BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (8), 2441—2442 (1978)

Infrared Spectra of ^{13}C-Labelled Diphenylcyclopropenone and Related Derivatives

Yoshikazu TAKEHIRA and Fumio TODA*

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790

(Received January 23, 1978)

Synopsis. The infrared spectra of diphenylcyclopropenone-1-^{13}C, its hydrate, 3-dicyanomethylene-1,2-diphenyl-1-cyclopropene-3-^{13}C, and 4-(2,3-diphenylcyclopropenylidene)-2-(diphenylmethylene)-1,3-cyclobutanedione-1′-^{13}C were studied.

Diphenylcyclopropenone (**3**) and related derivatives such as methylenecyclopropene (triafulvene) show complex IR bands. For example, **3** shows two strong bands at *ca.* 1850 and 1620 cm^{-1}, which were found to be mainly due to $\nu_{C=O}$ and $\nu_{C=C}$, respectively.[1] For the sake of confirmation and assignment of the IR bands of the hydrate of **3** (**4**),[2] 3-dicyanomethylene-1,2-diphenyl-1-cyclopropene (**5**),[3] and 4-(2,3-diphenylcyclopropenylidene)-2-(diphenylmethylene)-1,3-cyclobutanedione (**6**),[4] ^{13}C-labelled samples of these compounds were synthesized and their IR spectra were studied.

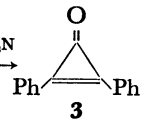
$$PhCH_2MgBr \xrightarrow{^{13}CO_2} PhCH_2{}^{13}COOH \xrightarrow{Ba(OH)_2}$$

$$(PhCH_2{}^{13}COO)_2Ba \xrightarrow{\Delta} PhCH_2{}^{13}COCH_2Ph \xrightarrow{Br_2}$$

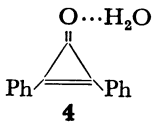
1

$$PhCHBr{}^{13}COCHBrPh \xrightarrow{Et_3N}$$

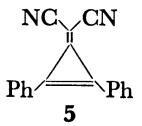
2



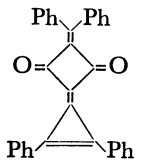
3



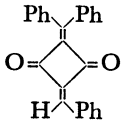
4



5



6



7

Experimental

^{13}C-Labelled Compounds. Phenylacetic acid-1-^{13}C (96.2 atom% ^{13}C) was prepared by carbonation of phenylmagnesium bromide with $^{13}CO_2$ evolved from $Ba^{13}CO_3$ (96.2 atom% ^{13}C), according to the standard procedure of isotope experiment.[5] From the phenylacetic acid-1-^{13}C, **3**-1-^{13}C was prepared successively *via* barium phenylacetate-1-^{13}C, 1,3-diphenyl-2-propanone-2-^{13}C (**1**-2-^{13}C), and 1,3-dibromo-1,3-diphenyl-2-propanone-2-^{13}C (**2**-2-^{13}C), according to the reported method[6] of preparation of non-labelled **3**. In ^{13}C-NMR spectrum, **3**-1-^{13}C showed a strong signal of the carbonyl carbon at 155.9 ppm (on $CDCl_3$, from TMS), which is comparable to that of **3**, 155.7 ppm (in $CDCl_3$, from TMS).[7]

Hydrate of **3**-1-^{13}C (**4**-1-^{13}C) was prepared according to the procedure of Toda and Akagi.[2] **5**-3-^{13}C and **6**-1-^{13}C were prepared by the condensation of **3**-1-^{13}C with dicyanomethane and 2-diphenylmethylene-1,3-cyclobutanedione,[4] respectively, following the preparation of non-labelled **5**[3] and **6**.[4]

IR Spectra. IR spectra were recorded with a Hitachi 285 grating spectrometer.

Results and Discussion

IR spectral data are summarized in Table 1. In the case of both **3** and **4**, the bands at *ca.* 1850 cm^{-1} shifts *ca.* 40 cm^{-1} towards lower frequencies when C-1 is labelled with ^{13}C, that at *ca.* 1620 cm^{-1} *ca.* 15 cm^{-1}. The results show that the bands are mainly due to their $\nu_{C=O}$ and $\nu_{C=C}$, respectively. The observed $\Delta\nu_{C=O}$ values agree with the calculated one, 41 cm^{-1}, for 1850 cm^{-1} band on the basis of $\nu^{12}{}_{C=O}/\nu^{13}{}_{C=O}=1.0227$.[8] Almost the same shift of $\nu_{C=O}$ by ^{13}C-labelling was observed for **1** and **2**.

TABLE 1. IR SPECTRAL DATA (cm^{-1})

Compound	State	ν(non-labelled)	ν(^{13}C-labelled)	$\Delta\nu$
1	Neat	1724[b]	1679	45
		1715[b]	1674	41
2	Nujol	1725[b]	1690	35
		1723[b]	1684	39
3	Nujol	1847[a]	1809	38
		1840[a]	1806	34
		1624[a]	1609	15
		1618[a]	1604	14
4	Nujol	1842[a]	1807	35
		1605[a]	1597	8
4	CCl_4	1861[a]	1817	44
		1640[a]	1626	14
5	Nujol	2206[b]	2207	1
		2197[b]	2198	1
		1872[c]	1854	18
		1867[c]	1849	18
6	Nujol	1888[d]	1888	0
		1847[c]	1828	19
		1843[c]	1821	22
		1756[d]	1757	1
		1659[a]	1659	0

a) Very strong. b) Strong. c) Medium. d) Weak.

Since the two bands of **5** at 1872 and 1867 cm^{-1} shift 18 cm^{-1} towards lower frequencies with ^{13}C-labelling, they seem to be mainly due to $\nu_{C=O}$ of *exo*-methylene moiety. However, a small shift of $\nu_{C\equiv N}$ of **5**, 2206 and 2197 cm^{-1}, was observed. No band of $\nu_{C=C}$ of cyclopropene moiety of **5** could be detected. The medium bands of **6** at 1847 and 1843 cm^{-1} would be mainly due to $\nu_{C=C}$ of *exo*-methylene of methylenecyclopropene moiety, since these bands of the ^{13}C-labelled sample appear at 19 and 22 cm^{-1} frequencies lower than those of the unlabelled compounds, respectively. The very

strong band of **6** at 1659 cm^{-1} not affected by ^{13}C-labelling could be assigned to $\nu_{C=O}$, since **7**[4] shows a similar $\nu_{C=O}$ band at 1680 cm^{-1}. However, neither 1888 nor 1756 cm^{-1} band could be assigned.

The authors wish to express their thanks to Professor Yoho Tsuno for his valuable suggestions on ^{13}C-labelling experiment.

References

1) A. Krebs, B. Schrader, and F. Höfler, *Tetrahedron Lett.*, **1968**, 5935.

2) F. Toda and K. Akagi, *Tetrahderon Lett.*, **1968**, 3735. Structural investigation of **4** by X-ray analysis has been reported; H. Tsukada, H. Shimanouchi, and Y. Sasada, *ibid.*, **1973**, 2455; H. L. Ammon, *J. Am. Chem. Soc.*, **95**, 7093 (1973).

3) Y. Kitahara and M. Funamizu, *Bull. Chem. Soc., Jpn.*, **37**, 1897 (1964).

4) F. Toda, *Chem. Lett.*, **1972**, 621.

5) A. Murray and B. L. Williams, "Organic Synthesis with Isotopes," Part I, Interscience, New York (1958).

6) R. Breslow, T. Eicher, A. Krebs, and R. A. Peterson, *J. Am. Chem. Soc.*, **87**, 1320 (1965).

7) M. T. W. Hearn and K. T. Potts, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 1918.

8) M. Halmann and S. Pinchas, *J. Chem. Soc.*, **1958**, 1703.