

Pulse Fourier Transform ^{13}C Nuclear Magnetic Resonance Spectra of Cyclopropenones and Related Derivatives

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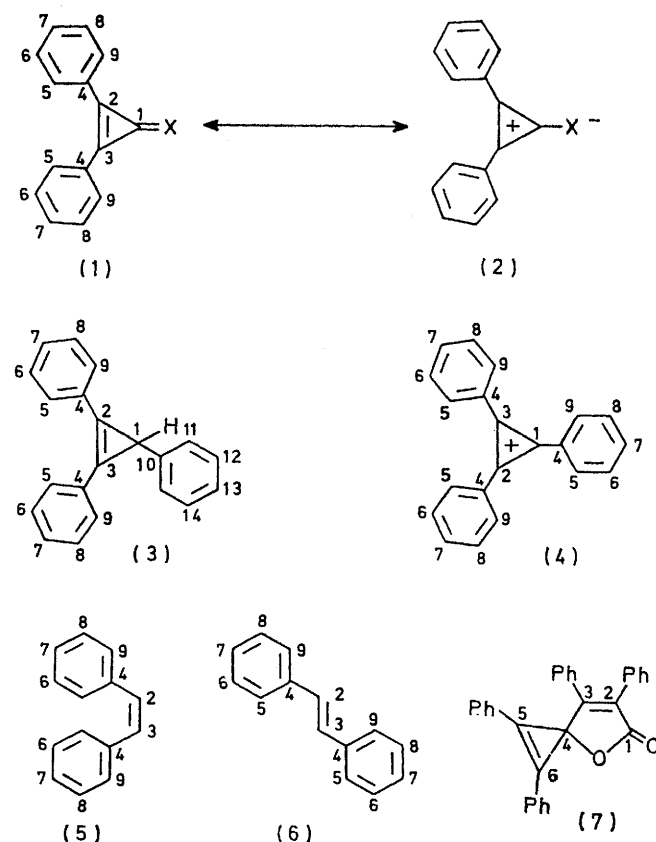
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Pulse Fourier transform ^{13}C n.m.r. spectra of diphenylcyclopropenone, diphenylcyclopropenethione, triphenylcyclopropene, diphenylcyclopropenone dimer, and other model compounds have been measured. The carbon chemical shift data, discussed in terms of the present concepts regarding the structures of these cyclopropene derivatives, provide further evidence for the pronounced polarization in these systems.

DIPHENYLCYCLOPROPENONE (1; $\text{X} = \text{O}$), prepared¹ initially in 1965, is a versatile intermediate in organic synthesis, providing numerous structures not readily available by other routes.² It is particularly effective in cycloadditions, a property also shared by diphenylcyclopropenethione (1; $\text{X} = \text{S}$) and triphenylcyclopropene (3). Cycloadducts have been formed with carbonyl ylides,³ heteroaromatic systems such as pyridine and pyridazine,⁴ 1,3-dipolar systems,⁵ 3H-azirines,⁶ and enamines and other electron-rich olefins.⁷

The high dipole moment (5.14 D) reported⁸ for diphenylcyclopropenone is strongly indicative of a highly polarized carbonyl group, a factor reflected also in its high basicity⁹ ($H_0 - 2.5$) and ready salt formation with acids.² Proposals have been advanced,² based on chemical reactivity as well as Hückel MO charge density and delocalization energy calculations, which suggest that the zwitterionic resonance form (2; $\text{X} = \text{O}$) contributes substantially to the ground state structure of cyclopropenones. I.r.^{1,10} and ^1H n.m.r.^{2,11} studies, although in

accord with these proposals, do not provide clear-cut evidence in this respect. ^{13}C N.m.r. data, capable of



Numbering of compounds has been chosen for convenience in presenting n.m.r. assignments.

showing changes in the chemical anisotropic environment of a carbon atom more clearly and directly than ^1H n.m.r. data,¹² should provide information of considerable

¹¹ R. A. Peterson, Ph.D. Thesis, *Diss. Abs.*, 1962, **23**, 1517.

¹² For recent reviews and compendia on ^{13}C n.m.r. spectroscopy see E. Breitmaier, G. Jung, and W. Voelter, *Angew. Chem. Internat. Edn.*, 1971, **10**, 673; E. F. Mooney and P. H. Winson, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 153; G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972; J. B. Stothers, *Carbon-13 N.M.R. Spectroscopy*, Academic Press, New York, 1972.

¹ R. Breslow, R. Haynie, and J. Mirra, *J. Amer. Chem. Soc.*, 1959, **81**, 247; M. E. Volpin, Yu. D. Koreshkov and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, **3**, 560; D. N. Kursanov, M. E. Volpin, and Yu. D. Koreshkov, *J. Gen. Chem. U.S.S.R.*, 1960, **30**, 2855.

² For reviews on cyclopropenone chemistry see A. W. Krebs, *Angew. Chem. Internat. Edn.*, 1965, **4**, 10; G. L. Closs, *Adv. Alicyclic Chem.*, 1966, **1**, 53; K. T. Potts and J. Baum, *Chem. Rev.*, 1974, **74**, 189.

³ J. W. Lown and K. Matsumoto, *Canad. J. Chem.*, 1971, **49**, 3444; K. T. Potts, A. Elliott, and M. Sorm, *J. Org. Chem.*, 1972, **37**, 3838.

⁴ J. W. Lown and K. Matsumoto, *Canad. J. Chem.*, 1971, **49**, 1165, 3119.

⁵ J. W. Lown, T. W. Maloney, and G. Dallas, *Canad. J. Chem.*, 1970, **48**, 584; J. W. Lown, R. K. Smalley, G. Dallas, and T. W. Maloney, *ibid.*, p. 49; J. W. Lown and K. Matsumoto, *ibid.*, 1972, **50**, 584; K. T. Potts, unpublished results.

⁶ A. Hassner and A. Kascheres, *J. Org. Chem.*, 1972, **37**, 2328.

⁷ M. A. Steinfelds and A. S. Dreiding, *Helv. Chim. Acta*, 1972, **55**, 702; V. Bilinski, M. A. Steinfelds, and A. S. Dreiding, *ibid.*, p. 1271; M. A. Steinfelds, H. W. Krapf, P. Riedl, J. Sauer, and A. S. Dreiding, *ibid.*, p. 1759.

⁸ R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 1965, **87**, 1320.

⁹ A. S. Kende and P. T. Izzo, *J. Amer. Chem. Soc.*, 1965, **87**, 1609.

¹⁰ R. Breslow and R. A. Peterson, *J. Amer. Chem. Soc.*, 1960, **82**, 4426; R. Breslow, J. Posner, and A. Krebs, *ibid.*, 1963, **85**, 234; B. E. Zaitsev, Yu. D. Koreshkov, M. E. Vol'pin, and Yu. N. Sheinker, *Doklady Akad. Nauk S.S.S.R.*, 1961, **139**, 1107; Yu. G. Borod'ka and U. K. Syrkin, *ibid.*, 1961, **136**, 1335.

interest about these cyclopropene derivatives. We report the ^{13}C n.m.r. spectra of diphenylcyclopropenone (1; X = O), diphenylcyclopropenethione (1; X = S), triphenylcyclopropene (3), and the dimer (7) of diphenylcyclopropenone. The recent synthesis¹³ of cyclopropenone itself makes this study particularly opportune.^{13a}

RESULTS AND DISCUSSION

The natural abundance, proton decoupled carbon-13 spectrum of diphenylcyclopropenone (1; X = O) consists of a simple six-line spectrum, derived from the six non-equivalent types of carbon atoms, in contrast to the complex pattern observed¹¹ for the ^1H n.m.r. spectrum.

Carbon-13 chemical shifts of triphenylcyclopropene and model systems

Compound	C-1	C-2, -3	C-4	C-5, -9	C-6, -8	C-7
(3)	23.9	111.0	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
(4) ^a	155.4	155.4	120.1	135.9	131.2	139.2
(5) ^b		127.0	137.3	128.8	128.1	130.2
(6) ^b		126.5	137.3	128.7	128.7	127.6

^a $\delta_{\text{C}}^{\text{OCS}}$ external = 193.7 p.p.m. conversion for refs. 18 and 20. ^b Cf. phenyl carbon resonances of styrene, *para* 126.2, *meta* 127.9, *ortho* 127.9, C-1 137.3 p.p.m. where C-1 is minimally affected although a *para*-resonance effect is operating. ^c Remaining resonances were observed at 129.8, 128.7, 128.1, 125.8, and 125.3 p.p.m.

The low-field resonance at 155.7 p.p.m. (measured from internal tetramethylsilane) is assigned to the carbonyl carbon atom C-1 and is in excellent agreement with the value 155.1 p.p.m. found for the carbonyl carbon atom of cyclopropenone.^{13b} The positions of normal ketone carbonyls have been found generally to occur¹² in the region 190–220 p.p.m. Carbonyl resonance frequencies have been shown to be very sensitive to both intramolecular and intermolecular influences,¹⁴ especially conjugation with unsaturated or electron-releasing systems.¹⁵ The ^{13}C chemical shift of the carbonyl carbon at 211.7 p.p.m. in cycloheptanone¹⁶ undergoes a high field shift to 172.0 p.p.m. in tropolone.¹⁷ The chemical shift of C-1 at 155.7 p.p.m. in diphenylcyclopropenone thus indicates a high degree of polarization of the carbonyl group to the extent that the dipolar form (2; X = O) must make a significant contribution to the ground state of the molecule. Similar conclusions can be made based on the recent X-ray diffraction and CNDO/2 comparisons.¹⁸ In the extreme cationic case of the triphenylcyclopropenium cation (4) the ring carbons have been shown¹⁹ to resonate at 155.4 p.p.m., a shift of 29 p.p.m. to higher field compared with the parent cyclopropenium cation,²⁰ and of 3 p.p.m. when compared to similar carbons in cyclopropenone itself.^{13b} The remaining ring carbons C-2 and -3 are tentatively assigned to the resonance at 148.4 p.p.m. which is consistent with the anticipated¹² shift to lower field of the olefinic carbons

¹³ (a) R. Breslow and M. Oda, *J. Amer. Chem. Soc.*, 1972, **94**, 4787; (b) R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *ibid.*, 1973, **95**, 2772.

¹⁴ T. T. Nakashima and G. E. Maciel, *Org. Magnetic Resonance*, 1972, **4**, 321.

¹⁵ K. S. Dhami and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 497.

¹⁶ F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 1347.

¹⁷ L. Weiler, *Canad. J. Chem.*, 1972, **50**, 1975.

due to their delocalized carbenium ion character. This results in a deshielding of those carbon atoms by *ca.* 21 p.p.m. when compared to the chemical shift observed for the olefinic carbons of *cis*-stilbene (5) at 127.0 and *trans*-stilbene (6) at 126.5 p.p.m., and by *ca.* 37.4 p.p.m. when compared to the olefinic carbons of triphenylcyclopropene (3). The chemical shifts of the ring carbons of diphenylcyclopropenone are thus intermediate between the covalent cyclopropenes, *e.g.* (3) and the cyclopropenium salts. A similar situation has been observed¹¹ in ^1H n.m.r. signals of the α -protons of alkyl-substituted cyclopropenones. An interesting feature of the spectra of diphenylcyclopropenone was the equivalence of the corresponding phenyl ring positions. Chemical shifts at 132.8, 131.5, 129.4, and 124.0 p.p.m. are assigned to the phenyl carbon atoms C-7 (*para*), C-5 + -9 (*ortho*), C-6 + -8 (*meta*), and C-4 in (1; X = O), respectively. This is consistent with the trend²¹ in a series of mono-substituted benzenes with electron-withdrawing substituents where the chemical shifts of the aromatic carbons are in the order $p > o > m$. Furthermore, the phenyl carbon resonance in triphenylcyclopropenium cation was also found¹⁹ to follow this order with $p > o > m > C-1$. The small downfield shift of carbon atoms C-5 + -9, and C-7 (*ortho* and *para*) relative to benzene indicates that the net amount of positive charge withdrawn from the cyclopropenone ring and delocalized over the phenyl ring is small, a situation in accord with the predictions based on Hückel MO calculations, and parallels the observed shifts of triphenylcyclopropenium cation.

The spectrum of diphenylcyclopropenethione (1; X = S) was similar to that of the oxygen analogue but reflected the decreased dipolar character of the molecule. The chemical shift of the thiocarbonyl carbon occurred at 168.6 p.p.m., a shift downfield by 13.0 p.p.m. This is indicative of reduced polarization of the thiocarbonyl group due partly to the $d_{\pi}-p_{\pi}$ bonding contribution but still at higher field than normally associated with thiones whose ^{13}C shifts fall in the range²² 190–205 p.p.m. These results conflict with X-ray diffraction data from which the conclusion was drawn that (2; X = S) does not make a significant contribution to the ground state.²² However, more recent X-ray and CNDO/2 data¹⁸ provide support for the cyclopropenium thioxide representation (2; X = S). Resonances at 133.5, 131.7, 129.1, and 122.1 p.p.m. may be assigned to C-7, C-5 + -9, C-6 + -8, and C-4, respectively, of the phenyl ring and the cyclopropene carbon atoms were observed at 152.7 p.p.m., only a small shift of 3.7 p.p.m. downfield from that of (1; X = O) above.

¹⁹ H. L. Ammon, *J. Amer. Chem. Soc.*, 1973, **95**, 7093.

²⁰ G. J. Ray, A. K. Colter, and R. T. Kurland, *Chem. Phys. Letters*, 1968, **2**, 324.

²¹ G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1970, **92**, 1430.

²² G. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. Pharm. Bull. (Japan)*, 1971, **19**, 2301; K. S. Dhami and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 510; H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731.

²³ L. L. Reed and J. P. Schaefer, *J.C.S. Chem. Comm.*, 1972, 528.

Although the spectra of triphenylcyclopropene (3) and diphenylcyclopropenone dimer (7) were more complex, each contained clearly resolved resonances which permitted partial assignment. The spectrum of triphenylcyclopropene (3) clearly shows the tertiary carbon atom at a chemical shift of 23.9 p.p.m., well downfield from cyclopropane derivatives.¹² The olefinic carbon atoms were observed at 111.0 p.p.m., an upfield shift of 16 p.p.m. from *cis*-stilbene or *ca.* 40 p.p.m. from the corresponding carbon atoms in (1; X = O or S). The chemical shift difference is most likely the result of more double bond character in the 2,3-bond of (3), a conclusion consistent with its chemical reactivity. This feature also influences the chemical shift of the phenyl carbon atoms, C-4 in (3), attached to the *sp*² carbons of the cyclopropene ring and assigned to a resonance at 143.0 p.p.m. The other sixteen aromatic carbon atoms are observed in a complex five-line multiplet with chemical shifts at 129.8, 128.7, 128.1, 125.8, and 125.3 p.p.m. Diphenylcyclopropenone readily gives²³ a dimer at 145–150° for which structure (7) has been proposed. The ¹³C spectrum is consistent with the assigned $\alpha\beta$ -unsaturated γ -lactone structure. Resonance frequencies were observed at 158.8 (lactone C-1), 125.8 (C-2), 116.3 (C-5 and -6), and 72.1 p.p.m. (γ -*sp*³ lactone C-4) and a complex seven line

²³ R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 1965, **87**, 1320.

multiplet at 131.1, 130.4, 129.7, 129.3, 129.0, 128.5, and 128.1 p.p.m. (aromatic carbons and C-3).

EXPERIMENTAL

¹³C Fourier spectra were recorded on a Bruker HFX 90 multinuclear spectrometer operating at 22.628 MHz. The spectra were produced by storing the frequency-independent data produced by a series of 10 μ s radiofrequency pulses in a computer (Fabritek 1074) of average transients. The interferograms which resulted were then Fourier transformed by a digital computer (PDP 81). The spectra were determined using 20–25% (w/w) solutions in CDCl₃ containing *ca.* 5% tetramethylsilane (w/w). Chemical shifts are in p.p.m. downfield from the carbon resonances of tetramethylsilane and are accurate to ± 0.2 p.p.m. Assignments follow from relative intensity measurements, single-resonance, off-resonance techniques, and the recognized¹² electronic effect that the *meta*-carbon atoms of phenyl rings with electron-withdrawing substituents are displaced least from benzene in chemical shift. Compounds (1; X = O and S), (3), and (7) were prepared by the reported procedures whilst compounds (5) and (6) were commercial samples, purified immediately prior to use.

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