

cessive deuteration showed the *meta* protons more deshielded than the *ortho* protons.¹²

(12) One of the referees called attention to unpublished and independent work of Dr. D. G. Farnum on phenyl and phenylmethyl carbonium ions and suggested simultaneous publication, which was arranged by mutual agreement. Having learned of Dr. Farnum's data, one can say that there is excellent agreement of the observed chemical shifts of the aliphatic protons and the over-all ring proton shifts. However, based on Dr. Farnum's data, supported by calculation of theoretical spectra with the use of a computer program, the deshielding sequence of the *ortho* and *meta* protons is reversed in the diphenyl- and phenylmethylcarbonium ions, as compared with that of the triphenylcarbonium ion.

CONTRIBUTION No. 114

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Chemical Shifts and Long Range Shielding Effects in the Nuclear Magnetic Resonance Spectra of Phenylmethyl, Diphenyl, Triphenyl, and Related Carbonium Ions

Sir:

Analyses of the n.m.r. spectra of triphenylcarbonium and methyl-diphenylcarbonium ions have been reported in the literature.¹⁻³ We wish to describe results of an analysis of the n.m.r. spectra of a number of phenyl-

TABLE I
RING PROTON CHEMICAL SHIFTS FOR SOME PHENYLCARBONIUM IONS⁴

Case	Carbonium ion	<i>para</i> , τ -units	<i>ortho</i> , τ -units	<i>meta</i> , τ -units	<i>ortho-para</i> , p.p.m.	<i>meta-para</i> , p.p.m.
1	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2^a$	2.80	2.80	2.80	0	0
2	$\text{C}_6\text{H}_5\text{C}(\text{OH})_2$	1.94	1.73	2.24	-0.21	+0.30
3	$(\text{C}_6\text{H}_5)_2\text{COH}$	1.85	1.88	2.17	+0.03	+0.32
4	$\text{C}_6\text{H}_5\text{C}(\text{OH})\text{CH}_3^b$	1.84	1.57	2.22	-0.30	+0.38
5	$(\text{C}_6\text{H}_5)_3\text{C}^+$	1.76	2.31	2.13	+0.55	+0.37
6	$(\text{C}_6\text{H}_5)_2\text{CCH}_3^c$	1.72	1.97	2.12	+0.25	+0.40
7	$(\text{C}_6\text{H}_5)_2\text{CH}^d$	1.62	1.54	2.02	-0.08	+0.40
8	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2^e$	1.45	1.20	2.03	-0.25	+0.58

^a Since sulfonation in chlorosulfonic acid was very rapid, the n.m.r. spectrum of this substance was determined in concentrated sulfuric acid. ^b CH_3 resonance at τ 6.69. ^c CH_3 resonance at τ 6.30. ^d $>\text{CH}$ resonance at τ 0.19. ^e CH_3 resonance at τ 6.43.

The *ortho*, *meta*, and *para* ring proton chemical shifts for a number of phenylcarbonium ions are given in Table I. Values were determined by comparing n.m.r. spectra of chlorosulfonic acid solutions of the appropri-

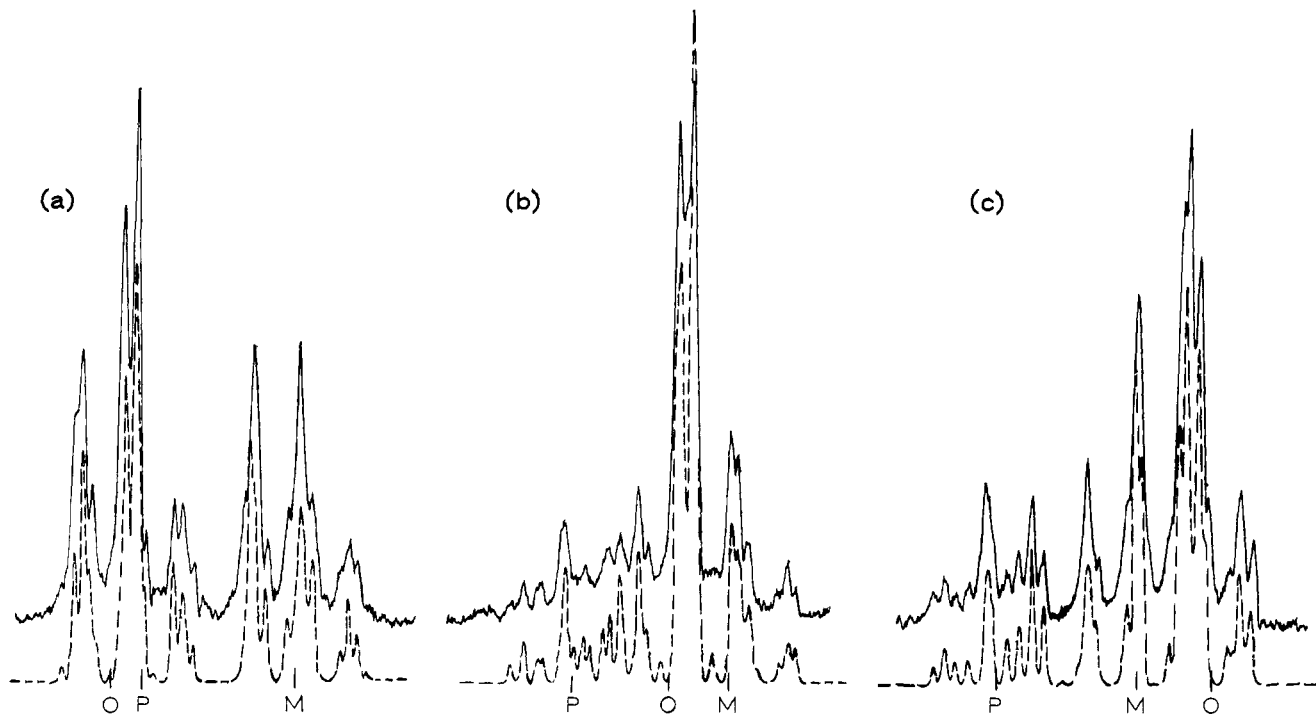


Fig. 1.—Calculated (dashed line) and experimental (solid line) n.m.r. spectra of some phenylcarbonium ions. Chemical shift differences (δ) and coupling constants (J) for the *ortho* (O), *meta* (M), and *para* (P) protons used for the calculation are given in c.p.s. Changes of 0.5 c.p.s. in chemical shifts or the large coupling constants gave noticeably poorer agreement. The small coupling constants are probably within 1 c.p.s. of the correct value. (a) Diphenylcarbonium ion: $\delta(\text{O-P}) - 5$, $\delta(\text{O-M}) + 24$; $J(\text{O, M}) 8.2$, $(\text{O, P}) 1.2$, $(\text{O, M}') 0.5$, $(\text{O, O}') 1.2$, $(\text{M, P}) 7.5$, $(\text{M, M}') 1.7$. (b) Methyl-diphenylcarbonium ion: $\delta(\text{O-P}) + 15$, $\delta(\text{M, P}) + 24.5$; $J(\text{O, M}) 8.2$, $(\text{O, P}) 1.2$, $(\text{O, M}') 0.5$, $(\text{O, O}') 1.2$, $(\text{M, P}) 7.5$, $(\text{M, M}') 1.7$. (c) Triphenylcarbonium ion: $\delta(\text{O-P}) + 33.5$, $\delta(\text{M-P}) + 22$; $J(\text{O, M}) 7.7$, $(\text{O, P}) 1.2$, $(\text{O, M}') 0.5$, $(\text{O, O}') 1.2$, $(\text{M, P}) 7.5$, $(\text{M, M}') 1.0$.

carbonium ions which (1) suggest that shielding of *ortho* protons by neighboring phenyl rings in di- and triphenylcarbonium ions is more important than has been recognized in earlier papers, and (2) permit a qualitative correlation of the extent of phenyl delocalization of the positive charge with the position of the *para* proton resonance.

(1) R. Dehl, W. R. Vaughan, and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); *J. Chem. Phys.*, **34**, 1460 (1961).

(2) D. E. O'Reilly and H. P. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960).

(3) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959).

ate carbinol or carbonyl compound⁴ with calculated spectra obtained using the computer program of Bothner-By and Naar-Colin.^{6,7} The calculated and de-

(4) Solutions were made up to approximately 10% concentration by dropwise addition of a 1:1 solution of the compound in thionyl chloride to vigorously stirred chlorosulfonic acid at -20° (-40° for phenyldimethylcarbonium ion). The n.m.r. spectra were determined on a Varian A-60 spectrometer at room temperature (-40° for phenyldimethylcarbonium ion). Chemical shifts are reported on the τ -scale with tetramethylammonium fluoroborate (τ 6.87) as an internal standard.⁵

(5) D. G. Farnum, M. A. T. Heybey, and B. Webster, *Tetrahedron Letters*, **No. 5**, 307 (1963).

(6) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231

terminated n.m.r. spectra for diphenyl-, methyl-diphenyl-, and triphenylcarbonium ions are given in Fig. 1a-c.

The structures of the carbonium ions were established by several observations. In cases 2, 3, 5, and 7 (Table I), the starting materials were recovered in 60% yield or greater by addition of aged solutions in chlorosulfonic acid to excess, ice-cold, vigorously stirred, aqueous base. The phenyl proton regions of the n.m.r. spectra in cases 2, 4, and 8 were very similar in appearance, though different in position. The ratio of the area of the phenyl proton resonances to that of the methyl (or methine) proton resonance in cases 4, 6, 7, and 8 was very close to the calculated value. The position of the methyl (or methine) proton resonance in cases 4, 6, 7, and 8 was as expected for the carbonium ions (see Table I). The spectra were stable and reproducible under the conditions of the n.m.r. determination.

The data in Table I show that the position of the *para* proton resonance is a reasonable measure of the extent of positive charge on the phenyl ring. Thus, the cases 1 through 8 are arranged in the anticipated order of increasing stabilization of the benzylic carbonium ion by electron release from the phenyl group. Collaterally, the *para* proton resonance moves progressively downfield. By contrast, the *ortho* proton chemical shifts show wide, noncorrelating variations. Columns 5 and 6 show that the separation of the *ortho* and *para* proton resonances fluctuates dramatically, while the separation of the *meta* and *para* proton resonances is more uniform.

A closer consideration of cases 3, 5, 6, and 7, however, puts the behavior of the *ortho* protons on a rational basis. Thus, as the substituent group on the benzylic carbon atom increases in size from hydrogen (case 7) to hydroxyl (case 3) to methyl (case 6) to phenyl (case 5), the *ortho* proton resonance moves upfield relative to the *para*. This is the expected behavior if the increasing bulk of the substituent causes the phenyl groups to twist further out of the plane of the carbonium ion, thus bringing the *ortho* protons more into the shielding region of the adjacent phenyl group. In order to account for the shielding of approximately 0.5 p.p.m. observed for the *ortho* protons of the triphenylcarbonium ion, an angle in the neighborhood of 40° from coplanarity is necessary. This may be compared with the 35° suggested by X-ray analysis of trityl perchlorate.⁸⁻¹¹

Acknowledgment.—The author is deeply indebted to Prof. C. F. Wilcox for his major contribution to this work in translation and modification of the computer program. Support from the National Science Foundation (NSF G 14454) is gratefully acknowledged.

(1961). We thank Dr. Bothner-By for a copy of the program and a deck of IBM cards.

(7) The computer program was run, after minor modifications, on a CDC 1604 computer. A resolution factor of 0.8 (approximately equal to the band width at half-height) gave calculated curves comparable in appearance to the best determined n.m.r. spectra.

(8) K. A. Eriks, A. H. Gomes de Mesquita, and P. S. Aggarwal, 5th Annual Report of the Petroleum Research Fund, 1960, p. 35.

(9) The large *ortho* shielding which we observe for the carbonium ion is claimed to be absent in the corresponding carbanion.¹⁰ Neither data nor space permits a detailed discussion of this discrepancy at present.

(10) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(11) After the completion of this work we were made aware of related work done independently by George A. Olah on the preparation of stable salts of some of the carbonium ions reported. We thank Dr. Olah for a republication account of his results and for his agreement to simultaneous publication.

(12) Fellow of the Alfred P. Sloan Foundation.

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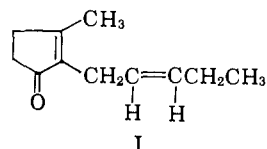
DONALD G. FARNUM¹²

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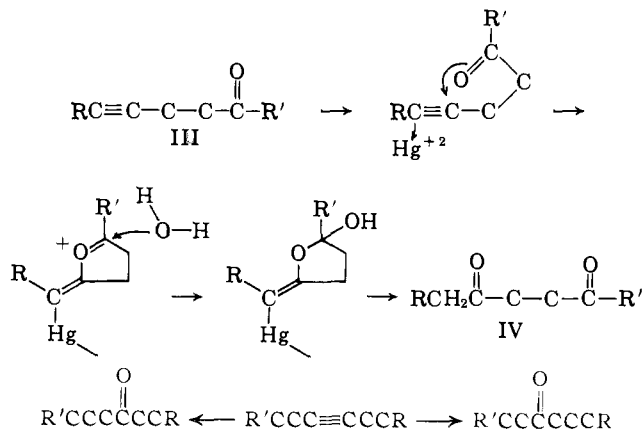
A New Synthesis of 1,4- and 1,5-Diketones

Sir:

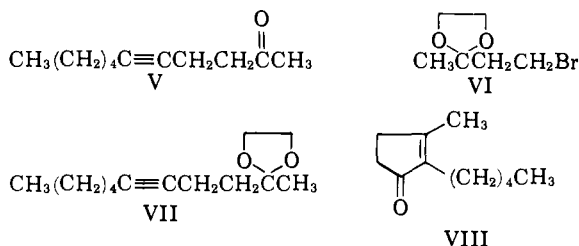
We have devised a new general synthesis of 1,4 and 1,5-dicarbonyl compounds which we have then utilized, *inter alia*, in an efficient synthesis of jasmone (I).¹ It is well known that an unsymmetrically disubstituted acetylene such as II will undergo mercuric ion catalyzed hydrolysis to form both possible carbonyl compounds,² and such hydrations are therefore not normally suited to synthetic purposes.



We were, however, attracted by the possibility that the hydration of an unsymmetrical acetylene of type II could become completely unidirectional when R (or R') is an acyl group (*cf.* III). In such a situation the participation of the carbonyl oxygen in the transition state for the hydration should sufficiently lower its energy to lead to only one of the two possible products, in this case the 1,4-diketone (IV).



The ketones of type III, which were necessary to test this hypothesis, were made by two different routes which we will illustrate with the synthesis of 5-undecyn-2-one (V). In the first sequence, methyl vinyl ketone was converted, by addition of hydrogen bromide followed by exchange ketalization, into the cyclic ketal of 2-bromoethyl methyl ketone (VI)³ which thus becomes readily available, and which served to alkylate



the lithium salt of 1-heptyne in refluxing dioxane to give acetylenic ketal VII in 50% yield, b.p. 85-88° (0.05 mm.). Deketalization with methanolic sulfuric acid led to the desired V in 93% yield, b.p. 79-81° (0.3 mm.), semicarbazone m.p. 104-104.5°.

(1) G. Stork and R. Borch, *J. Am. Chem. Soc.*, **86**, 936 (1964).

(2) For general references, *cf.* R. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths Publications Ltd., London, England, 1955.

(3) For an earlier synthesis of this substance see L. Willmann and H. Schinz, *Helv. Chim. Acta.* **32**, 2151 (1949).