The Addition of Bromotrichloromethane to α,β-Unsaturated Ketones. A Nuclear Magnetic Resonance Study of the Addition Products

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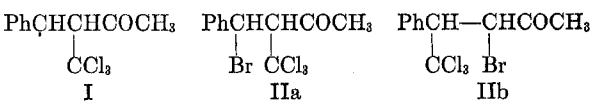
The free-radical addition of bromotrichloromethane to benzylideneacetone and benzylideneacetophenone yielded mainly $PhCHBrCH(CCl_3)COCH_3$ and $PhCHBrCH(CCl_3)COPh$, respectively. The structures of the adducts have been assigned unambiguously through nmr study involving solvent effects on acyclic ketones and comparison of data of several related compounds of known structures.

The free-radical addition of bromotrichloromethane to unsymmetrical olefins RCH=CHR′ has been studied,[1,2] and the mode of addition in each case afforded an intramolecular comparison of the stabilizing influences of the substituents R and R′ on the free alkyl radicals. The scale of relative stabilizing effects[1] was found to be Ph > CN ≈ CO > CO_2Et ≈ CO_2H > Me. Considering the stabilizing effects of the phenyl and ketonic groups, the addition of bromotrichloromethane to benzylideneacetone would be expected to lead to the intermediate radical I and hence the product IIa.



I IIa IIb

Although this reaction was reported, attempts to degrade the adducts to known products were not successful.[1] Further, it was also recorded[3] that in the addition of thiyl radicals (R·) to α,β-unsaturated ketones, including benzylideneacetone, the radical (R·) adds at the carbon β to the carbonyl. In view of the difference in the orientation of free-radical addition, we thought that it would be important to determine the structure of the adduct II.

Nmr study of several acyclic ketones indicates that protons α to the carbonyl group are subject to benzene-induced solvent shifts, as in the case of alicyclic ketones,[4] and thus can be distinguished from other protons. Therefore the nmr signals can be accurately assigned to the protons in II. By comparing the chemical-shift data of several related compounds of known structures, it is possible to determine unambiguously the positions of the Br and CCl_3 groups. This study was extended to the reaction of bromotrichloromethane and benzylideneacetophenone. The adduct III is expected to have the structure IIIa. Detailed discussion of the nmr study is given below.

IIIa IIIb

The nmr signals of protons α to the carbonyl group in alicyclic compounds are known to shift upfield in benzene solution relative to deuteriochloroform solution.[4] The nmr spectra of several acyclic ketones have been obtained in both benzene and deuteriochloroform solutions. The chemical-shift data are tabulated below.

TABLE I
NMR CHEMICAL-SHIFT DATA FOR ACYCLIC KETONES[a]

Compd	Formula	Protons	$\tau_{C_6H_6}$	τ_{CDCl_3}	$\Delta = \tau_{C_6H_6} - \tau_{CDCl_3}$
IV	$CH_{3a}COCH_{3a}$	a	8.44	7.85	0.59
V	$CH_{3a}COCH_b(CH_{3c})_2$	a	8.32	7.87	0.45
		b	7.90	7.43	0.47
		c	9.16	8.90	0.26
VI	$CH_{3a}COCH_{2b}CH_{3c}$	a	8.42	7.86	0.56
		b	8.18	7.54	0.64
		c	9.17	8.95	0.22
VII	$PhCOCH_{2b}CH_{3c}$	b	7.54	7.03	0.51
		c	8.95	8.78	0.17
VIII	$(CH_{3c}CH_{2b})_2CO$	b	8.11	7.57	0.54
		c	9.10	8.94	0.16
IX	$PhCH_cCH_bCOCH_{3a}$ (Br Br)	a	8.05	7.54	0.51
		b	5.38	5.07	0.31
		c	4.73	4.69	0.04

[a] Values are in parts per million. All determinations were carried out in dilute solutions (<2%).

Table I shows that, for compounds IV–VIII, methyl protons α to the carbonyl group shift upfield by 0.45–0.59 ppm in benzene solution relative to deuteriochloroform solution; methylene or methine protons α to the carbonyl also shift upfield by about the same amount. Methyl protons β to the carbonyl group are also observed to shift upfield in these compounds, but by lesser amounts. These results are used to assign the pair of AB doublets due to protons b and c in the nmr spectrum of compound IX.

These chemical-shift data observed for acyclic ketones in benzene and chloroform solutions are consistent with similar data observed for alicyclic ketones, such as keto steroids.[4] Certainly, it is the same solute–solvent interaction that gives rise to this benzene-induced upfield shift in these ketones. An explanation in terms of a collision complex between the ketone compound and the benzene molecule has been offered by Bhacca and Williams.[4]

The upfield shift of protons α to the carbonyl group may be used to help in elucidating the correct structures of the reaction products II and III described above. The nmr spectra of these compounds have been determined in both benzene and deuteriochloroform solutions at *ca.* 0.25 *M* or less.

The nmr spectrum of II consists of a pair of AB doublets and a methyl peak, plus the phenyl-proton peaks, with parameters shown in Table II. As the methyl peak and the higher field doublet (τ 5.78)

(1) R. L. Huang, *J. Chem. Soc.*, 1342 (1957).
(2) J. I. G. Cadogan, E. G. Duell and P. W. Inward, *ibid.*, 4164 (1962).
(3) F. W. Stacey and J. F. Harris, Jr., *Org. Reactions*, **13**, 150 (1963).
(4) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 7.

shift upfield in benzene solution, this higher field doublet may be assigned to the proton α to the carbonyl group.

TABLE II
NMR DATA FOR COMPOUND II

AB doublets, τ, ppm		AB doublets, J, Hz	Methyl, τ, ppm	Solvent
4.52	5.52	10.3	7.37	$CDCl_3$
4.55	5.78	10.0	7.75	C_6H_6
$\Delta = \tau_{C_6H_6} - \tau_{CDCl_3}$ 0.03	0.26		0.38	

The nmr spectrum of III consists of a pair of AB doublets for the aliphatic protons, plus the phenyl-proton peaks, with parameters shown in Table III. In this case the relative shifts in the two solvents are too small to be significant. In view of the large groups near the aliphatic protons, the lack of any significant relative shift in the two solvents can be explained in terms of steric factors preventing any substantial interaction between the molecule and the solvent molecules.

TABLE III
NMR DATA FOR COMPOUND III

AB doublets, τ, ppm		AB doublets, J, Hz	Solvent
4.26	4.54	10.2	$CDCl_3$
4.19	4.57	10.2	C_6H_6

The benzene-induced solvent shifts found for the benzylidene–acetone product assign chemical shifts to the protons α and β to the carbonyl group, respectively. Reference compounds may be used to establish the chemical shifts of protons adjacent to bromine and trichloromethyl groups and thus to locate these groups relative to the carbonyl group. To this end the nmr spectra of the following compounds have been obtained, with the chemical-shift data in deuteriochloroform solution indicated below the respective protons.

$PhCHBrCH_2Br$	$PhCHBrCH_2CCl_3$
X	XI
4.91 6.01	4.60 6.25
$PhCHBrCHBrPh$	$PhCHBrCHCCl_3Ph$
XII	XIII
4.55	4.13 5.70

Comparison of the τ values in compounds X and XI shows that the protons in the fragment CH_2Br have a lower τ value than those in the fragment CH_2CCl_3. This may indicate that Br as a substituent in a molecule confers a lower τ value on protons attached to the same carbon atom than does the substituent CCl_3, other conditions being the same. This point, together with the chemical-shift datum of the aliphatic protons of compound XII, may be used to assign the nmr spectrum of the aliphatic protons of compound XIII.

Compound IX–XIII show that the proton in the fragment PhCHBr in various molecular environments has a τ value less than 5. In compound IX, if the Br on the carbon adjacent to the carbonyl group is replaced by a trichloromethyl group, CCl_3, to give $PhCHBrCHCCl_3COCH_3$ (IIa), it is expected that the proton in the PhCHBr fragment has a τ value less than 5 and that of the proton in the fragment $CHCCl_3CO$ has a τ value higher than 5. If compound II is assigned the structure as shown, the observed τ values of the aliphatic protons, which are 4.52 and 5.52 ppm in deuteriochloroform solution, would be consistent with this structure.

If compound II is assigned the alternative structure $PhCHCCl_3CHBrCOCH_3$ (IIb), the proton in the fragment $PhCHCCl_3$ should be assigned the higher τ value, 5.52, on the basis of the data for compound XIII. However, it has been shown above that the benzene-induced solvent shift involves the proton associated with this τ value, and the resonance signal of the proton in this fragment, $PhCHCCl_3$, is not expected to involve this shift in this structure. Hence this structure is ruled out.

The τ values 4.26 and 4.54 for III indicate that the fragment $PhCHCCl_3$ is not present. This is obvious from examination of the data for compound XIII, in which the proton in the fragment $PhCHCCl_3$ has a τ value of 5.70. This rules out structure IIIb for the adduct. Further, by analogy with the reaction of benzylideneacetone, it may be deduced that the adduct has structure IIIa.

Experimental Section

The nmr measurements were made with a Hitachi Perkin-Elmer R-20A high-resolution nmr spectrometer. Proton chemical shifts are reported in parts per million with respect to tetramethylsilane (TMS) as internal standard and frequently checked with the cyclohexane signal at 1.42 ppm from TMS. Thus the chemical-shift data are accurate to within ± 0.02 ppm.

Acetone, methyl isopropyl ketone, methyl ethyl ketone, diethyl ketone, and propiophenone were of reagent grade and distilled twice before use. Benzylideneacetone dibromide, mp 123.5–124.5° (lit.[5] mp 124–126°), styrene dibromide, mp 74–75° (lit.[6] mp 74–74.5°), and stilbene dibromide, mp 236–238° (lit.[6] mp 237°), were prepared from benzylideneacetone, styrene, and stilbene, respectively, by the addition of bromine in carbon tetrachloride. 1-Bromo-2-trichloromethylethylbenzene,[7] mp 51–52°, 1-bromo-2-trichloromethylhydrostilbene,[2] mp 112–113°, and 4-bromo-4-phenyl-3-trichloromethylbutan-2-one,[1] mp 98–99°, were prepared according to the methods reported in the literature.

The addition of bromotrichloromethane (80 g, 400 mmol) to benzylideneacetophenone (14.3 g, 69 mmol) catalyzed by benzoyl peroxide (4.0 g, 17 mmol) was carried out under the same conditions as in the preparation of 4-bromo-4-phenyl-3-trichloromethylbutan-2-one.[1] The crude adduct, yield 13 g (46%), mp 118–133°, was recrystallized from methanol to give 2-bromo-2-phenyl-1-trichloromethylethyl phenyl ketone, mp 140.4–141°.

Anal. Calcd for $C_{16}H_{12}OBrCl_3$: C, 47.3; H, 2.9. Found: C, 47.4; H, 3.2.

Registry No.—Bromotrichloromethane, 75-62-7; IIa, 22431-13-6; IIIa, 22431-14-7; IV, 67-64-1; V, 563-80-4; VI, 78-93-3; VII, 93-55-0; VIII, 96-22-0; IX, 6310-44-7.

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