

mixture with an authentic sample of triethyl 1,2,3-cyclopropanetricarboxylate¹⁰ confirm the absence of this anticipated "trimer" of carboethoxycarbene.

Diphenyldiazomethane gives no detectable insertion product when decomposed catalytically in cyclohexane with cupric sulfate or cuprous chloride. Gaspar and Jones, *et al.*, likewise report⁷ that the cuprous chloride catalyzed decomposition of unsubstituted diazomethane in cyclohexane fails to produce any detectable methylcyclohexane. Thus the conjugation of copper carbenoids with a carbonyl group appears to play a crucial role in determining the feasibility of intermolecular C-H insertion. The mechanism of C-H insertion by copper carbenoids is not known but may involve dissociation of the carbenoid to free carbene.⁶

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Assignment of ¹³C Nuclear Magnetic Resonance Signals. Fingerprints in Off-Resonance ¹³C, {¹H} Nuclear Magnetic Double Resonance Spectra¹

Sir:

One of the most widely used techniques for the assignment of ¹³C nmr signals is off-resonance continuous wave spin decoupling.² Not only can the resonances of quaternary carbons, CH-, CH₂-, and CH₃- groups, be readily identified³⁻⁵ but, in a more refined stage, the residual one bond ¹³C,¹H coupling constant J_R measured in these partially decoupled spectra may frequently be used to interrelate carbon and proton chemical shifts, since J_R is given² by

$$J_R = J_0 \Delta\nu / \gamma H_2 \quad (\dot{\gamma} = \gamma / 2\pi) \quad (1)$$

where J_0 is $^1J(^{13}\text{C}, ^1\text{H}_i)$, $\Delta\nu$ is the frequency difference between the proton resonance ν_i and the decoupler frequency ν_2 , and γH_2 is the power of the decoupling field.⁶ Chemically different carbons that bear the same number of protons may thus be discriminated, provided that: (1) the ¹H nmr spectrum is correctly assigned, (2) the $^1J(^{13}\text{C}, ^1\text{H})$ data are known, and (3) the difference in the $\Delta\nu$ values for individual protons yields variations in J_R that are larger than the experimental error.

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(6) The more rigorous relation $J_R = \Delta\nu J_0 / (\Delta\nu^2 + \gamma^2 H_2^2)^{1/2}$ has been derived by Pachler.⁷

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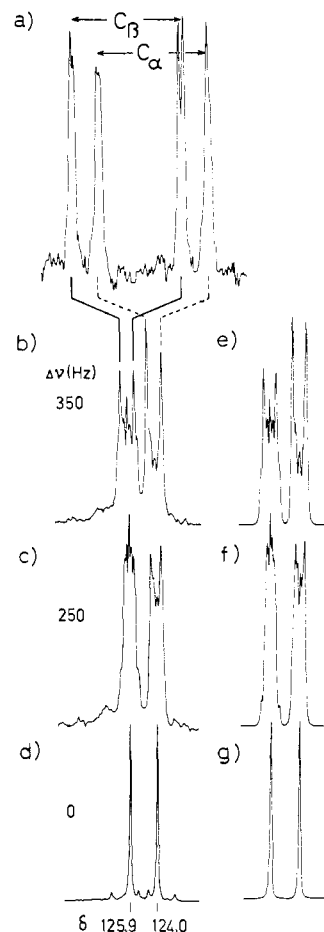
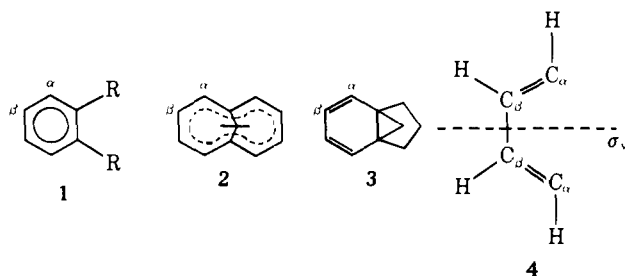


Figure 1. ¹³C nmr spectrum of the methine carbons of indan at 22.63 MHz: (a) ¹H undecoupled; (b), (c) ¹H off-resonance decoupled with ν_2 at high field from the proton resonances; (d) ¹H decoupled, δ values refer to internal tetramethylsilane; (e)-(g) calculated spectra (see text).

Recently we have shown⁸ that characteristic splitting patterns or fingerprints in the ¹H-undecoupled ¹³C nmr spectra of compounds of types 1-3, which have in common a C₄H₄ fragment of four methine groups and a plane of symmetry (4), allow an unequivocal assign-



ment of the C_α and C_β resonances, even in cases where off-resonance decoupling fails.

We now report that these fingerprints are also retained in the off-resonance decoupled spectra of 1-3, thereby eliminating certain restrictions imposed on this assignment technique.

As an example, Figure 1 shows the experimental ¹³C nmr spectra of the α - and β -carbons of indan, where $\delta(C_\alpha) = 124.0$ and $\delta(C_\beta) = 125.9$ ppm have been firmly