^{13}C Nuclear Magnetic Resonance Spectroscopy of Evolving Reactions. Indanones via $AlCl_3$- and H_2SO_4-Catalyzed Cyclialkylations

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Abstract: Aluminum chloride catalyzed Friedel-Crafts cyclialkylations of 2- and 3-bromo- and -chloro-4′-fluoro-2-methylpropiophenones **1b, 1c, 6b,** and **6c** have been studied in detail by in situ ^{13}C NMR spectroscopy as well as by the more conventional techniques requiring reaction quench. Clear evidence removes the historical mechanistic ambiguity relative to 2-methyl-1-indanone formation from **1** and establishes cyclization as proceeding through the methacrylophenone **3.** With the β-halo isomers, skeletal rearrangement leads to 3- as well as 2-methylindanones. A stable oxonium ion by-product **10** has been observed which requires the equivalent of a transformation of a secondary carbonium ion to a primary carbonium ion. This is rationalized in terms of a neighboring group effect by the carbonyl group. Cyclialkylations with β-halo compounds **6b** and **6c** have been studied in H_2SO_4 for purposes of comparison. Facile oxidation of Br^- to Br_2 in H_2SO_4 intrudes upon the simplicity of the reaction of **6b,** relative to **6c,** leading to brominated products.

In his review on cyclialkylation of aromatics, Barclay,[1] citing the work of Layer and MacGregor,[2] pointed out that α-bromo aralkyl ketones are considered to undergo aluminum chloride catalyzed cyclization to indanones through the corresponding unsaturated ketone **3** (Scheme I). Formation of the tertiary carbonium ion **2** by aluminum chloride initiates the sequence. Barclay mentioned as an alternative possibility a pathway which requires a hydride shift and conversion of a tertiary to a primary carbonium ion (**2** → **5**).[1]

In another chapter of the same treatise, Gore[3] reported the reaction of 2-bromo-2-methylpropionyl bromide with benzene to give **1a** as a first intermediate which lost HBr to form both the unsaturated ketone **3a** and the indanone **4a.** He continued, "If **4a** arises, as seems probable, by cyclization of **3a,** a likely intermediate may be the β-bromoketone, $C_6H_5COCH(CH_3)$-CH_2Br" (**6a**). It is one purpose of this paper to settle these mechanistic ambiguities.

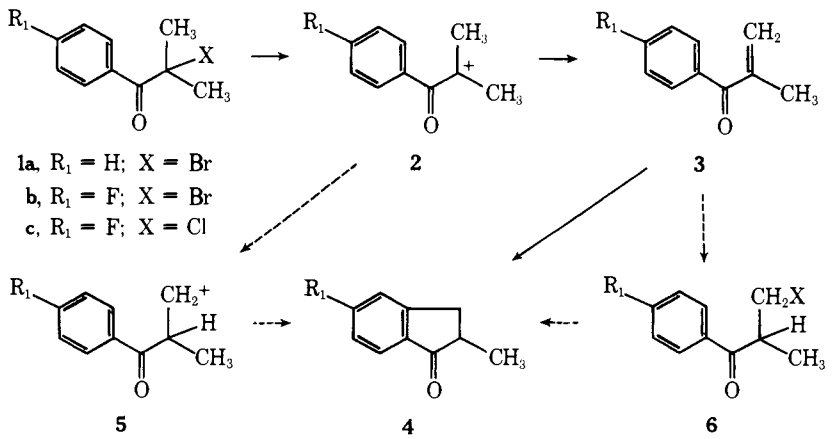
We have chosen to do so by examining the reaction of 2-bromo-4′-fluoro-2-methylpropiophenone (**1b**), by in situ ^{13}C NMR spectroscopy as well as by more conventional chromatographic analysis of reaction mixtures following workup. The power of the ^{13}C NMR spectroscopic method has been made abundantly clear in identifying, e.g., stable carbocations.[4a] Its use in studying evolving reactions is seldom if ever cited,[4b] and reports of the study of ongoing Friedel-Crafts reactions are to our knowledge nonexistent.

We have also studied and report upon related cyclialkylations of halo analogues and isomers of **1b.** For some of these, H_2SO_4 catalysis was also examined. In all cases, intermediates and products have been identified and characterized. We have developed new mechanistic insight to these reactions principally through the in situ study, and have even discovered a neighboring group effect not previously observed in Friedel-Crafts reactions. These experiments and others convince us that Professor Olah's suggestion[5] to restudy this segment of Friedel-Crafts chemistry with modern tools has merit.

Results and Discussion

When quenched aliquots of the reaction of 2-bromo-2-methylpropionyl bromide, fluorobenzene, and $AlCl_3$ in CS_2 were examined by gas chromatography and mass spectrometry, a reaction profile was observed (Figure 1) which indicated that the rapidly formed bromo ketone **1b** was converted to both the unsaturated **3b** and isomeric β-bromo ketone **6b** in keeping with Gore's[3] suggestion. The latter two intermediates appeared to decay simultaneously and cleanly to indanone **4b.** However, when the same reaction was observed *directly* by ^{13}C NMR, *no signals attributable to* **6b** *could be seen.* All signals were accounted for by **1b, 3b,** and **4b,** as indicated in Figure 2. The β-bromo ketone, then, was an artifact of the quench procedure and not an intermediate in the reaction. In fact, a mixture of authentic **6b** and $AlCl_3$ remained practically unchanged after 4 h exposure to the same reaction conditions (but see below). It later became clear that the amount of **6b** depended in part

Scheme I[a]



[a] For clarity, the oxygen-complexed $AlCl_3$ is not shown here or in Schemes II and III.

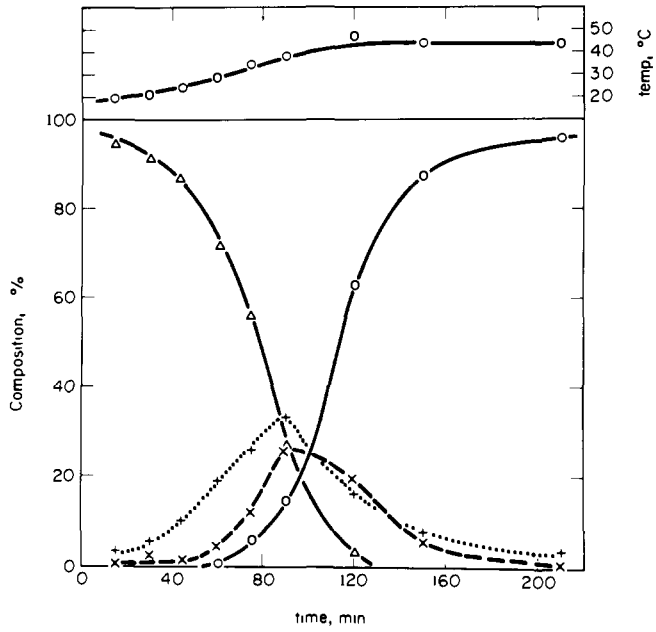


Figure 1. Reaction composition after acylation of fluorobenzene (0.26 mol) with 2-bromo-2-methylpropionyl bromide (0.25 mol)-$AlCl_3$ (0.55 mol) in CS_2 (33 ml). Zero time marks end of 15–20 °C acid bromide addition period; temperature was then gradually raised to 45 °C. Values are given as GC area percent of quenched aliquots: (-△) **1b**; (-○) **4b**; (···+) **3b**; (- - - ×) **6b**. Compound **6b** is an artifact (see text).

upon the volume of water in which the aliquot was quenched; thus, conjugate addition of HBr to **3b** explains its formation.

Cyclization rates of the α-halo ketones **1b** and **1c** and the acrylophenone **3b** were measured by GC under the same reaction conditions, and they are shown in Figure 3. Note that plots for the latter two are coincident. The first (15 min) sample taken from the reaction of **1c** showed that dehydrochlorination was virtually complete in a surprisingly fast step and thus indanone formation from either **1c** or **3b** is kinetically indistinguishable.[6] Curvature in the rate plot of the α-bromo ketone (**1b**) reaction reflects slower dehydrobromination. Stated differently, $AlCl_3$ ionization of the C-Br bond is more difficult than that of the analogous C-Cl bond, which is in line with observed faster Friedel-Crafts alkylations with alkyl chlorides vs. alkyl bromides.[8]

Traces of β-chlorophenone **6c** were observed while gathering the kinetic data for **1c** and **3b**, but they, too, reflect conjugate addition during the quench. The inaccuracy which this artifact introduced into the data ranges from 0.5 to 2.5 mol % of **3b** remaining in its reaction with $AlCl_3$. This is near the usual GC precision. All these reactions, then, are straightforward, and we may consider the mechanism of cyclization of **1b**, **1c**, and **3b** to be established.

We also studied the cyclization of the isomeric β-halo aralkyl ketones. Because the β-chlorophenone **6c** reacted much more slowly than the α-halo compounds, it was examined in a solvent-free mixture with $AlCl_3$ at 100 °C.

In situ ^{13}C NMR spectroscopy showed that the diminution of signals for starting material was accompanied by the appearance of spectra readily attributable to **4b**, the indanone we sought, *and* its isomer, 5-fluoro-3-methyl-1-indanone (**8**) in a ca. 3:1 ratio. The remaining lines of significance, which grew in concert and were therefore related, accounted for ca. 15% of the total after 4 h. These lines could not be assigned to any of the compounds identified after conventional workup and therefore represented an unisolable intermediate. It contained three aliphatic carbons at δ_C 23.1, 41.1, and 91.4 ppm (from external Me_4Si), each of which possessed two protons according to off-resonance decoupling experiments. In order that it appear near 90 ppm and possess, as it does, $^1J_{CH}$ = 161–162 Hz, a methylene carbon must bear an unprecedentedly polar single substituent or two ordinary polar ones, or else it must be an olefinic CH_2.[9] There was also an apparent carbonyl carbon at δ_C 218.5, and two equivalent aromatic carbons at δ_C 142.2, $^3J_{CF}$ = 12.9 Hz, corresponding to $C_{2',6'}$. The other aromatic carbon atoms of this species could not be identified in

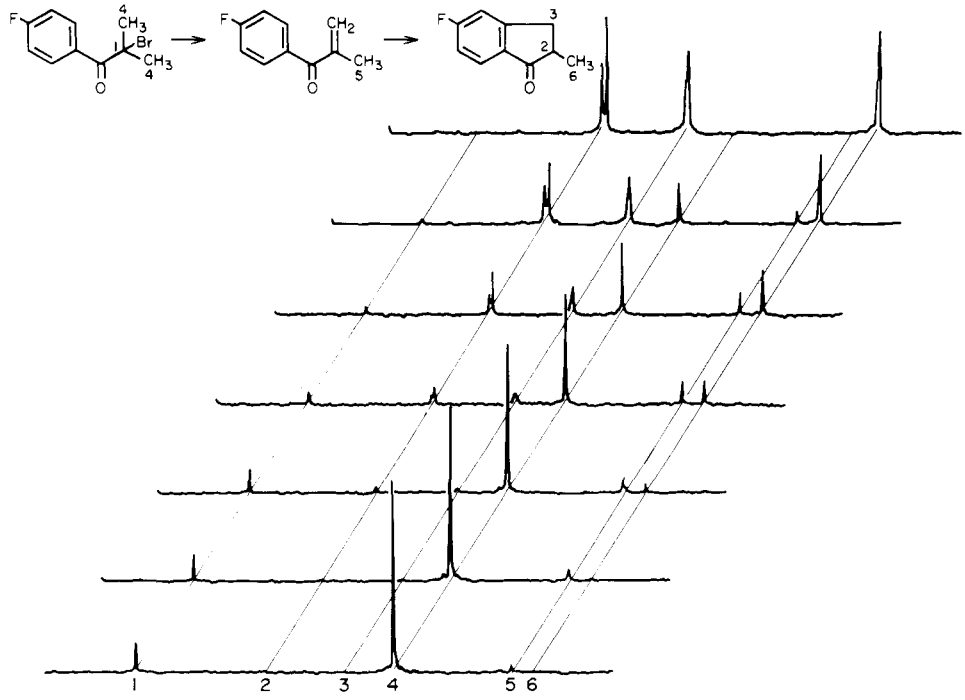


Figure 2. Time-lapse plot of ^{13}C NMR spectra (aliphatic carbons only) of the reaction of **1b** with $AlCl_3$ at ~30 °C. Reaction times are 0.5, 1, 2, 4, 8, and 18 h, and 4 days, bottom to top, respectively, representing the mid-point of half-hour accumulations. The numbered signals (ordinate) are assigned to specific carbon atoms as shown for the reaction at the upper left of the figure. Signals due to the product indanone are split due to the existence of two forms of aluminum chloride-ketone complex in solution which have different stoichiometries.

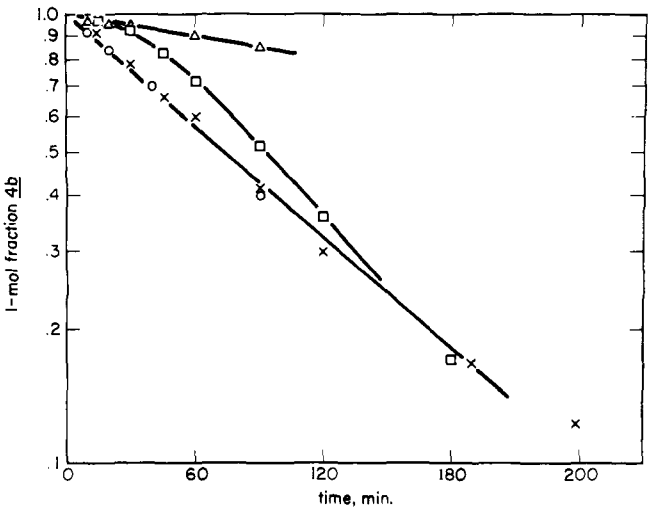


Figure 3. Cyclization rates at 50 °C, determined by GC: (○) **3b** in CS_2; (△) **3b** in CH_3NO_2; (□) **1b** in CS_2; (×) **1c** in CS_2. Each experiment employed 1.5 equiv of $AlCl_3$. The concentration function was chosen to demonstrate the differences in rate of dehydrohalogenation of **1b** and **1c**.

the complex reaction mixture. Careful chromatography of a similar experiment which was quenched after 50% reaction revealed the presence of only one other compound in quantity sufficient to have been responsible for the signals, namely, 4′-fluoro-4-hydroxybutyrophenone (**11**). Therefore, based upon both spectral and chemical considerations, the observed intermediate was assigned the structure 2-(4′-fluorophenyl)-1-oxoniacyclopent-1-enyl cation (**10**), which is discussed further below.

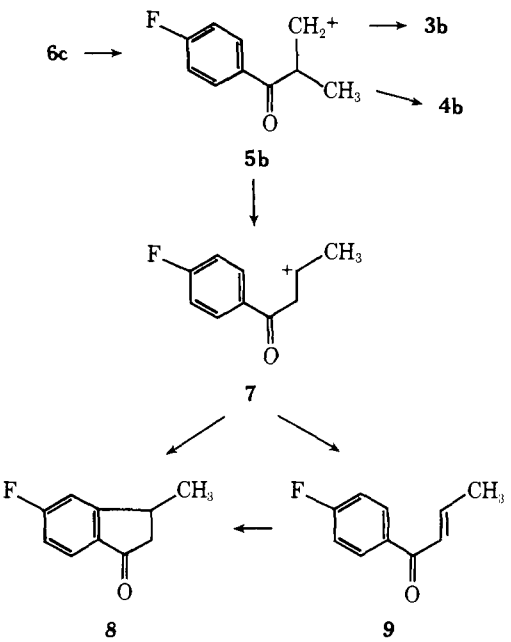
No other NMR signals were observed save a small (ca. 2–3% of the total) methyl signal early in the reaction which diminished with time. Its chemical shift was δ_C 23.7 ppm and it was assigned to 4′-fluorocrotonophenone (**9**). The other carbons of this compound were not seen. Methacrylophenone **3b** was found during workup as ca. 1% of the mixture.

In presenting our interpretation of this multipath reaction, we would prefer to describe only the chemistry that we can "see". We do, however, invoke carbonium ions in their traditional sense in order to connect the visible with the invisibly fast (under our viewing conditions). Accordingly, ionization of **6c** may be considered to form a primary carbonium ion, **5b**, which undergoes intramolecular cyclization to provide the major product of the reaction, indanone **4b** (Scheme II). Intervention of **3b** is neither necessary nor excluded in this path by our observations. Its presence after quench can reflect proton loss from **5b**.

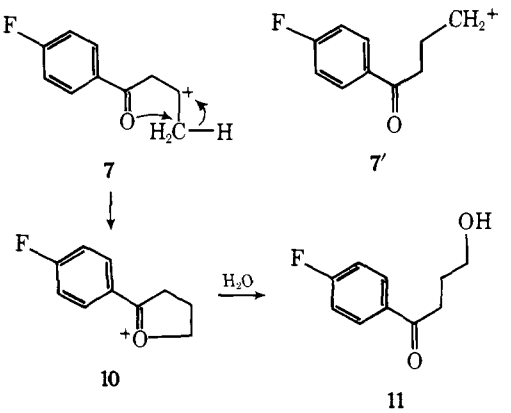
Skeletal rearrangement precedes[10a,b] formation of the other products. Historically, it has been convenient and sometimes experimentally justified to invoke rapid alkyl and hydride migrations to account for these rearrangements. In this specific case, aroyl migration[12b] could explain the results with equal ease.[12c] Ion **7**, whether formed by concurrent methyl and hydride shifts or acyl migration, may be transformed to **8** by intramolecular cyclization and to **9** by loss of a proton. Sketchy literature rate data for the cyclization of crotonophenone[11] support the path **9** → **8** under our conditions, but do not require it.

Access to the oxonium ion **10** is conveniently portrayed as a concerted process (Scheme III) whereby hydride migration accompanies the formation of the O → C donor bond. Prior hydride migration would not be energetically favored, since it creates a primary carbonium ion (**7′**) from a secondary one. The inherent stability of **10** permits its accumulation under these reaction conditions. Aqueous hydrolysis of **10** to **11** has precedence.[13]

Scheme II



Scheme III

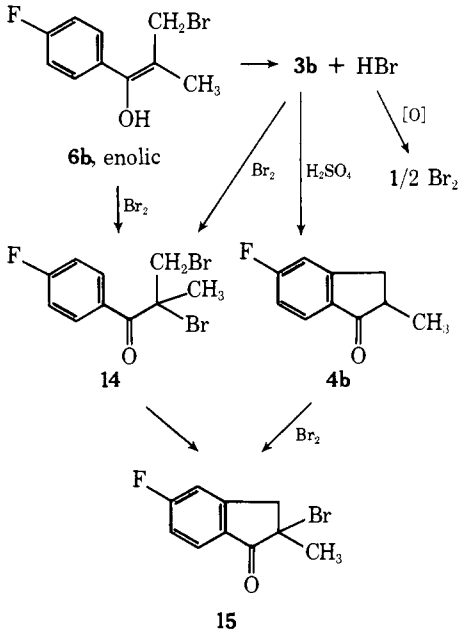


One other potential pathway deserves mention. Carbonium ion **5b** could be considered a precursor to ring-protonated 4-fluorobenzoylcyclopropane (**12**). Its intermediacy here must be rejected even though **3b**, **4b**, **8**, and **9** would be expected as its ultimate products.[11] We find that 4-fluorobenzoylcyclopropane is sufficiently stable in solutions with $AlCl_3$ to have been observed in these reactions, had it been formed.

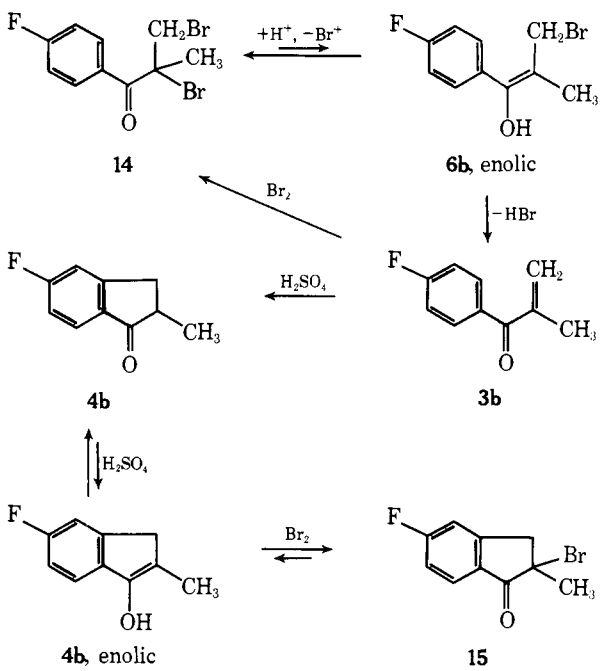
Oxonium ion **10** was an unexpected finding, and it vividly demonstrates the value of ^{13}C NMR spectroscopy for following evolving reactions. Further justification for the structure comes from examination[12a] of the Friedel-Crafts chemistry of 4-chloro-4′-fluorobutyrophenone (**13**)[14] from which its spectrum is generated under milder conditions than used here. Since both **6c** and **13** undergo (conceptually) initial ionization to primary carbonium ions, and the latter more readily, we consider the formation of **10** from **13** to demonstrate a neighboring group effect,[15] most often exemplified in the past in solvolytic reactions.[16] Intermediate ions like **10** have heretofore been neither observed nor postulated for these reactions.[17] We suspect they will be found to be commonplace where five-membered rings can form.

When the same conditions (100 °C, 2 equiv of $AlCl_3$) were applied to β-bromophenone **6b**, a slower but qualitatively similar reaction ensued. The same intermediate and product pattern emerged with but one significant difference: formation of chloro analogue **6c** in appreciable quantity was evident from our first observation onward. Its presence must be attributed

Scheme IV



Scheme V



to a displacement reaction rather than an ionization. Were exchange to follow ionization, the intervening carbonium ion should have produced the indanones directly. Formation of **6c** from **6b** may also have been responsible for the lack of a kinetic fit in this overall reaction.

Up to now, we have pointedly avoided mention of enolization in the reactions of **6b** and **6c** for reasons which become evident after a study of their reactions in sulfuric acid (see below). Suffice it to say that we believe **6b, 6c,** and the like are *not* enolized by $AlCl_3$. Nonenolization of acetophenones by $AlCl_3$ could readily explain, for that matter, the useful "swamping catalyst" method developed by Pearson et al., by which ring halogenation without side-chain attack is achieved.[18]

Reactions in Sulfuric Acid. The ready cyclization of β-chlorophenones in H_2SO_4[20] was studied with **6c:** a 1 M solution was converted rapidly at 50 °C ($t_{1/2}$ = 20 min) in near-quantitative yield to indanone **4b.** The enolic form of **6c,** which was not seen per se, readily underwent HCl elimination affording the methacrylophenone **3b** as a true intermediate which was observed in situ by both ^1H and ^{13}C NMR spectroscopy. Acrylophenone **3b,** subjected to the same conditions, cyclized with $t_{1/2}$ = 16 min.

The behavior of the β-bromo analogue **6b** in H_2SO_4 was more involved (Scheme IV); however, its half-life was the same as that of **6c,** confirming enolization as the essential rate-limiting step. Oxidation of bromide by H_2SO_4 led to α-brominated products, further supporting the argument for enolization. Thus, accompanying the cyclization to **4b** was formation of 2,3-dibromo-4′-fluoro-2-methylpropiophenone (**14**). Bromoindanone **15** also formed, much more slowly, and at the expense of both **4b** and **14.** Bromination of **6b** was, in fact, faster than cyclization since the initial ratio of **14** to **4b** exceeded unity. After 4 h at 50 °C, the product ratio was reversed: 65% **4b** and 34% **14.** Obviously, no more than one-half the substrate can be converted to **14** because of its requirement for two atoms of bromine.

The conversion of **4b** to **15** was unexceptional, considering the presence of bromide and H_2SO_4. Cyclization of **14** to **15** was unusual, and slow, as observed in a separate experiment. Only ~30% conversion occurred in 18 days at 50 °C. No mechanistic clues were visible by ^{13}C NMR. We suggest the pathway of Scheme V, which rests upon the reversibility of acid-catalyzed bromination of ketones, so elegantly demonstrated by Altschul and Bartlett.[21]

Granting this reversibility, **14** is in equilibrium with the enol of **6b** which may lose HBr as was seen in our ^{13}C NMR observations. Not only can **3b** revert to **14** via bromination, but it can also cyclize to **4b,** whose enolic form will suffer bromination to **15.** The irreversibility of this cyclization step, and the excess of bromine, assures accumulation of **15.**

Finally, a note on the comparison of $AlCl_3$- and H_2SO_4-catalyzed cyclization of methacrylophenone **3b** is in order. The ^{13}C NMR data in Table I include the shifts of the β-olefinic and ortho-aromatic carbons ($C_{2',6'}$), between which the new C–C bond is formed. The deshielding of these carbons upon treatment with either acid indicates a depletion of negative charge at these centers. That the new bond is formed at all might most easily be ascribed to an electrophilic attack by the severely electron-impoverished β-olefinic carbon at the admittedly electron-poor but spatially proximate ortho-aromatic carbon. Indeed, initial attack may take place upon the ortho C–H bonding electrons such that the aromaticity of the phenyl ring is never lost along the reaction coordinate. It is interesting to speculate whether the greater acidification shift at C_β in H_2SO_4 is correlated with the ca. fivefold faster cyclization of **3b** in H_2SO_4 vs. $AlCl_3$.

Summary

In summary, we have analyzed in detail some aspects of the cyclialkylation reactions of haloaralkylphenones. In the case of α analogues, **1,** a definitive mechanism for the cyclization step, carbon–carbon bond formation between two unsaturated centers, has been "seen", and it can now supplant an ambiguity of the past.[1,3] In the considerably more complicated case of β analogues, a ketone neighboring group effect has been discovered which leads to an oxonium ion. This requires, in principle, the transformation of a secondary carbonium ion to a primary carbonium ion.

The H_2SO_4 cyclization method, long used with β-chlorophenones,[20] has been applied to a β-bromophenone revealing distinctions caused by the facile oxidation of bromide in the medium. Nevertheless, the products which were formed support an enolization-initiated mechanism. Finally, and perhaps most important, we have illustrated the power of ^{13}C NMR spectroscopy for the study of evolving chemical reactions not otherwise amenable to scrutiny prior to workup.

Table I. ^{13}C Chemical Shifts[a] of 4′-Fluoro-2-methylacrylophenone (**3b**) in Various Media

Carbon	Medium		
	Neat	$AlCl_3$[b,c]	H_2SO_4[b]
C=O	196.3	210.7 (+14.4)	211.3 (+15.0)
C_α	144.6	144.4 (−0.2)	141.7 (−2.9)
C_β	126.4	147.0 (+20.6)	152.0 (+25.6)
$C_{1'}$	134.8	131.1 (−3.7)	127.6 (−7.2)
$C_{2',6'}$	132.8	140.0 (+7.2)	140.4 (+7.6)
$C_{3',5'}$	116.0	119.2 (+3.2)	119.7 (+3.7)
$C_{4'}$	165.9	171.6 (+5.7)	172.9 (+7.0)
CH_3	19.1	20.6 (+1.5)	19.3 (+0.2)

[a] Reference was Me_4Si, external, ~25% v/v in $(CD_3)_2CO$. [b] Acidification shifts are given in parentheses, where a positive value indicates a deshielding effect. [c] Two complexed forms appear in the $AlCl_3$ treatment, as with some other ketones studied in this work. Data for only the dominant form are reported here.

Table II. Cyclialkylation Reaction, Half-Life of Starting Material

Ketone	$t_{1/2}$, min under condition[a]			
	A	B	C	D
1b	27			
1c	~2.5[b]			
3b	75		>360[c]	16
6b		>700[c,d]		20
6c		175		20

[a] Conditions: (A) 50 °C, 1.5 equiv of $AlCl_3$, saturated with CS_2; ca. 2 M; (B) 100 °C, 2 equiv of $AlCl_3$, solvent-free; (C) 50 °C, 1.5 equiv of $AlCl_3$, 1 M CH_3NO_2 solution; (D) 50 °C, 1 M in concentrated H_2SO_4. [b] Estimate; complete in 15 min. [c] Extrapolated. [d] Includes both **6b** and **6c** remaining.

Experimental Section[22,23]

2-Bromo-4′-fluoro-2-methylpropiophenone (1b). Twenty-three grams (100 mmol) of 2-bromo-2-methylpropionyl bromide was added over 15 min at 15 °C to a stirred slurry of 14 g (105 mmol) of $AlCl_3$ in 14.4 g (150 mmol) of fluorobenzene and 15 ml of CS_2. After 15 more min, the reaction was quenched on ice and worked up in the usual way. GLC analysis showed less than 1 area % of **3b**.[24] The yield was 80% after distillation.

Ketones 6b, 6c, and 14 and 4′-fluoro-2-methylpropiophenone (16) were obtained in near-quantitative yield from the appropriate acid chloride similarly, except that the reaction was allowed to age several hours at room temperature before quench to ensure complete acylation. The products **6b, 6c,** and **14** were not distilled. The first two are readily dehydrohalogenated thermally.

Authentic 8 and 9 both came from similar acylation with crotonyl chloride. The crotonophenone **9** was isolated by distillation of a portion of the reaction worked up *before* 4 h heating at 100 °C for cyclization. The 5-fluoro-3-methyl-1-indanone (**8**) was purified by chromatography on SiO_2 (C_6H_6-0.5% MeOH).

4′-Fluoro-2-methylacrylophenone (3b). Methacryloyl chloride (0.4 mol) was added to fluorobenzene (0.8 mol) and $AlCl_3$ (0.6 mol) with stirring at 15–20 °C over 30 min. The temperature was brought to 30 °C for 7 min; then the reaction was quenched and worked up. The yield of **3b** after distillation was 50%. The compound is susceptible to polymerization on long storage.

From the higher boiling residue were identified (by GC–MS and ^1H and ^{19}F NMR) two isomeric acylation–alkylation[25] by-products, 3-(2-fluorophenyl)-4′-fluoro-2-methylpropiophenone and 3-(4-fluorophenyl)-4′-fluoro-2-methylpropiophenone, in a ca. 1:4 ratio, which accompanied every attempt to acylate or directly annelate fluorobenzene with methacryloyl chloride.

2-Chloro-4′-fluoro-2-methylpropiophenone (1c). Warming **16** in 50% excess sulfuryl chloride overnight at 70 °C after the initial gas evolution subsided gave clean and complete α-chlorination. The product was distilled directly and obtained in 96% yield.

Cyclialkylations with $AlCl_3$. We describe one typical kinetic experiment, and record differences from this procedure for other substrates. Half-life data are summarized in Table II.

1b. $AlCl_3$ (1.1 g; 8.25 mmol) was overlayered with 3 ml of CS_2, and to it was added 1.34 g (5.5 mmol) of **1b** rinsed in with 0.8 ml of CS_2. The reaction was stirred magnetically in a 50 °C oil bath under a reflux condenser. Some of the CS_2 did not dissolve in the red oil. We estimated the reactive layer to be above 2 M in substrate. Gas evolution was evident. Samples were taken periodically, quenched on ice, extracted with CS_2 or CH_2Cl_2, and assayed by GC. The GLC area response was generally converted to molar response by applying the measured response factors, or in some cases, through the use of internal standard methods.

1c. The procedure for **1c** had the same molar composition as that for **1b.**

3b. This substrate was run identically with **1b** and **1c.** Another experiment in which CS_2 was replaced by CH_3NO_2 (1 M solution) showed ca. fivefold rate reduction.

6c. One equivalent of substrate was added to 2 equiv of $AlCl_3$ and the mixture stirred in a 100 °C oil bath. It became fluid in a few moments. Aliquot treatment was as above. An experiment with only 1.65 equiv of $AlCl_3$ was distinctly slower, but qualitatively similar.

A 255-mg experiment, $AlCl_3$ ratio 2:1, was quenched after ~50% reaction. The organic extracts were chromatographed on 2 × 1 mm, 20 × 20 cm, SiO_2 plates with C_6H_6–0.5% MeOH. Five bands were removed and eluted as follows (in order of increasing polarity).

Band A: 123 mg; essentially pure **6c** by GLC, TLC, and ^1H NMR.

Band B: 9.6 mg; 80% **9**, and a little overlap material from bands A and C.

Band C: 71.6 mg, which is virtually all indanones **4b** and **8** in a 2.6:1 ratio (GC).

Table III. Physical Constants and Analyses

Compd no.	Bp, °C (mm)	n^tD	Formula	Calcd			Found		
				C	H	Br (Cl)	C	H	Br (Cl)
1b	60–61 (0.2)	1.5365[24]	$C_{10}H_{10}BrFO$	49.00	4.11		49.14	4.25	
1c	57–58 (0.2)	1.5124[24]	$C_{10}H_{10}ClFO$	59.86	5.02		59.79	5.24	
3b	40–42 (0.1)	1.5181[24]	$C_{10}H_9FO$	73.16	5.53		72.93	5.51	
4b	79–80 (0.3)	1.5339[21.5]	$C_{10}H_9FO$	73.16	5.53		73.14	5.80	
6b			$C_{10}H_{10}BrFO$	49.00	4.11	32.6	49.61	4.19	32.08
6c			$C_{10}H_{10}ClFO$	59.86	5.06	(17.67)	59.94	5.14	(17.66)
8			$C_{10}H_9FO$	73.16	5.53		72.62	5.65	
9	27–28[a]		$C_{10}H_9FO$	73.16	5.53		73.13	5.52	
14			$C_{10}H_9Br_2FO$	37.07	2.80	49.33	37.78	2.94	49.33
15	85–87[a]		$C_{10}H_8BrFO$	49.41	3.32		49.29	3.42	
16	43 (0.2)	1.4970[23]	$C_{10}H_{11}FO$	72.27	6.67		72.24	6.57	

[a] Melting point.

Band D: 9.3 mg; the major portion (GC, ^{1}H NMR) is the hydroxybutyrophenone **11.** Traces of less polar materials are seen on re-TLC. It was estimated that if *any* tetralone-like product were present, it would have been less than 0.2% of the entire reaction.

Band E: 20.1 mg, consisted of ca. 80:20 ratio (^{1}H NMR) of **11** and 5-fluoro-2-hydroxy-2-methyl-1-indanone (**17**). This by-product was found in each of the $AlCl_3$ reactions.

6b. Run like **6c** using 2 equiv of $AlCl_3$. The results were qualitatively similar, but nonlinear. A significant fraction of **6b** was rapidly converted to **6c.**

Cyclialkylations with H_2SO_4. One molar solutions were heated at 50 °C and sampled for assay by GC. In the case of **6c**, the yield of **4b** was 92% after 4 h. The following yields were noted with **6b:** after 50% conversion, there was 23% **3b,** 12% **4b,** and 18% **14.** After 4 h, an aliquot showed 65% **4b** and 34% **14.** Accumulation of appreciable amounts of bromoindanone **15** was not observed for several hours.

Preparative layer chromatography on a 2 mm–20 × 20 cm SiO_2 plate (C_6H_6 development) of a 30-h reaction of 250 mg of **6b** gave, in order of increasing polarity 99 mg of **14,** 42 mg of **15,** and 54 mg of **4b.** Small amounts of other nonidentified materials were observed.

"One Pot" Indanone (4b) Synthesis from 1b. The procedure is described in the caption for Figure 1. Similar reactions worked up for product gave yields of distilled **4b** in excess of 90%.

^{13}C NMR Experiment. Portions of reactions mixed as above were transferred to 8-mm NMR tubes for observation. In the case of the solvent-free reactions, CS_2 was added as diluent to each aliquot. Observations were made with a Varian Associates CFT-20 Fourier transform spectrometer with external reference/lock tubes of 3 mm o.d. inserted concentrically. ^{13}C chemical shifts were referenced to external tetramethylsilane (Me_4Si) at ~10 to 25% in $(CD_3)_2CO$ by volume. Air cooling of samples at 15 ft^3/h and limited sample volumes (~0.8 cm^3) resulted in observation temperatures of ~30 °C. Typical signal accumulations were performed for 0.5-h periods with pulse widths equivalent to approximately $\pi/4$ with a 0.5-s repetition rate. Smoothing before Fourier transformation was performed by multiplication of the accumulated free induction decay with the function $\exp[-t/0.4]$. No other apodization was employed.

Semiquantitative analyses of reaction mixtures by ^{13}C NMR have been based upon intensity comparisons for carbon atoms with similar motional characteristics and an equal number of attached protons. Differences in relaxation times and nuclear Overhauser effect enhancements should therefore be negligible. The degree of rf saturation should be quite comparable for CH_2 groups of **3, 4, 6, 8,** and **10,** for example, in accord with our experience in a number of similar cases.

Supplementary Material Available: Tables IV (^{1}H NMR spectra), V (mass spectra), and VI (^{13}C NMR spectra) (6 pages). Ordering information is given on any current masthead page.

References and Notes

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(4) (a) See, for example, G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801–5810 (1969). (b) Cf. J. B. Stothers, *Top. Carbon-13 NMR Spectrosc.*, **1**, Chapter 6 (1974).
(5) G. A. Olah, "Friedel-Crafts Chemistry", Wiley, New York, N.Y., 1973, p 427.
(6) This suggests that "one pot" acylation–cyclization of C_6H_5F with 2-chloro-2-methylpropionyl chloride will give the lesser results which were obtained with methacryloyl chloride, i.e., lower yields due to competitive intermolecular alkylation by intermediate **3b** before all the C_6H_5F is consumed[7] (see the Experimental Section).
(7) D. G. Kundiger and H. Pledger, Jr. [*J. Am. Chem. Soc.*, **78**, 6098–6101 (1956)] have reported a 47% yield of 5-chloro-2-methyl-1-indanone from reaction of chlorobenzene and 2-chloro-2-methylpropionyl chloride.
(8) G. A. Olah, "Friedel-Crafts Chemistry", Wiley, New York, N.Y., 1973, p 41.
(9) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, Chapters 3 and 5.
(10) (a) Our own and prior studies[11] rule out isomerization of **4b.** Both indanones are stable to the reaction conditions used. (b) No such rearrangement occurs with $AlCl_3$-CH_3NO_2 as catalyst. This observation[12a] will be discussed in a future paper.
(11) G. Combaut and L. Giral, *Bull. Soc. Chim. Fr.*, 3710–3714 (1970).
(12) (a) Work in progress in these laboratories. (b) We thank Dr. P. C. Radlick for this suggestion and other stimulating discussion. (c) We are undertaking a labeling experiment which may provide a firm choice of pathways. See also: P. K. G. Hodgson and S. Warren, *J. Chem. Soc. Perkin Trans. 2*, 372–380 (1975), where acyl migration might have occurred in a solvolysis, but did not.
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(14) The reaction of γ-chlorobutyrophenone was mentioned briefly in 1966: A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89–95 (1966).
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(17) But see their formation in sulfuric acid, ref 13.
(18) D. E. Pearson, H. W. Pope, W. W. Hargrove, and W. E. Stamper, *J. Org. Chem.*, **23**, 1412–1419 (1958). In a later paper[19] the requirement of an eight-membered cyclic complex was discounted.
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(20) F. Mayer and P. Müller, *Chem. Ber.*, **60**, 2278–2283 (1927).
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(22) Boiling points are uncorrected. Elemental analyses (Table III) were performed by Mr. J. P. Gilbert and associates of these laboratories. ^{1}H NMR spectra (Table IV) were obtained by Messrs. R. Reamer and R. Zerfing with JEOL (USA) C-60HL and Varian A-60A spectrometers in $CDCl_3$ unless otherwise noted. Mass spectra (Table V) were obtained courtesy of Messrs. J. Smith and H. Flynn with an LKB 9000 or Varian/MAT 111 at 70 eV. For brevity only parts of some spectra are reported. ^{13}C NMR data are presented in Tables I and VI. Tables IV–VI are found in the Supplementary Material (see paragraph at end of article). GLC analyses were performed on a Hewlett Packard 5830A gas chromatograph using thermal conductivity detection. Three columns, a 6 ft × 0.125 in. stainless steel packed with 10% SP2401, a 7 ft × 0.125 in. stainless steel packed with 10% OV-101, and a 20 ft × 0.125 in. stainless steel packed with 10% OV-17, all on 80–100 mesh Supelcoport, were used with helium as the carrier gas. Internal standard methods were used in some experiments to ensure reliability. The "usual workup" involves aqueous washing of the organic solvent solutions followed by magnesium sulfate drying and evaporation to dryness in vacuo. New compounds mentioned in the text, characterized with data, but with no specifically described synthesis were isolated from cyclialkylations by preparative layer chromatography on commercial silica gel plates. Where possible, the characterization data of the new compounds of this work are tabulated for conciseness and ready comparison.

(23) We thank Messrs. N. L. Abramson and W. E. Shearin for assistance with some of the preparations.

(24) GLC data are reported as mole percent unless otherwise indicated.
(25) This problem was noted by E. P. Kohler, *Am. Chem. J.*, **42**, 375–401 (1909).

Competing Photocyclization and Photoenolization of Phenyl α-Diketones

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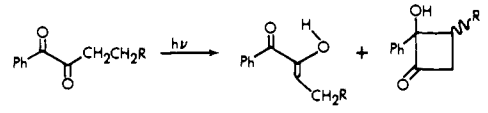
Abstract: The photochemistry of several phenyl alkyl α-diketones has been studied in solution. Photocyclization of 2-phenyl-2-hydroxycyclobutanones competes with photoenolization to 1-phenyl-2-hydroxy-2-alken-1-ones. Both processes compete with phosphorescence, whereas fluorescence quantum yields are independent of the alkyl group. Quantum yields of cyclization are higher in wet acetonitrile than in benzene and increase as the C–H bonds γ to the 1-keto group are made more labile. Cyclization apparently proceeds by the expected γ-hydrogen atom abstraction, exclusively by the 1-keto group, to yield a 1-hydroxy-2-keto-1,4-biradical which cyclizes in high efficiency even in hydrocarbon solvents. Relative reactivities of primary:secondary:tertiary C–H bonds are 1:60:390. Quantum yields and rates of enolization are strongly dependent on the type of C–H bonds α to the 2-keto group, the relative reactivities of primary:secondary:tertiary being 1:1000:300 000. In α-ketovalerophenone, the rate ratio for γ-hydrogen abstraction/enolization is 2.3/1. There is no evidence that photoenolization of these phenyl diketones involves an upper triplet. Photoenolization may involve β-hydrogen abstraction by the 1-keto group to yield an oxyallyl intermediate. It is suggested that the lowest n,π* triplet of these α-diketones has significant zwitterionic character.

Spectroscopists and photochemists have been intrigued by the excited-state behavior of 1,2-diketones for some time. Energies of the long-wavelength n-π* transition of diketones have been correlated with ground-state conformations of the carbonyl groups.[2-5] Although biacetyl and other acyclic aliphatic α-diketones are most stable with trans, coplanar conformations,[5,6] the carbonyl groups of benzil and other phenyl α-diketones are presumably twisted.[2-5] The large Stokes loss observed with the twisted α-diketones has been attributed to major configurational differences between ground and excited states[5] and suggests planar excited states. By analogy to conjugated dienes,[7] diketone triplets have been suggested to exist as nonequilibrating mixtures of cis and trans stereoisomers.[8] The concept of stereoisomeric excited states is consistent with the simple LCAO-MO representation for the lowest excited state of biacetyl.[9] However, a detailed vibrational analysis of the spectra of solid biacetyl indicates that the predicted increase in bond order between the carbonyl carbons does not occur in either the singlet or triplet state.[10] Moreover, photoelectron spectra of α-diketones[11] are now interpreted as demonstrating a large splitting of n orbitals due to through-bond coupling,[12] such that the formally conjugated π orbitals may not interact very strongly.[13]

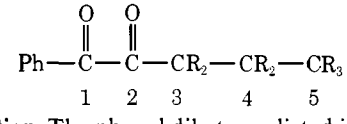
Despite the uncertainty about the nature of its excited states, biacetyl has played a key role in early spectroscopic studies of energy transfer because of its relatively intense phosphorescence in fluid solution.[14] Photoreactions of α-diketones are varied, often paralleling those of monoketones.[15,16] The most important photoreaction of biacetyl in the vapor phase is cleavage of the bond between the carbonyl carbons.[17] In solution, quantum yields for cleavage of biacetyl are considerably reduced.[18] Photoenolization has been observed of biacetyl in the vapor phase[19] and of biacetyl[20] and other aliphatic α-diketones[21] in solution. In a detailed study of the enolization, Lemaire found that the quantum yield is temperature and wavelength dependent.[20] The kinetics for quenching of biacetyl by a variety of substrates in solution have been investigated,[22,23] but quantitative studies of photoreactions of other α-diketones are surprisingly scarce. Aliphatic α-diketones with γ-hydrogens undergo photoinduced 1,5-hydrogen transfer to yield exclusively 2-hydroxycyclobutanones,[24] at the expense of their phosphorescence efficiencies.[25] A kinetic study of this photoreaction has been reported.[26] That suitably substituted aliphatic α-diketones fail to form acylcyclobutanols and do not undergo type II cleavage is one of the most intriguing aspects of their photochemistry.[21,24,27]

Our two laboratories, working independently, have both studied the photocyclization of 1-phenyl-1,2-diones in solution, discovered a competing photoenolization, and communicated our findings separately.[28] In this paper, we report our joint findings in full and attempt to correlate the chemistry with recent advances in the understanding of the spectroscopy of α-dicarbonyls.

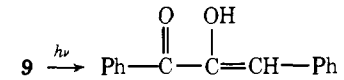


Results

Below is drawn a general structure for the diketones with the carbons numbered to facilitate discussion.



Photoreaction. The phenyl diketones listed in Table I have been studied. Irradiation of diketones with hydrogens on carbon 4, which is γ to the 1-keto group, results in the formation of 2-phenyl-2-hydroxycyclobutanones, as expected.[24] However, the chemical yields vary markedly with structure, ranging from 100% for **8** to 3% for **7**. Although 1-phenyl-4,4-dimethyl-1,2-pentanedione (**6**) and 1,3-diphenyl-1,2-propanedione (**9**) possess no such γ-hydrogens, they also photoreact very efficiently. Vapor phase chromatographic (VPC) analysis of irradiated **6** indicated only one product, which by its spectroscopic and chemical behavior is the enol **10**. Reaction of **10** with bromine leads to formation of the α-bromodiketone **11** and HBr. Under the same conditions diketone **6** itself does not brominate. A brief look at the IR and NMR of the photoproduct from **9** suggests an enol structure. Enol **10** is stable for



days at room temperature in dilute solutions and can be analyzed by VPC with low injector temperatures; but it is reconverted to **6** in a hot (200 °C) VPC injector or by treatment with aqueous acid or base.[29] Infrared and NMR analysis of the