

mixture with an authentic sample of triethyl 1,2,3-cyclopropanetricarboxylate<sup>10</sup> 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 report<sup>7</sup> 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.<sup>6</sup>

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### Assignment of <sup>13</sup>C Nuclear Magnetic Resonance Signals. Fingerprints in Off-Resonance <sup>13</sup>C, {<sup>1</sup>H} Nuclear Magnetic Double Resonance Spectra<sup>1</sup>

Sir:

One of the most widely used techniques for the assignment of <sup>13</sup>C nmr signals is off-resonance continuous wave spin decoupling.<sup>2</sup> Not only can the resonances of quaternary carbons, CH-, CH<sub>2</sub>-, and CH<sub>3</sub>- groups, be readily identified<sup>3-5</sup> but, in a more refined stage, the residual one bond <sup>13</sup>C,<sup>1</sup>H 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 given<sup>2</sup> 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  $\nu_i$  and the decoupler frequency  $\nu_2$ , and  $\gamma H_2$  is the power of the decoupling field.<sup>6</sup> Chemically different carbons that bear the same number of protons may thus be discriminated, provided that: (1) the <sup>1</sup>H 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.<sup>7</sup>

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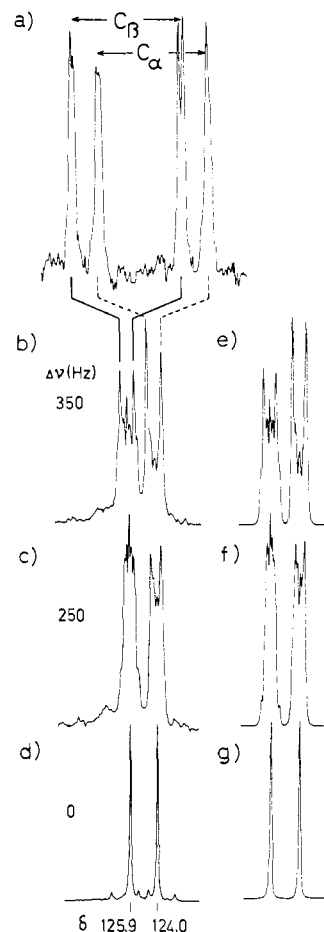
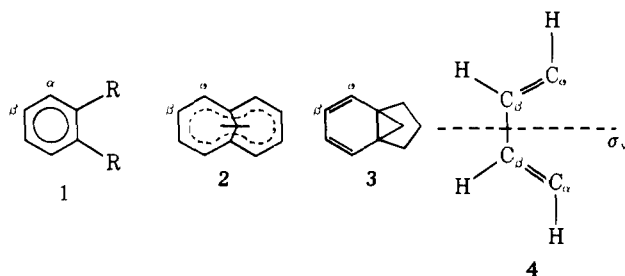


Figure 1. <sup>13</sup>C nmr spectrum of the methine carbons of indan at 22.63 MHz: (a) <sup>1</sup>H undecoupled; (b), (c) <sup>1</sup>H off-resonance decoupled with  $\nu_2$  at high field from the proton resonances; (d) <sup>1</sup>H decoupled,  $\delta$  values refer to internal tetramethylsilane; (e)-(g) calculated spectra (see text).

Recently we have shown<sup>8</sup> that characteristic splitting patterns or fingerprints in the <sup>1</sup>H-undecoupled <sup>13</sup>C nmr spectra of compounds of types 1-3, which have in common a C<sub>4</sub>H<sub>4</sub> fragment of four methine groups and a plane of symmetry (4), allow an unequivocal assign-



ment of the  $C_\alpha$  and  $C_\beta$  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 <sup>13</sup>C nmr spectra of the  $\alpha$ - and  $\beta$ -carbons of indan, where  $\delta(C_\alpha) = 124.0$  and  $\delta(C_\beta) = 125.9$  ppm have been firmly

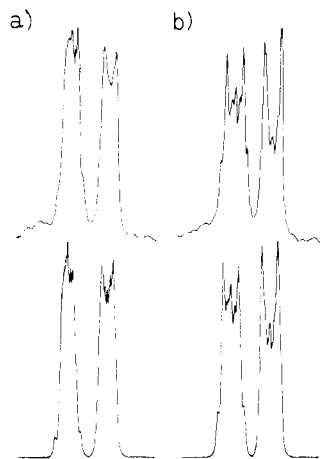


Figure 2. Experimental (upper trace) and calculated (lower trace) off-resonance  $^1\text{H}$  decoupled  $^{13}\text{C}$  nmr spectra of the methine carbons of indan with  $\nu_2$  at low field from the proton resonances: (a)  $\Delta\nu = -230$  Hz; (b)  $\Delta\nu = -290$  Hz.

established.<sup>8,9</sup> The different fine structure in the doublets of the undecoupled  $\text{C}_\alpha$  and  $\text{C}_\beta$  resonance<sup>8</sup> (Figure 1a) becomes more distinct on off-resonance decoupling (Figure 1b,c), thus enabling a better differentiation. This is of special interest in cases with small  $^1\text{H}$  chemical shift differences (less than 10 Hz), where normal off-resonance decoupling fails because condition 3 is violated and where the fingerprints in the single resonance spectrum disappear.<sup>8</sup> Even more important, calculations (see below) show that fingerprints in the off-resonance  $^{13}\text{C},\{^1\text{H}\}$  nmr spectra are also observed for zero chemical shift between  $\text{H}_\alpha$  and  $\text{H}_\beta$ . Furthermore, since part of the Overhauser enhancement<sup>12</sup> is retained during partial decoupling, the fingerprint method becomes more sensitive than in the undecoupled  $^{13}\text{C}$  nmr spectrum.

As shown in Figure 2, the fingerprints reappear after the decoupler frequency has been swept through the proton resonances. This corresponds to a reversal of the  $^1\text{H}$  chemical shifts and demonstrates that the technique does not depend on the  $^1\text{H}$  assignment.

To provide a firm basis for the interpretation of our

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experimental findings, we have calculated theoretical off-resonance decoupled spectra using the well-known double-resonance Hamiltonian<sup>13</sup>

$$\mathcal{H} = \sum_i (\nu_i - \nu_2) \mathbf{I}_z(i) + \sum_{i < j} J_{ij} \mathbf{I}(i) \mathbf{I}(j) - \sum_i \gamma H_2 \mathbf{I}_x(i) \quad (2)$$

With a decoupler power of  $\gamma H_2 = 3000$  Hz (obtained by calibration using eq 1 and  $J_R$  in the  $^{13}\text{CHCl}_3$  resonance), the  $^{13}\text{C},^1\text{H}$  coupling constants of benzene,<sup>15</sup> and the relevant  $^1\text{H}$  nmr data of indan,<sup>16</sup> the spectra given in Figure 1e-g were obtained in excellent agreement with experiment (Figure 1b-d).<sup>17</sup>

As an application of the new technique, the  $\text{C}_\alpha$  and  $\text{C}_\beta$  resonances for benzocycloalkenes up to benzocyclooctene were assigned by inspection of the off-resonance  $^1\text{H}$ -decoupled  $^{13}\text{C}$  nmr spectra after the fingerprints for  $\text{C}_\alpha$  and  $\text{C}_\beta$  had been clearly identified by the indan experiment and the calculations (Figure 1). The results<sup>9</sup> show that the assignment given by Maciel, *et al.*,<sup>10</sup> and by Buchanan and Wightman<sup>11</sup> must be reversed.

Taking advantage of the increasing number of  $^{13}\text{C},^1\text{H}$  and  $^1\text{H},^1\text{H}$  coupling constants available, typical splitting patterns in off-resonance  $^{13}\text{C},\{^1\text{H}\}$  nmr spectra existing in other cases may be identified easily with the help of calculated spectra, thus leading to a facile  $^{13}\text{C}$  nmr assignment of high sensitivity. Alternatively, for a class of structurally similar compounds, the experimental spectra of one member with established  $^{13}\text{C}$  chemical shifts may be used for fingerprint identification.

**Acknowledgments.** We are indebted to Dr. R. E. Moore for reading the manuscript. Support of this research by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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(16) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970). The  $^1\text{H}$  assignment based on long-range coupling given there was confirmed by the spectrum of indane-5-d.

(17) A close inspection of the fine structure in each carbon resonance (Figures 1 and 2) reveals that each multiplet is changed to its mirror image upon reversal of the proton chemical shift, i.e., upon sign change for  $\Delta\nu$ ;  $^1\text{H}$  resonances may thus be assigned.

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## Book Reviews\*

**Comprehensive Biochemistry.** Edited by M. FLORKIN and E. H. STOTZ. **Volume 30. A History of Biochemistry.** By M. FLORKIN (University of Liege). Elsevier Publishing Co., New York, N. Y. 1972. xviii + 343 pp. \$27.75.

According to the author, this book is "intended to retrace the long process of evolution in the science of biochemistry framed in a

conceptual background and in a manner not recorded in recent treatises." He has accomplished this in an interesting and informative manner.

The central themes of the historical development are the "matter-of-life" and the "forces-of-life." The first is concerned with the chemistry and mechanism of metabolic processes and the second