Elucidation of the Structure of the Double [6+4]Adduct of Tropone and Dimethylfulvene by Nuclear Magnetic Resonance and the Nuclear Overhauser Effect

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Summary The complete structure of the 2 : 1 adduct of tropone and dimethylfulvene was elucidated by analyses of the twenty-two proton n.m.r. spectra in various solvents and by N.O.E. experiments.

THE thermal cycloaddition of tropone to dimethylfulvene has been reported recently.[1] As there are thirty-eight possible primary 1 : 1 adducts of tropone and dimethylfulvene (excluding carbonyl additions), twenty-two of which are thermally allowed, there are several hundred reasonable thermally allowed 2 : 1 adducts of tropone and dimethylfulvene. The isolation of a single 2 : 1 adduct (I) in up to 88% yield by the Scheme illustrated is an example of both a novel and a phenomenally specific cycloaddition. We report the details of the total elucidation of structure of (I) by a variety of n.m.r. techniques.

The n.m.r. spectra of (I) at 100 MHz in common deuteriated solvents were too complex for analysis.

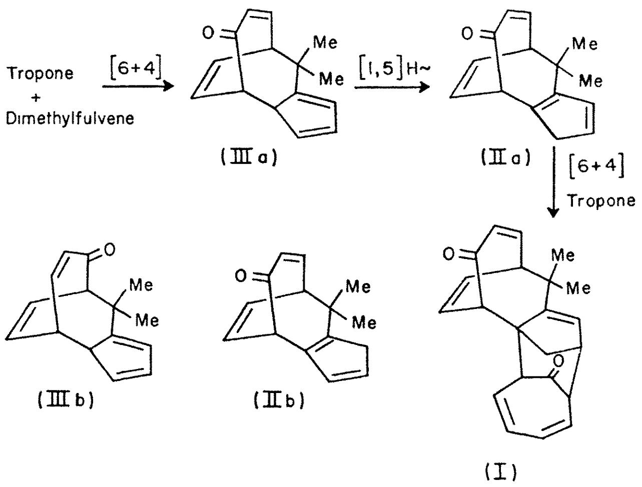
At 220 MHz, the thirteen aliphatic proton resonances of (I) were best resolved in C_6D_6, but the spectral patterns of most of the olefinic protons remained complex. However, by mixing C_6D_6 and $CDCl_3$ in varying proportions and observing changes in the spectral patterns, it was possible to identify the resonance of every proton in the molecule. The spectral assignments were then confirmed by conducting spin-decoupling experiments on a HA-100 spectrometer operating in the frequency sweep mode. Finally the stereochemistry of the molecule was determined by N.O.E. experiments. Additional assistance in deciphering the spectra of (I) was afforded by preparation of tetradeuterio-(I) from the reaction of dimethylfulvene and 2,7-dideuteriotropone.[†]

Assignments of the resonances of the aliphatic protons in C_6D_6 solution (Figure, a) were made as follows: the sharp three proton singlets at δ0·87 and 1·03 are assigned to methyls A and B, respectively (*vide infra*). The sixteen-line multiplet at δ1·26 is assigned to H-19A in light of its geminal coupling with H-19B (12·0 Hz) and vicinal coupling with H-9 (5·0 Hz), the dihedral angle between H-19A and H-9 being approximately 30°. The two long-range couplings with H-3 (2·0 Hz) and H-8 (1·0 Hz) imply that H-19A is disposed in a "W" arrangement with respect to both H-3 and H-8 which, in turn, indicates the "second" tropone moiety is disposed *exo* to the cyclopentadiene moiety, since the *endo*-arrangement would place neither H-19A nor H-19B in a "W" arrangement with H-3 and H-8.

The broad doublet (12·0 Hz) at δ1·92 represents H-19B. The broadening of the H-19B doublet is caused by three small couplings of unequal magnitude. H-19B is coupled to vicinal H-9 by a small coupling (0·8 Hz) compatible with the measured dihedral angle of 85°. The larger long-range coupling of H-19B with H-10 (1·5 Hz) is due to their "W" type arrangement, while the smallest coupling of H-19B is with H-17 (0·5 Hz).

The doublet of triplets at δ2·21 is assigned to bridgehead H-13 which is coupled to both vicinal olefinic neighbours H-14 and H-18 with identical couplings (8·5 Hz). The additional splitting is an allylic coupling with H-17 (1·0 Hz).

The slightly broadened doublet of overlapping triplets at δ2·34 is assigned to bridgehead H-9. The two small equal couplings (3·0 Hz) are due to spin interactions with vicinal aliphatic H-8 and olefinic H-10. The dihedral angles formed by H-9 with H-8 and H-10 are 50° and 30°, respectively, when the tropone and cyclopentadiene moieties are *exo*, while they would be 0° and 30°, respectively, for the corresponding *endo*-adduct. The remaining splittings of H-9 by H-19A (5·0 Hz) and H-19B (0·8 Hz) have been noted earlier.



SCHEME

The remaining aliphatic resonances at δ2·97, 3·23, and 3·47 all were absent in the spectrum of tetradeuterio-(I),[†] which indicated these resonances were due to H-1, H-3, and H-8. The broadened doublet of overlapping triplets at δ2·97 and the doublet of doublet of doublets at δ 3·47 are ascribed to H-8 and H-3, respectively. These assignments were based on double resonance experiments which indicated that the two large couplings of 8·0 Hz in the δ2·97 and 3·47 signals were due to the spin interactions of H-8 and H-3 with those of the vicinal olefinic neighbours H-7 and H-4, respectively. The intermediate size splittings of 3·0 Hz observed in the two resonances are due to the long range "W" type coupling between H-8 and H-3. The second 3·0 Hz splitting in the H-8 resonance at δ2·97 represents the coupling between H-8 and its vicinal neighbour H-9. The smallest splitting (2·0 Hz) in the H-3 adsorption and the broadening of the H-8 resonance

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[†] Prepared from hydroxytropinone by base-catalysed exchange of α-protons for deuterons followed by conversion into tropone by the method of van Tamelen,[2] modified by the use of deuteriated solvents.

result from the aforementioned "W" type interactions of these two protons with H-19A.

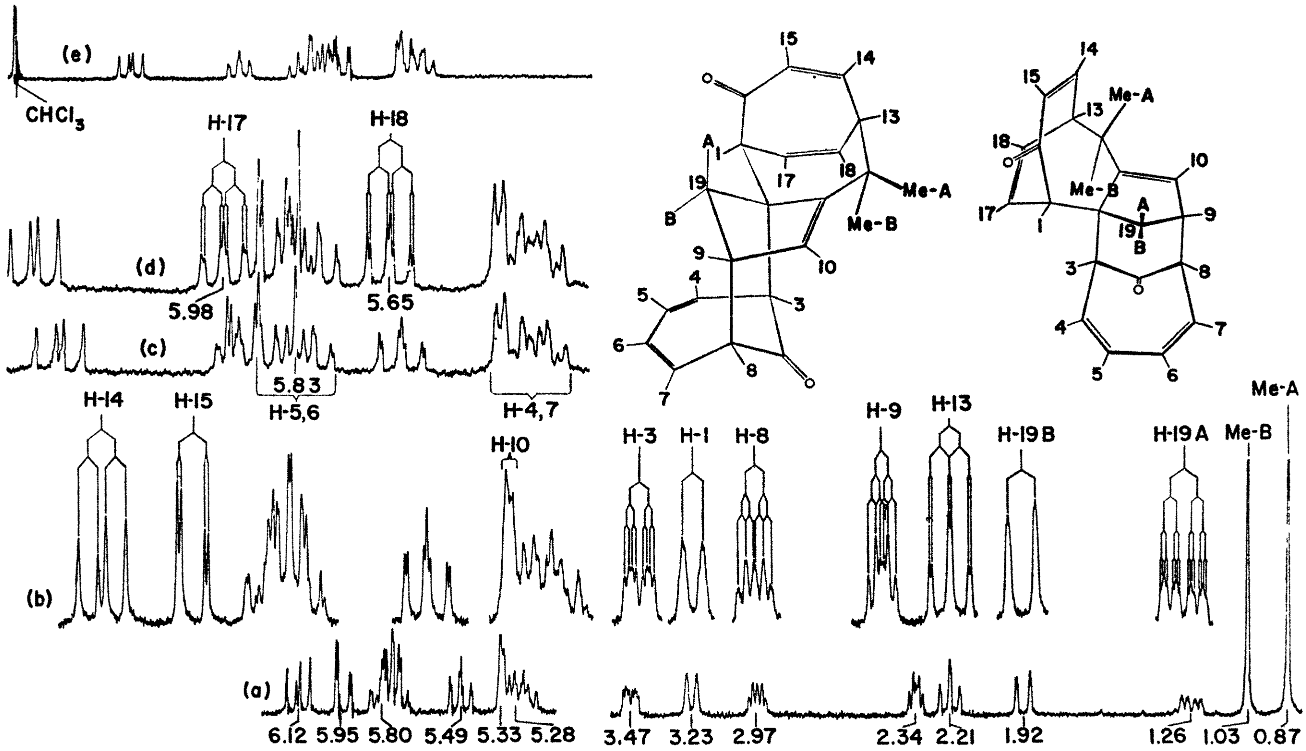

FIGURE. 220 *MHz spectra of* (I) (a) *in* C_6D_6; (b) *expansion of* (a); (c) *in* ca. 2 : 1 C_6D_6 : $CDCl_3$; (d) *in* ca. 1 : 2 C_6D_6: $CDCl_3$; (e) *in* $CDCl_3$.

The remaining aliphatic proton resonance at δ3·23 is assigned to H-1. This broad doublet arises from vicinal coupling with H-17 (8·5 Hz). Expansion of this resonance results in partial resolution of the broad doublet into a pair of pseudoquartets arising from three nearly equal long-range couplings (*ca.* 1·5 Hz) with H-15, H-18, and H-10 *via* a "W" type coupling, an allylic coupling, and an uncommon five-bond coupling, respectively.

Although most of the olefinic resonances overlapped in C_6D_6, the lowest-field resonances were well separated from other resonances. The absence of the resonance at δ5·95 in tetradeuterio-(I), the characteristic vicinal coupling between the protons resonating at δ5·95 and 6·12 (11·5 Hz), as well as the chemical shifts of these protons resulted in the assignment of the resonances at δ 5·95 and 6·12 to H-15 and H-14, respectively. H-15 exhibits an additional "W" type coupling with H-1 (1·5 Hz), while H-14 exhibits a vicinal coupling with H-13 (8·5 Hz).

The remaining olefinic proton resonances were identified when the C_6D_6 solution was gradually diluted with $CDCl_3$, and the 220 MHz spectra obtained at various concentrations were compared (see Figure, b—d).

The broad resonance at δ5·33 in C_6D_6, which overlaps with the two-proton multiplet centred at 5·28 p.p.m., retains virtually the same pattern in the mixed solvent and is ascribed to H-10. Irradiation of the H-10 resonance and observation of changes in the aliphatic proton resonances resulted in confirmation of the assignment through observation of previously mentioned couplings with H-9 (3·0 Hz), H-19B (1·5 Hz), and H-1 (1·5 Hz).

In the mixed solvent (Figure, d), the very similar doublet of doublet of doublet patterns at δ5·65 and 5·98 are ascribed to H-18 and H-17, respectively. Double-resonance experiments verified the assignments. H-17 and H-18 were shown to be mutually coupled by a *cis*-coupling of 8·0 Hz. H-17 is also coupled to vicinal H-1 (8·5 Hz) and allylic H-13 (1·0 Hz), while H-18 is also coupled to vicinal H-13 (8·5 Hz) and allylic H-1 (1·5 Hz). Additional broadening in the H-17 resonance is due to long-range coupling with H-19B (0·5 Hz).

Irradiation of the H-3 resonance resulted in simplification of the portion of the two-proton multiplet at 5·28 p.p.m., revealing the position of resonance due to H-4. Similarly, irradiation of H-8 simplified that portion centred at 5·33 p.p.m. due to H-7. These vicinal couplings were 8·0 Hz in both cases.

The previously unassigned resonances of the vicinal olefinic H-5 and H-6 are most clearly observed as a symmetrical pattern centred at 5·83 p.p.m. in the mixed solvent (Figure, c). The coupling constants between H-4, 5, 6, and 7 were not determined, although the similarity with related patterns in cyclohexadienes[3] leaves no doubt as to the origin of these resonances.

The n.m.r. spectra of tropone Diels–Alder adducts with a number of dienophiles[4] have been analysed and are fully in accord with our analysis in regards to mutual couplings between H-1, 17, 18, 13, 14, and 15 in (I). The only significant differences in coupling constants between this work and that preceding are in the vicinal couplings 8·5 Hz) between H-1 and H-17 and between H-13 and H-18. In the bicyclo[3,2,2]nona-3,6-dien-2-one systems, the analogous couplings range from 6·2 to 7·4 Hz.[4] In (I), the dihedral angles between these protons are about 0°, while in the earlier adducts, the corresponding dihedral angles approach 10°.

Apart from the proof of the gross structure and connectivity of adduct (I), the assignments of all the resonances and couplings in the n.m.r. spectra resulted in elimination from consideration all isomers resulting from *endo*-addition of tropone to (II). There remained the possibility that (IIIb) rather than (IIIa) was the initial adduct, or that three [1,5] sigmatropic shifts of hydrogen from (IIIa) to form (IIb) precede addition of the second tropone. Of the eight possible structures arising from these various combinations and addition of tropone to either the "top" or "bottom" of the cyclopentadiene ring, the combination leading to (I) was proved by double-resonance experiments carried out under N.O.E. conditions[5] in a mixed solvent system at 100 MHz.

Irradiation of the higher-field methyl resonance (A) resulted in increases in intensity of 15% of the resonances due to both H-10 and H-13. The proximity of H-13 and a methyl group requires that the initial [6 + 4] cycloaddition led to (IIIa) rather than (IIIb), while the proximity of H-10 and a methyl requires that (IIa) rather than (IIb) should be the immediate precursor of (I).

Irradiation of the lower-field methyl resonance (B) resulted in an increase in intensity of 13% in the H-3 resonance. In the hypothetical adduct in which tropone added to the "top" of cyclopentadiene ring (nearest the $\alpha\beta$-unsaturated ketone), the methyl near H-3 would be expected to be shielded since it would of necessity lie directly over the C-14,15 double bond. Since B lies downfield from A, the structure of (I) in which tropone has added to the "bottom" of the cyclopentadiene is preferred.

The origin of the remarkable periselectivity,[1] regiospecificity, and stereospecificity of this reaction will be the subject of future communications.

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