Tetrahedron Letters No.9, pp. 817-822, 1967. Pergamon Press Ltd. Printed in Great Britain.

SOLVENT EFFECTS IN N.M.R. SPECTROSCOPY. DETERMINATION OF CONFIGURATIONS OF THREE-MEMBERED RING CARBONYL COMPOUNDS BY BENZENE INDUCED CHEMICAL SHIFTS (1)

David W. Boykin, Jr. (2), Andrew B. Turner and Robert E. Lutz
Cobb Chemical Laboratory, University of Virginia
Charlottesville, Virginia 22901

(Received 7 December 1966; in revised form 30 December 1966)

Interpretable chemical shifts of protons in compounds containing polar functional groups induced by solvents which have diamagnetic anisotropic properties are now well documented (3,4,5). Recent studies on solvent induced shifts of the signals of substituents on cyclopropane rings (6) prompt us to make this preliminary report on an investigation of the benzene-induced chemical shifts of the ring protons of three-membered ring ketones. This work stems from our earlier observation of such a shift for a three-membered ring proton signal of 1,2,2-triphenyl-1-benzoylcyclopropane (7).

As has been suggested by several authors and recently summarized (8), it is reasonable to discuss the shifts observed by comparing proton-signals in a magnetically isotropic solvent (e.g. $CDCl_3$) with the signals observed in an anisotropic solvent (e.g. C_6H_6) in terms of a time averaged complex between the anisotropic solvent and a polar functional group. It has been useful to assume as a working model a 1:1 complex with a geometry such that the complexed benzene molecule and the polar functional group (in our examples, the carbonyl group) occupy parallel planes. The negative π-system of the benzene molecule is attracted to the positive site (the carbonyl carbon) of the functional group and is repelled by the negative site (the carbonyl oxygen) (5,8).

The solvent shift data may be interpreted by using a model such as represented in Fig. 1. The conformation of the -CO-CH-bond depicted is assumed to be the favored one on steric grounds. The protons on the side of the ring opposite the carbonyl group lie in the shielding region of the complexed benzene molecule, whereas protons on the same side of the ring as the carbonyl group lie in the very slight shielding or deshielding region of the complexed benzene molecule depending upon the rotomer distribution of the carbonyl group. When compared to $CDCl_3$, the signals for protons in the shielding region of benzene are moved upfield, whereas the signals of the protons not in the shielding region of the complexed molecule remain unchanged or moved slightly downfield.

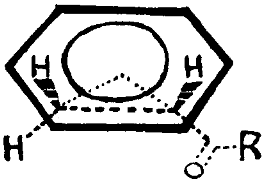


Fig. 1

If this model is reasonably accurate, the assignment of the configuration of three-membered ring ketones may be made by comparison of the chemical shifts of the ring protons in $CDCl_3$ to C_6H_6. To test this model we selected trans- and cis-1-benzoyl-2-phenylcyclopropane (I,II). To make unequivocal proton assignments, I and II were synthesized with deuterium labels. The trans-3,3-dideuterio isomer III was obtained by the Corey reaction (9) of trimethylsulfoxonium iodide-d_9 with trans-chalcone, and the cis-isomer IV was obtained from III by photoisomerization (10). The trans-1-deuterio isomer V was obtained by base catalyzed d-exchange of I using $NaOCH_3/CH_3OD$, and the cis-isomer VI was obtained from V by photoisomerization.

The Table contains the proton chemical shift data for the three-membered ring ketones. The proton resonance values are expressed in cps relative to TMS as an internal standard, and Δ is defined as $\delta CDCl_3 - \delta C_6H_6$. Proton assignments were made by following conventional n.m.r. rules and by deuterium labelling as indicated in the Table.

The chemical shift for the proton on the side of the ring opposite the carbonyl group in III is moved upfield by 11 cps in C_6H_6 as compared to $CDCl_3$, whereas the signal of the proton cis to the carbonyl group is unaffected. In a similar solvent comparison the signals of both protons in IV, which are on the opposite side of the ring from the carbonyl group, are moved upfield by ca. 20 cps.

For protons on the side opposite the carbonyl group of the monoketocyclopropanes listed in the Table, the range of Δ is 10 to 26 cps. The range of Δ is -10 to 4 cps for protons *cis* to the carbonyl group.

The *trans*-isomers in the monoketoaziridine series listed in the Table have Δ values of 3 to 12 cps for the proton on the side of the ring opposite the carbonyl group and have Δ values of ca. -5 cps for the proton *cis* to the carbonyl group. For the *cis*-aziridines studied, the Δ values for the ring protons are 16 to 29 cps.

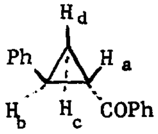
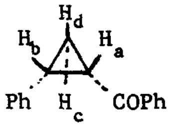
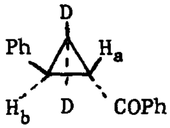
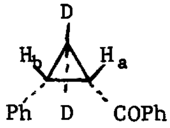
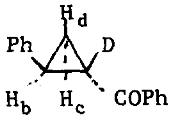
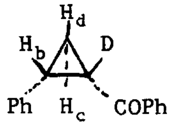
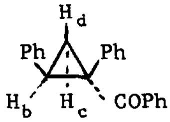
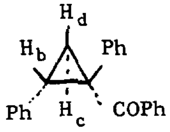
The *cis*- and *trans*-dibenzoyl-cyclopropanes and -aziridines also exhibited characteristic behavior when their proton signals were compared in the above solvents. The signals for the protons α to the carbonyl groups in the *cis*-isomers were moved upfield ca. 30 cps in benzene, whereas the signals for the α-protons for the *trans*-isomers were only slightly affected.

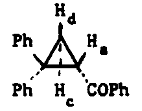
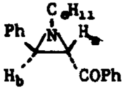
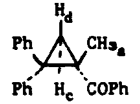
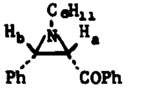
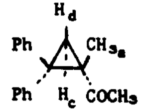
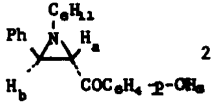
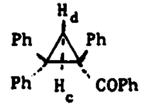
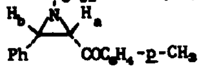
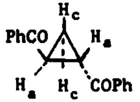
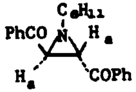
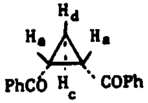
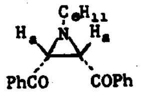
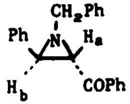
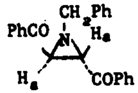
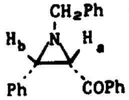
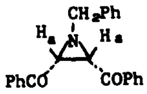
The configurations of the three-membered ring ketones included in this study may be assigned by the direction of the benzene induced chemical shifts. The magnitude of these shifts may also be of value in configurational determinations. Generally, for protons on the side of the three-membered ring opposite the carbonyl group, for the examples in the Table, the Δ values for the *cis*-isomers (ca. 20 cps) are larger than the Δ values for the corresponding *trans*-isomers (ca. 10 cps). Comments on the significance of this observation are deferred until more examples are investigated.

For the compounds reported herein, as well as in other systems, we have noted in the two solvents that nonequivalent protons which are magnetically equivalent in one solvent often become magnetically nonequivalent in the other. We have found this phenomenon to be of value in structural elucidations.

The generality of these observations is now being studied by testing more examples of three-membered ring systems, including oxiranes, larger ring analogs and cycloalkanones.

TABLE (11)

			δcps $CDCl_3$				δcps C_6H_6				Δ			
			a	b	c	d	a	b	c	d	a	b	c	d
I		(12)	176	162	115	91	164	164	116	74	12	-2	-1	17
II		(12)	186	171	130	87	160	150	132	64	26	21	-2	23
III		(12)	173	162			162	162			11	0		
IV		(12)	185	170			160	150			25	20		
V		(12)		163	114	89		163	114	73		0	0	16
VI		(12)		172	129	86		152	130	63		20	-1	23
VII		(13)		208	119	134		218	118	108		-10	1	26
VIII		(13)		203	153	86		192	157	74		11	-4	12

	δcps $CDCl_3$				δcps C_6H_6				Δ					δcps $CDCl_3$		δcps C_6H_6		Δ	
	a	b	c	d	a	b	c	d	a	b	c	d		a	b	a	b	a	b
	210		152	103	197		156	88	13		-4	15	 (15)	215	215	208	218	7	-3
	82		158	90	75		161	78	7		-3	12	 (16)	193	193	169	169	24	24
	73		141	86	65		137	72	8		4	14		217	217	214	223	3	-6
			156	156			154	143			2	13	 (16)	193	193	177	167	16	26
	205		107		200		99		5		8			244		251		-7	
	187		128	92	155		136	61	32		-8	31		199		171		28	
	219	219			207	222			12	-3				245		246		-1	
 (15,16)	203	194			174	174			29	20				203		170		33	

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1. Supported in large part by NSF Grant 25029.

2. (a) Eastman Kodak Company Fellowship (1964-1965). (b) A small part of this work was carried out at Georgia State College, Atlanta, Georgia.

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11. The compounds were prepared by methods in the literature and their physical properties were consonant with those published. The spectra were determined in ca. 10% solutions at normal operating temperature on a Varian A60 spectrometer.

12. The δ values reported are based on those obtained from the d-substituted isomers, since in the undeuterated isomers the signals for some of the protons overlapped and accurate values were not readily assigned. Furthermore, signals for protons in the d-isomers were broadened by deuterium coupling and therefore the accuracy of the δ values is probably no better than ± 4 cps.

13. New compounds gave satisfactory carbon and hydrogen analyses and were prepared by addition of phenyl lithium to the appropriate carboxylic acid (14). VII: mp 94.5-96°; ν 1655^{-1}, λ_{EtOH} 246 mμ (ϵ 13,600). VIII: mp 110-111°; ν 1660 cm^{-1}, λ_{EtOH} 246 mμ (ϵ 11,700).

14. A. R. Patel, *Acta Chem. Scand.*, **20**, 1424 (1966). We wish to thank Dr. Patel for a copy of this manuscript prior to publication.

15. Proton assignments based upon d-exchange experiments; see R. E. Lutz and A. B. Turner to be published shortly.

16. The value in $CDCl_3$ is for the center of an overlapping pair of doublets.