ray analysis (2) and has been chemically correlated with I (3). We now wish to report that 2-methoxytropone and cycloheptatriene afford two new adducts, one being the methoxy derivative of I and the other a new type of cage compound. The structures of the two compounds were determined by mass spectrometry.

The mass spectrum of I (FIG. Ia) exhibits very strong peaks corresponding to cycloheptatriene (m/e 92) and tropylium ion (m/e 91), besides the molecular ion (m/e 198) and characteristic peaks due to M-CO (m/e 170) and M-C_7H_7 (at m/e 107, hydroxytropylium ion). This tendency is also shown in the mass spectrum of II (FIG. Ib), the last two peaks being by far the largest. Peaks due to M^+ (232), M-CO (204), M-Cl (197), M-CO-Cl (169), and chlorohydroxytropylium ion (m/e 141) are also present. This indicates that, in both cases, the molecule preferentially cleaves to give cycloheptatriene ion and tropylium ion. However, the mass spectrum (FIG. Ic) of the trideuterated chloro-adduct III, prepared by the same reaction from 2-chlorotropone-3, 5, 7-d_3 (4), shows that, although the fragmentation is similar to II, the base peak is now due to dideuteriotropylidene (m/e 94) and the corresponding dideuteriotropylium ion peak (m/e 93) is the second highest. This reveals that both modes of fragmentation a and b lead to the formation of m/e 92 and m/e 91 peaks in both I and II as shown below.

This characteristic fragmentation was used to determine the structure of the cage compounds formed by the

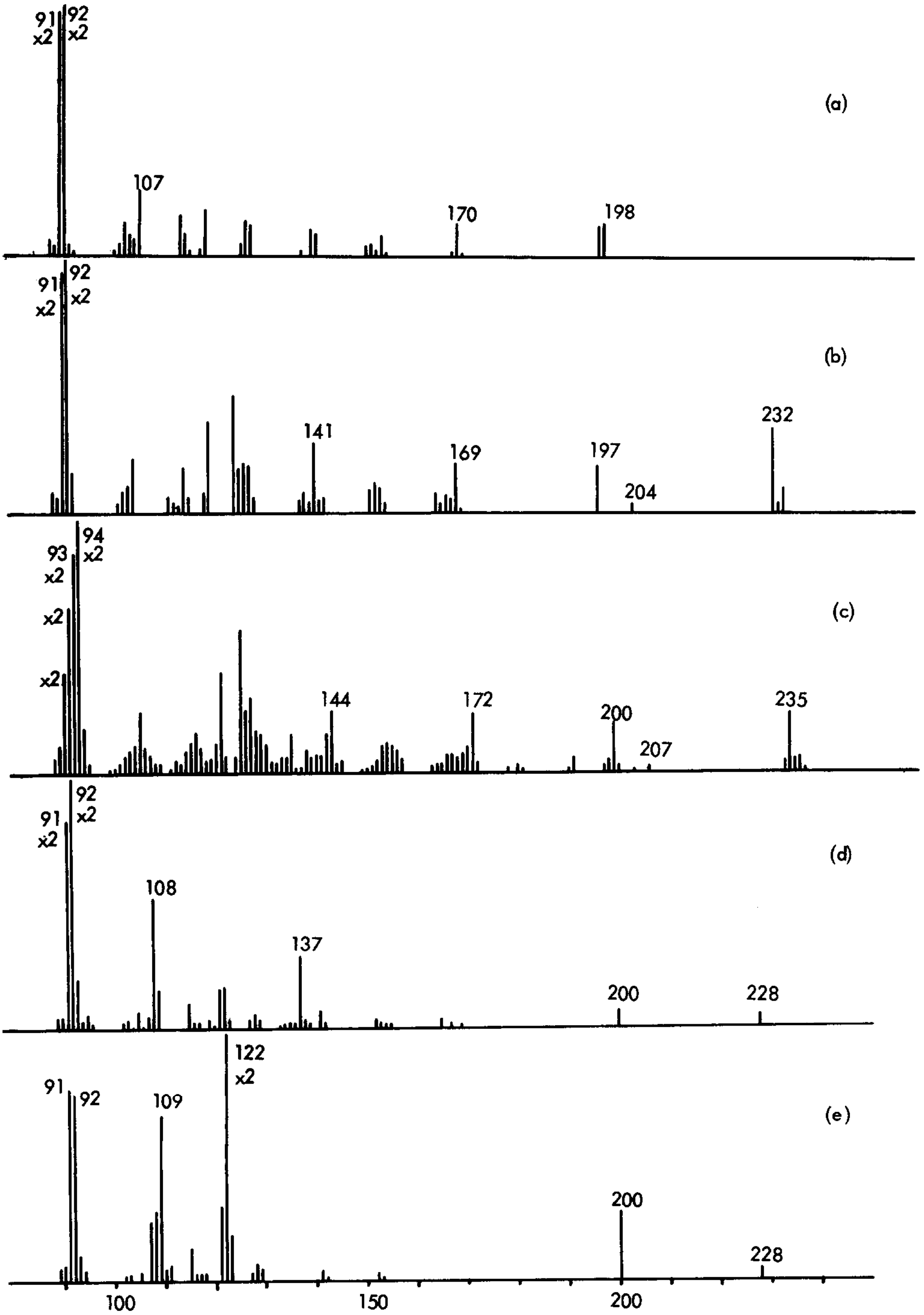
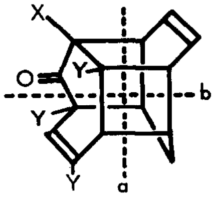
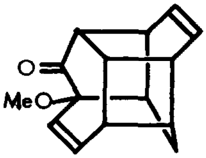


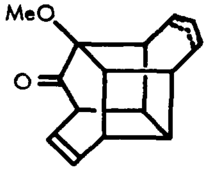
FIGURE 1. Mass Spectra of the Adducts I, II, III, IV and V



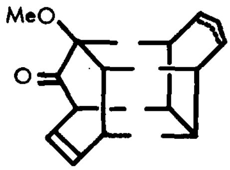
I: X=Y=H
II: X=Cl, Y=H
III: X=Cl, Y=D
IV: X=OCH_3, Y=H



IVa



V



Va

reaction of 2-methoxytropone and cycloheptatriene.

Heating of 2-methoxytropone (5) and tropylidene at 200° for 15 hours yielded, after silica gel chromatography, two adducts: Adduct IV (6), m.p. 107.5-109°, and adduct V, m.p. 89-93°. Both of them have a cyclopentanone grouping (ν 1744 cm^{-1}) with the carbonyl group located β to an olefinic linkage as shown by their UV spectra [IV, λmax 310 mμ (ϵ 179) and V, λmax 308 mμ (ϵ 404)]. The NMR spectrum of IV in $CDCl_3$ is very similar to those of I and II (1), showing signals due to four olefinic protons at 5.66 (1H) and 6.0 ppm (3H), and one methylene bridge at 2.06 ppm in addition to that of a methoxyl group at 3.24 ppm. Although a detailed analysis of the spectrum was not possible, NMDR experiments clearly disclosed that the methylene group is not connected directly with the double bonds and that all of the olefinic protons have at least one hydrogen in allylic positions. Mass spectrum of IV (shown in FIG. Id) exhibits very strong peaks ascribed to tropylidene and tropylium ion (m/e 92, 91), the only other prominent peaks being the ones due to methoxy-hydroxytropylium ion (m/e 137) and anisole (m/e 108), and lacks a peak due to methoxytropylidene (m/e 122) or methoxytropylium ion (m/e 121) which might be expected through the fragmentation b if the compound had the structure IVa.

NMR spectrum (FIG. II) of the second adduct V in benzene-d$_6$ also shows signals due to one methoxyl at 3.30 ppm and four olefinic protons at 5.55, 5.79, 6.02, 6.18 ppm, but lacks the characteristic high-field signals due to the methylene bridge (1). The overall pattern is also different from those of I, II and IV. Complete analysis of the NMR spectrum was again impossible, but NMDR experiments revealed that each olefinic hydrogen is coupled to at least two hydrogens. This evidence, when coupled with the UV and IR data mentioned above, eliminates all possible structures except those resulting from the three difference combination of the two seven-membered rings shown in Va. The mass spectrum of V (FIG. Ie) shows the

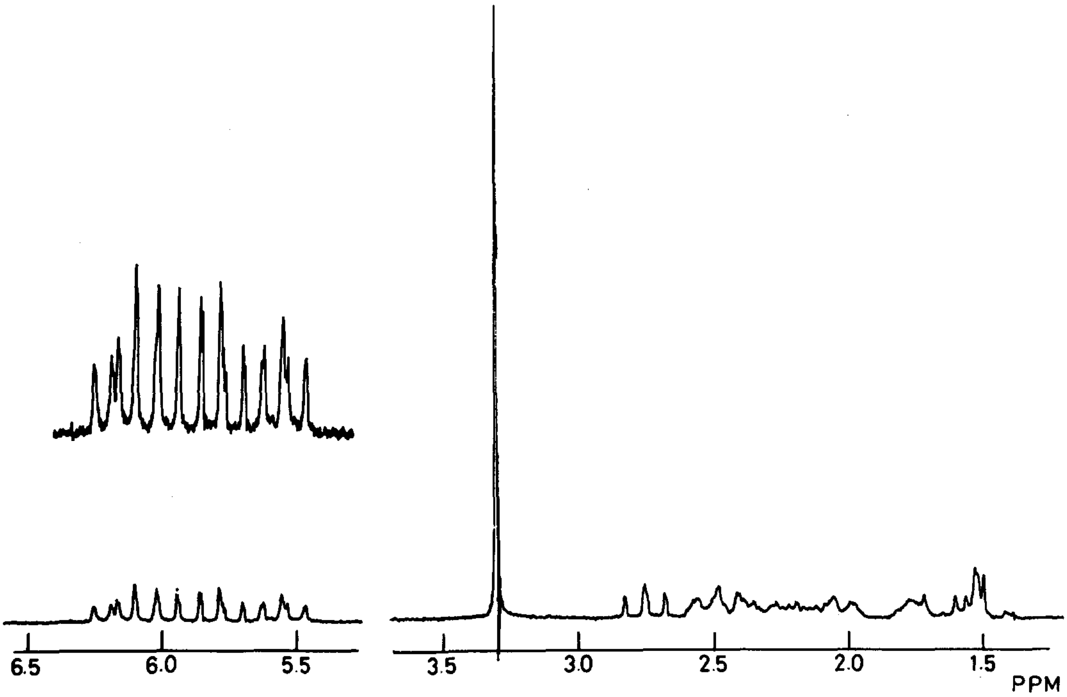


FIGURE 11. NMR Spectrum of the Adduct V in C_6D_6

base peak at m/e 122, due to methoxytropylidene ion, as well as peaks at m/e 92 and 91. The formation of methoxytropylidene ion is only compatible with the structure V with one double bond unlocated.

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References and Footnotes

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6) UV and IR spectra were measured for methanol solutions and KBr discs, respectively. NMR spectra were measured at 60 MHz or 100 MHz. Chemical shifts δ are expressed in ppm from internal TMS. All compounds gave satisfactory elemental analysis.