CIDNP-Assisted Assignment of ^{13}C NMR Lines. Alkyl Phenyl Ketones[1]

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Abstract: The reversible abstraction of hydrogen from hydrogen donors by photoexcited aromatic aldehydes and ketones leads to CIDNP in the ^{13}C NMR spectra of these compounds. Additional information gained from the phase of the polarization in the CIDNP spectrum is used to assign the carbon-13 lines of alkyl phenyl ketones. The carbon-13 spectra of the ketones PhCOR with R = n-C_xH_{2x+1}, x = 0, 1, . . . , 6; c-C_yH_{2y-1}, y = 3, 4, 5, 6; as well as i-C_3H_7, i-C_4H_9, sec-C_4H_9, and t-C_4H_9 are completely assigned and their chemical shifts reported. The measurements show that for all ketones listed above the chemical shift of the aromatic ring carbon C-2′ (ortho) is upfield of the C-3′ (meta) regardless of whether R is a primary, secondary, or tertiary alkyl group. Only for benzaldehyde is the resonance of C-3′ found at lower shift values than that of C-2′. The application of the assignment technique to phenolic compounds is also discussed.

The assignment of resonance lines in ^{13}C NMR spectroscopy generally proceeds without great difficulty owing to the large spectral dispersion, the existence of extensive parametrization lists, and the ready observation of spin-coupled multiplicity. However, in cases such as the C-2′ (ortho) and C-3′ (meta) carbons of phenyl rings a clear assignment is not always possible. A case in point is the alkyl phenyl ketones. The ^{13}C NMR spectra of several of these compounds were first reported by Dhami and Stothers in 1965.[3] In their investigation resolution was not sufficient to distinguish distinct resonance lines for C-2′ and C-3′ carbons of the phenyl ring. With modern spectrometers these two lines are easily resolved, but their assignment to C-2′ or C-3′ remains ambiguous in some cases—e.g., in the various collections of ^{13}C NMR data[4–7] the assignment of these lines is not always conclusive. Recently, we have shown that chemically induced dynamic nuclear polarization (CIDNP)[8] may be used to assign carbon-13 resonance lines in aromatic hydroxy and carbonyl compounds.[9] In this paper we describe the method in more detail and demonstrate its applicability to the definitive assignment of the carbons in alkyl phenyl ketones.

Method

It is known[10] that photoexcited carbonyl compounds in their triplet state can abstract a hydrogen atom from a hydrogen donor like phenol according to Scheme I. In methanol as a solvent this reaction is reversible and may be described as a nonreaction.[11] The ^{1}H NMR spectra recorded during UV irradiation of such systems show CIDNP.[12] Both radicals formed as intermediates during the reaction (Scheme I) are odd alternant radicals, and have an alternating spin density in the aromatic ring, as confirmed by molecular orbital calculations, e.g., INDO.[13] According to Kaptein's rules[14] the sign Γ of the NMR line i is determined by

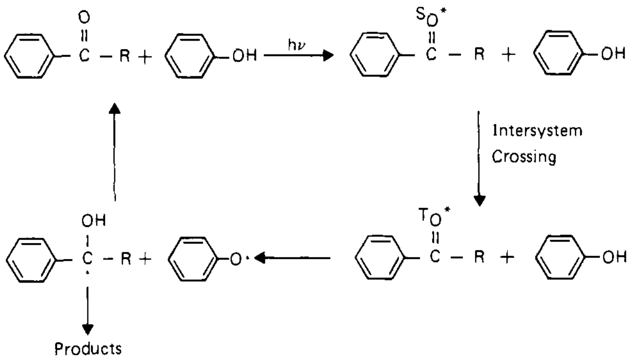
$$\Gamma(i) = \mu\epsilon\Delta g A_i \qquad (1)$$

Because μ (multiplicity of the precursor), ϵ (out-cage or in-cage product), and Δg (difference in g values of both radicals) are constant for the systems studied here, the sign of the polarization of the NMR lines follows the sign of the hyperfine coupling constant A_i at atom i. The alternating sign of the spin density in aromatic radicals of the type mentioned above thus allows unequivocal assignment of the resonance lines arising from the neighboring ring carbons. The method is outlined below for benzophenone.

The proton coupled carbon-13 spectrum of benzophenone shows two triplets for carbon C-2′ due to the coupling J_{CCCH} with 4′H and 6′H but only two doublets for C-3′ due to the coupling with 5′H (C-1′ does not carry a hydrogen).[15,16] As these multiplets do not overlap, the assignment of the resonances is straightforward as demonstrated by earlier investigators.[17,18] The proton decoupled ^{13}C NMR spectrum of benzophenone/benzene-1,3,5-triol during UV irradiation is shown in Figure 1. The resonances of the carbonyl carbon, as well as those of C-2′/6′, and of C-4′ of benzophenone show emission, while those of C-1′ and of C-3′/5′ show enhanced absorption. This serves as an experimental proof that the signs of the hyperfine coupling constants are indeed alternating in the aromatic ring. An analogous behavior is also found for benzene-1,3,5-triol, where the line for C-1′/3′/5′ (labeled α in Figure 1) shows emission and that for C-2′/4′/6′ (labeled β) enhanced absorption. This result can be used for the assignment of carbon-13 resonance lines. Since the carbonyl resonance can always be assigned in a straightforward way owing to the low-field value of its chemical shift, its phase (emission) may serve as a calibration standard in the CIDNP spectrum. Consequently, the neighboring carbon (C-1′) must appear in absorption. There are two absorption lines in the spectrum, but from the different intensities of these lines in the dark ("normal") spectrum it follows that the line at δ 138.5 ppm belongs to C-1′ while that at 129.2 ppm belongs to C-3′/5′. Again from the intensities in the dark spectrum the two emission lines can be assigned, namely, the emission line at 133.4 ppm to C-4′ and that at 130.7 ppm to C-2′/6′. Thus, the complete assignment for benzophenone can be achieved from the intensity information gained from the dark spectrum and the alternating sign pattern of the CIDNP spectrum.

Even though for benzophenone this result can also be obtained from the interpretation of the proton coupled spectrum as indicated above, the assignment of the carbons in the aromatic ring for the alkyl phenyl ketones is more difficult. Here the multiplets of the coupled spectra overlap, which compli-

Scheme I



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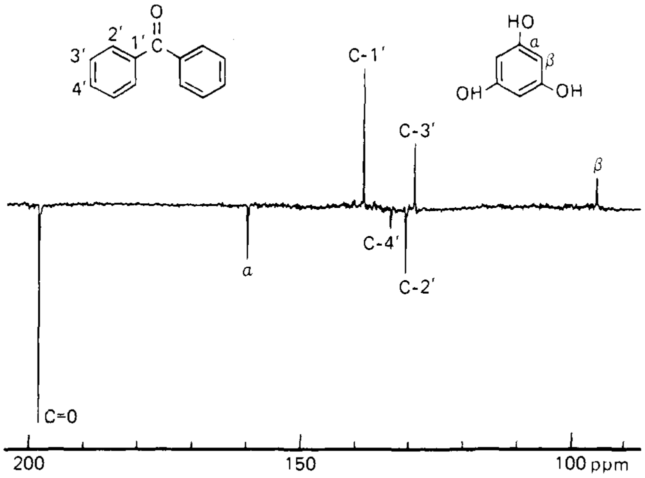

Figure 1. Proton decoupled pulse FT ^{13}C NMR spectrum of benzophenone (0.2 M) and benzene-1,3,5-triol (0.2 M) in methanol-d_1 during UV irradiation showing CIDNP. Chemical shifts are given downfield from internal Me_4Si. 1000 accumulations, flip angle 45°.

cates the interpretation or makes it even impossible. In the following we demonstrate that with the additional information from the CIDNP spectra the assignment of the ^{13}C NMR lines becomes straightforward.

Results

The values for the carbon-13 chemical shifts of benzaldehyde (**1**), of the *n*-alkyl ketones from acetophenone (**2**) to heptanophenone (**7**), of the cycloalkyl phenyl ketones with cyclopropyl **8** up to cyclohexyl **11** groups, of isobutyrophenone (**12**), and of branched isomers of valerophenone **13–15** are given in Table I. As an example the dark and the photo-CIDNP spectra of propiophenone (**3**) are given in Figure 2. The carbonyl resonance is observed in emission. This observed sign (−) is in agreement with eq 1 assuming a triplet precursor (μ = +), in-cage product (ϵ = +), Δg = (−) (g = 2.0030 for the 3-phenyl-3-hydroxypropyl radical[19] and g = 2.0055 for the phenoxy radical[20]), and a positive sign (A_{CO} = +) for the corresponding hyperfine coupling constant of the ketyl radical as calculated by the INDO[13] method. The g values of the various hydroxy radicals formed from the carbonyl compounds **1–15** should vary only in a very limited range (e.g., g = 2.003 11 for α-hydroxybenzyl and g = 2.0030 for 2-phenyl-2-hydroxyethyl);[21] therefore, the phase of the polarization of the carbonyl resonance should be the same for all compounds. This is indeed found to be true for the photo-CIDNP experiments of **1–15**, which all show emission for the carbonyl resonance. The ketyl radicals, formed during the photoreaction (cf. Scheme I), are odd alternant (benzyl) radicals as demonstrated in the case of the phenyl hydroxybenzyl radical. It can thus be concluded that the resonance lines of all the C-1′ aromatic carbons, which are next to the carbonyl carbon atom, as well as all C-3′/5′ should show enhanced absorption. As outlined above, the assignment of C-1′ is obvious from the low-field shift and the low intensity in the dark spectrum; therefore, the second absorption line must belong to C-3′/5′. The emission lines for C-2′/6′ and C-4′ are assigned using the analogous argument.

Since the carbonyl resonances are observed in emission, the same CIDNP pattern applies to all compounds studied here. Therefore, C-2′/6′ is always an emission line and C-3′/5′ an absorption line. Although the differences in chemical shift are small (0.15–0.63 ppm), the assignment method is definite for any of the 15 carbonyl compounds of Table I. Table I and Figure 3 show that the resonance line with the lower shift value belongs to C-2′ for all alkyl phenyl ketones investigated. C-3′ is found at lower values of chemical shift than C-2′ only for benzaldehyde (**1**) and benzophenone in contrast to the situation found in the alkyl phenyl ketones.

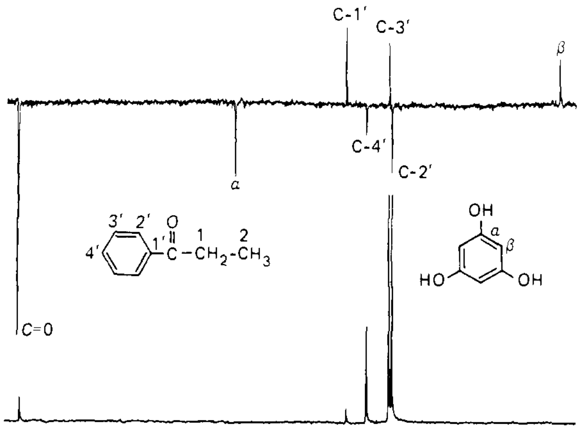

Figure 2. Proton decoupled pulse FT ^{13}C NMR spectra. Lower trace, 10 mol % propiophenone (**3**) in methanol; upper trace, propiophenone (0.2 M) and benzene-1,3,5-triol (0.2 M) in methanol-d_1 during UV irradiation showing CIDNP.

The symmetric benzene-1,3,5-triol was used as a hydrogen donor for all CIDNP experiments throughout this investigation because it gives rise to only two resonance lines. Figures 1 and 2 show that these two lines are located at the extreme ends of the chemical shift range for aromatic carbons, and thus can hardly be confused with other lines.

For ketones with three or more carbons in the alkyl chain, Norrish type II cleavage may occur during the UV irradiation.[10] However, this is in fact observed in the CIDNP spectra to only a limited extent. Acetophenone, formed as one product of this cleavage, can subsequently become photoexcited leading to additional polarized lines. Other than that, resonance lines of any reaction products are typically not detected in the CIDNP spectra. The ketones with secondary or tertiary alkyl groups may undergo α-cleavage[10] caused by the irradiation. We could not detect any α-cleavage or evidence for other reactions from the CIDNP spectra which were taken both with or without benzene-1,3,5-triol added to the solution. In some special cases, as, for instance, in *p*-hydroxypropiophenone, the carbonyl and the hydroxy function may be part of the same molecule. Accordingly, a solution of this compound alone in CH_3OD exhibits CIDNP during UV irradiation. This is believed to be the consequence of an intermolecular process, whereby some molecules act as hydrogen donors and some as hydrogen abstractors.

Figure 2 shows another interesting fact. The concentrations of the ketone used for the dark spectrum and the photo-CIDNP spectrum are different. A dark spectrum recorded with the same low concentration of 0.2 M and the same spectrometer conditions as used for the photo-CIDNP spectra shows only the resonance lines for C-2′ to C-4′ with a low signal to noise ratio and no signal for C-1′ and C=O. This demonstrates that the resonance lines in the CIDNP spectra are significantly enhanced. This amplification is strongest for the carbon atoms which do not carry a hydrogen, and thus have long relaxation times (i.e., C-1′ and C=O). This enhancement allows the ^{13}C NMR spectra of those compounds with a low solubility or which are available in small quantities to be obtained in a shorter accumulation time.

Discussion

The ^{13}C NMR spectra of benzaldehyde (**1**) and *n*-alkyl phenyl ketones **2–6** are reported in the literature. In many cases

Table I. Carbon-13 Chemical Shifts for Alkyl Phenyl Ketones (10 mol % in Methanol) Downfield from Internal Me_4Si

compd	R	C-1′	C-2′/6′	C-3′/5′	C-4′	C==O	C-1	C-2	C-3	C-4	C-5	C-6
1	H	137.7	130.5	129.9	135.4	194.0						
					n-Alkyl							
2	CH_3	138.1	129.2	129.5	134.1	200.1	26.5					
3	C_2H_5	137.9	128.8	129.4	133.8	202.5	32.4	8.4				
4	C_3H_7	138.2	128.9	129.5	133.9	202.1	41.1	18.6	14.0			
5	C_9H_9	138.1	128.9	129.5	133.9	202.1	39.0	27.4	23.2	14.2		
6	C_5H_{11}	138.1	128.9	129.4	133.8	202.0	39.2	25.0	32.4	23.4	14.2	
7	C_6H_{13}	138.1	128.9	129.4	133.8	202.0	39.3	25.3	29.9	32.6	23.4	14.3
					Cycloalkyl							
8	c-C_3H_5	138.9	128.8	129.4	133.8	202.4	17.7	12.1				
9	c-C_4H_7	136.6	129.1	129.5	133.9	202.5	43.1	25.9	18.8			
10	c-C_5H_9	137.9	129.3	129.4	133.7	204.3	47.3	30.8	27.0			
11	c-C_6H_{11}[a]	137.4	129.1	129.6	133.8	205.5	46.4	30.4	26.6	26.9		
					Branched Alkyl							
12	*i*-C_3H_7	137.3	129.1	129.6	133.8	206.3	36.2	19.4				
13	*i*-C_4H_9	138.5	129.0	129.5	133.9	201.9	48.2	26.1	22.9			
14	*sec*-C_4H_9	137.9	125.1	129.6	133.8	206.1	42.9	27.6	11.9	17.1[b]		
15	*t*-C_4H_9	139.8	128.6	129.0	131.7	210.8	44.9	28.3				

[a] Saturated solution. [b] Methyl group bound to C-1.

the resonance lines for the aromatic carbons C-2′ (ortho) and C-3′ (meta) are not assigned definitely. This holds for benzaldehyde (**1**) in ref 4 and 17, but the resonance lines are assigned in ref 6 and 22 in agreement with our findings. The carbon-13 spectrum of acetophenone (**2**) is given in the collections of ^{13}C data[4-6] but it is not completely assigned, and assignments in the literature are not consistent, as already mentioned.[9] The assignment of propiophenone (**3**) found in ref 16 and 23 is in agreement with our experiments[24] and may be included in ref 5 and 6. For butyrophenone (**4**) to hexanophenone (**6**) our results support the assignment of ref 5. As evident from Figure 3, the chemical shifts of the aromatic carbons show only very little variation for the ketones with longer *n*-alkyl chains. This is not unexpected, and it may be further deduced that the ketones with alkyl chains longer than six carbons have a very similar aromatic carbon-13 spectrum with C-2′ and C-3′ in the same order as found for **2–7**.

To our knowledge, out of the group of cycloalkyl ketones, only the carbon-13 spectrum of cyclopropyl ketone **8** has been measured so far. Again for **8**, the assignment of the ortho and meta carbon resonances was not conclusive[25,26] but followed in a straightforward manner from our CIDNP results. Within the series of cycloalkyl ketones, the chemical shifts of carbons C-2′, C-3′, and C-4′ are fairly constant (cf. Figure 3). Only C-1′ shows a somewhat larger variation, for which no explanation can be offered.

The carbon-13 spectrum of isobutyrophenone (**12**) is the only member out of the series of ketones with branched alkyl groups for which the assignment is given in the literature.[4,5] According to our results, the assignment of C-2′ and C-3′ in ref 5 must be interchanged, however. Ketones with a secondary alkyl group like cyclohexyl ketone **11**, which is considered to have no ring strain, isobutyrophenone (**12**), and *s*-valerophenone (**14**) all have comparable chemical shifts, both for their carbonyl and their aromatic carbons (cf. Figure 3). A tertiary alkyl group, as found in pivalophenone (**15**), has the strongest influence on the chemical shift. The carbonyl shift is found approximately 5 ppm higher than those of the secondary ketones, which in turn are about 4 ppm higher than those of the primary ketones. The resonances of the carbons C-1′ to C-4′ of **15** show stronger deviations from the average position than those of any other ketone. It should be mentioned that C-2′ and C-3′ are both shifted in the same direction. From the data of ketones **2–15** it may be deduced that C-2′ has a lower shift value than C-3′ for all alkyl phenyl ketones, which have no substituents in the aromatic ring.

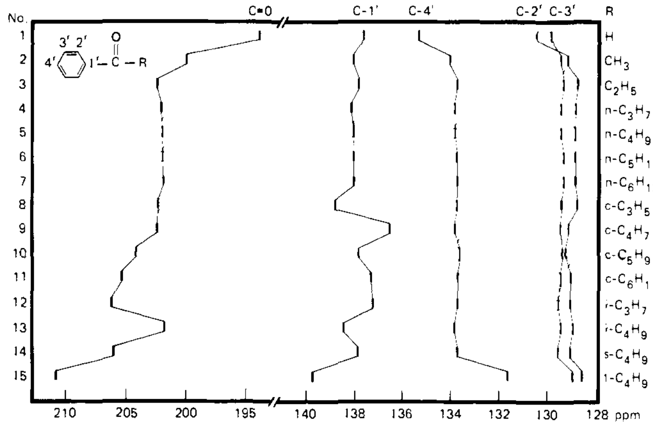

Figure 3. Variation of carbon-13 chemical shifts of alkyl phenyl ketones.

So far we have only discussed the CIDNP spectra of the aromatic carbons. Polarization of the carbon resonance lines in the alkyl groups of the ketones is observed as well. This polarization is weaker than that of the aromatic ring carbons, and it is not observed for all alkyl groups. For those ketones which do show CIDNP in the alkyl group, C-2 exhibits emission which is stronger than the enhanced absorption found for C-1. α-Cleavage can be excluded as the reason for this polarization, as it is not found for solutions of the ketones without benzene-1,3,5-triol. There are only very limited data about carbon-13 hyperfine splittings of γ carbons, so that we cannot offer a set of generally applicable parameters[27] to assist in the assignment of alkyl carbons as well. The assignment is hardly doubtful; however, from our CIDNP experiments it may be suggested that the hyperfine splitting constant has a positive sign for the γ carbon (=C-2) in the ketyl radicals derived from the alkyl phenyl ketones.

In this paper we have described the assignment of unsubstituted phenyl carbonyl compounds, but the technique is by no means limited to these compounds.[28] CIDNP was observed as well and may be used to assign the resonance lines in carbonyl compounds with the following substituents in the aromatic ring: alkyl, Cl, OH, NH_2, and OCH_3. From experiments with various carbonyl compounds we conclude that only those compounds with carbonyl groups attached to an aromatic ring show CIDNP under the conditions described here. Another prerequisite seems to be that the carbonyl compounds have a (n, π^*) as their lowest excited triplet state. Accordingly, fluorenone and other substances, which do not fulfill this condition, did not give rise to CIDNP in their carbon-13 spectra. The same technique has also been employed for the assignment of carbon resonances of aromatic hydroxy compounds which show CIDNP as well (cf. Figures 1 and 2). Preliminary results for naturally occurring phenolic substances, e.g., vitamin E and tyrosine, exhibit CIDNP in their carbon-13 spectra under similar conditions as described here.

Conclusion

The method described above requires only a minor modification of a commercial spectrometer (cf. Experimental Section). It is shown to aid the assignment of the ^{13}C NMR lines in the aromatic ring of alkyl phenyl ketones. In general the technique may be used to (1) assign the ^{13}C NMR lines in aromatic ketones, aldehydes, or phenolic compounds; (2) identify which carbon resonance arises from a phenolic or benzylic ring in compounds containing additional aromatic rings; (3) amplify the resonance lines (reducing the sampling time) of compounds with low solubility or which are only available in small quantities, e.g., natural products.

Experimental Section

Chemicals. Benzophenone and compounds **1–13** were commercially available products and used without further purification. Commercial benzene-1,3,5-triol was recrystallized from water. The ketones **14** and **15** were obtained by oxidation of 2-methyl-1-phenyl-1-butanol and 2,2-dimethyl-1-phenyl-1-propanol, respectively, with chromium trioxide and acetic acid.[29] Their purity was checked with GC and ^{1}H NMR.

Spectrometer Modification. The CIDNP spectra were recorded on a Varian CFT-20 spectrometer using a modified carbon-13 room temperature probe, which allowed irradiation of the sample in the spectrometer. For irradiation, the light of a 1000-W short arc high-pressure mercury-xenon lamp (Hanovia) was passed through a water-cooled solution of aqueous $NiSO_4/CoSO_4$, to filter out the infrared and visible radiation allowing light within 350 nm $\geq \lambda \geq$ 230 nm to pass.[30] With a simple optical system consisting of two quartz lenses the beam is focused on the end of a light guide (Suprasil, diameter 10 mm, length 40 cm, both ends polished), which leads into the probe. A hole, directed to the receiver coil, is drilled into the metal frame of the probe. The axis of the light guide is not horizontal, in contrast to previous modifications of other instruments, but deviates by an angle of 30° from the horizontal position (rod pointing down, looking out of the probe). The 30° angle makes the modification of a carbon-13 probe of a Varian CFT-20 very easy, because there is no interference of the light guide with the air cooling, any electronic part, or the external lock of the more recent instruments. In the probe the rod ends near the Faraday shield, which has been cut away to allow the light to pass through a hole, into the receiver coil, which was rewound on a quartz tube and glued at the opposite side only. The spacing between the windings of the coil equaled the diameter of the coil wire allowing the light to pass through. These modifications had only a minor influence on the performance of the probe.

Carbon-13 Spectra. All ^{13}C NMR spectra were measured with the modified room temperature probe of a Varian CFT-20 as described above. The values of the chemical shifts, reported in Table I, were obtained from solutions of 10 mol % of the substances in methanol, except for those of cyclohexyl phenyl ketone, where the values for a saturated (lower concentration) solution are given. All chemical shifts are measured downfield from internal Me_4Si. The lock signal was derived from D_2O, enclosed in a 5-mm tube, which was held by Teflon rings in the center of the 10-mm tubes containing the ketone solutions. Assignment was obtained as explained under Results. The photo-CIDNP spectra were recorded using quartz tubes of 10-mm outer diameter with solutions of ketones (0.2 M) and benzene-1,3,5-triol (0.2 M) in CH_3OD. The solutions were not degassed.

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