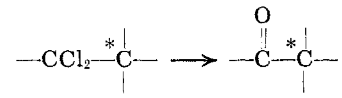
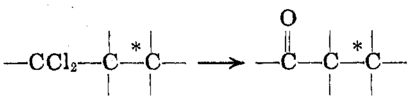
Table XI
Comparison of ^{13}C Chemical Shifts of Carbons Adjacent to a Carbonyl and a Dichloromethylene Group


$-CCl_2-\overset{*}{C}- \longrightarrow -\overset{O}{\overset{\|}{C}}-\overset{*}{C}-$


$-CCl_2-C-\overset{*}{C}- \longrightarrow -\overset{O}{\overset{\|}{C}}-C-\overset{*}{C}-$

Carbon	Δδ, ppm	Carbon	Δδ, ppm
C-1 (**81**)–C-1 (**8**)	+11.2	C-4 (**84**)–C-3 (**16**)	+2.5
C-2 (**85**)–C-3 (**16**)	+16.5		
C-5 (**84**)–C-4 (**16**)	+12.0		
[C-5 (**83**)–C-4 (**16**)]/2[a]	+14.5		
[C-5 (**86**)–C-4 (**16**)]/2[a]	+16.1		

[a] An additive effect is assumed for the two carbonyl groups in compounds **83** and **86**.

14310-17-9; **16**, 706-78-5; **17**, 6317-25-5; **18**, 1128-20-7; **19**, 1680-65-5; **20**, 3424-05-3; **21**, 6928-57-0; **22**, 50565-48-5; **23**, 50565-49-6; **24**, 34004-45-0; **25**, 15725-07-2; **26**, 50565-47-4; **28**, 21703-93-5; **29**, 50565-50-9; **30**, 50565-51-0; **31**, 2626-30-4; **32**, 27376-18-7; **33**, 37820-33-0; **34**, 50558-31-1; **35**, 50558-34-4; **36**, 50479-39-5; **37**, 2227-17-0; **38**, 27425-40-7; **39**, 27425-42-9; **40**, 27425-41-8; **41**, 33234-21-8; **42**, 2626-29-1; **43**, 27425-43-0; **44**, 27396-27-6; **45**, 156-59-2; **46**, 156-60-5; **47**, 79-01-6; **48**, 71-55-6; **49**, 594-89-8; **50**, 3849-33-0; **51**, 21400-41-9; **52**, 695-77-2; **53**, 50565-55-4; **54**, 16177-47-2; **55**, 50565-56-5; **56**, 50565-57-6; **57**, 3389-71-7; **58**, 14446-77-6; **59**, 50565-58-7; **60**, 2440-02-0; **61**, 2439-87-4; **62**, 38672-05-8; **63**, 2439-88-5; **64**, 50565-59-8; **65**, 28021-60-5; **66**, 26770-94-5; **67**, 50565-60-1; **68**, 50565-61-2; **69**, 50565-62-3; **70**, 35960-34-0; **71**, 4659-42-1; **72**, 50565-63-4; **73**, 50565-64-5; **74**, 50565-65-6; **75**, 50565-66-7; **76**, 50479-40-8; **77**, 6914-86-9; **78**, 50565-67-8; **79**, 29272-51-3; **80**, 50565-68-9; **81**, 116-16-5; **82**, 3200-96-2; **83**, 15743-13-2; **84**, 2514-52-5; **85**, 15743-12-1; **86**; 50565-69-0; **87**, 50565-70-3; **88**, 21306-21-8; **89**, 23326-66-1; **90**, 50565-71-4; **91**, 50565-72-5; **92**, 50565-73-6; **94**, 50565-74-7; **95**, 50565-75-8; **96**, 2207-27-4; **97**, 50565-76-9; **98**, 50479-41-9.

References and Notes

(1) (a) Supported by the National Science Foundation, and by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Services. Some of the data in this paper has been reported earlier by V. Mark and E. D. Weil, *J. Org. Chem.*, **36**, 676 (1971). (b) NATO Postdoctoral Fellow, 1970–1972.

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(5) Care should be taken in interpreting integrated signal intensities which might be obtained for cmr spectra measured by the CAT technique with fairly rapid sweeps and high power levels. Under these conditions (which tend to optimize the signal to noise ratios for a given total time of observation), we have found very substantial and disturbing deviations from the predicted integrals on samples of known structure. After considerable hassling over the source of the difficulty, it was finally traced to the relatively long relaxation times of carbon in chlorocarbons which, with rapid sweeps, may not permit return of the equilibrium magnetization between sweeps. We have been able to show with the aid of a program for numerical integration of the Bloch equations developed here by Donald W. Roberts, somewhat along the lines of that described by R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **36**, 1696 (1965), that the first in a rapid series of sweeps gives normal integrals, but further sweeps do not, and, after three or four sweeps, a quasi-equilibrium is set up, which leads to an overall accumulation of signal intensities which may give up to 100% errors in relative signal integrals.

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(10) One obvious exception is the unusual low-field resonance at 75.0 ppm in the spectrum of **17** which we originally assigned to C-6, but which, from the work of J. B. Grutzner, reported by E. T. McBee, E. P. Wesseler, R. Hurnaus, and T. Hodgins, *J. Org. Chem.*, **37**, 1100 (1972), clearly seems to arise from C-2. This shift is some 15 ppm upfield of any other =CCl– cyclopentene carbon resonance we have measured, and it is interesting that no comparable shift occurs in **14**, **20**, **21**, or **22**.

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(17) For an explanation of the notation, see the footnote to Table IV.

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Spectral Comparison of Steric Inhibition of Resonance in Some Hindered *p*-Arylacetophenones as Neutrals and as Gaseous Ions

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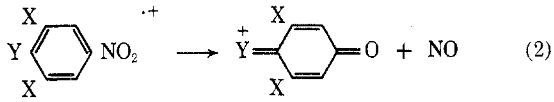
The infrared and ultraviolet absorption spectra of a series of *p*-phenylacetophenones substituted ortho to the aryl–aryl bond indicate steric inhibition of interaction between the rings by the substituent. The mass spectra, within error limits established earlier for multiple substitution, indicate that steric inhibition of resonance is not important in the ions.

The remarkable correlation of ion intensities in the mass spectra of acylbenzenes with Hammett σ constants[1] is probably the result of a correlation of onset potentials for formation of the pertinent ions unobscured by the various factors which cannot be correlated by such constants and which apparently are unimportant in the acylbenzenes.[2] Ion intensities in these systems, then, serve in the general case as an empirical gauge of ion energetics for processes associated with their formation.[3]

One of the poorest correspondences between solution behavior and mass spectral behavior is found for the *p*-phenyl substituent.[1] The ion abundances for the reactant and product in eq 1 have a ratio suggesting, on comparison with similar reactions in other acylbenzenes, that the *p*-phenyl substituent is more electron donating in this sort of cleavage than it is in the dissociation of *p*-phenylbenzoic acid in water, the reaction which defines the Hammett substituent constant. It was suggested[1] that the origin of this behavior might be the same as that of the increased electron donation by the *p*-phenyl substituent in solution reactions when electron demand on the reaction center is high: variable response of the *p*-phenyl substituent as the requirement for resonance stabilization becomes more important and overcomes repulsion between ortho hydrogen atoms of the two rings.[4,5]

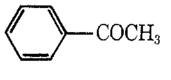
$$p\text{-}C_6H_5C_6H_4COC_6H_5^{\cdot +} \longrightarrow C_6H_5CO^+ + C_{12}H_9\cdot \qquad (1)$$

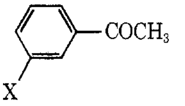
A comparison of the energetics of rotation about the bond between the two aromatic rings in *p*-phenylacetophenone and 2-fluoro-4′-acetylbiphenyl, as calculated by the semiempirical INDO method, reinforces this view.[6] In the molecular ion as compared to the neutral compound, there is a lower energy barrier to rotation and the ion can assume a more nearly planar configuration. Consideration of the likely energy distribution in *p*-arylacetophenones[6] suggests that the most important factor governing ion abundances in these compounds is again onset potentials, as in the general case, and not some peculiarity of the internal energy distribution of the ion. The problem can therefore be discussed in terms of activation energies.

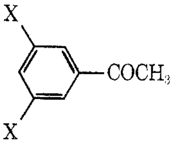

(2)

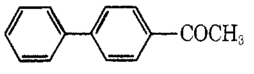
Empirical observations of effects on ion abundances consistent with steric inhibition of resonance have been made in the mass spectra of nitrobenzenes.[7,8] The process in eq 2 is important when Y is small or when X is hydrogen, but, for the special combination when Y is as large as dimethylamino and X is as large as the chloro, bromo, or methyl substituents, eq 2 is only of slight importance. We thought it important to determine, therefore, whether in this same fashion blocking groups on either side of a *p*-phenyl substituent could influence the reactivity of this group in a process where substituent effects can be monitored successfully, *viz.*, cleavage of acylbenzenes. Studies of the effect of multiple substitution in acylbenzenes have shown that multiple substitution in the absence of steric interaction gives an additive substituent effect for this cleavage.[9] Deviations from additivity then could be ascribed to steric interactions, provided that they are qualitatively consistent with such an interpretation and that they are not so small as to be ambiguous. The size of the deviation to be considered significant has been discussed.[9]

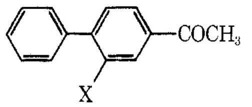
Accordingly, the following scheme for comparison of substituent effects was proposed. The compounds I-IV form the set to which the more highly substituted compounds can be compared. Compounds V and VI may be compared with II and IV and III and IV, respectively. If substituent effects are additive, as they are when there is no chance for steric interaction in other model systems,[9] then there is no steric interaction in compounds V and VI; on the other hand, substantial deviation from strict additivity compatible with the reduction of the substituent effect found in IV will indicate steric interaction. Within rather wide limits[9] it may be possible, if the latter case obtains, to evaluate the effective size of the blocking groups X in V and VI. Compounds VII and VIII do not have immediately obvious model compounds with which they can be compared. However, the electronic effect of blocking groups so far removed from the reaction site (*i.e.*, the ring C–acyl C bond) is expected to be less than it is in II and III and might be sufficiently small that it can be ignored within the error limit expected, 0.12 log unit or twice the standard deviation of model systems.[9] Another estimate of the small effect of a halogen substituent in this position can be gained from the INDO charge distribution in the molecular ions of IV and 2-fluoro-4′-acetylbiphenyl (VI, X = F).[6]

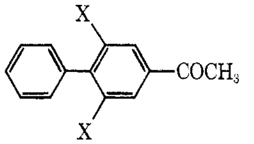

I

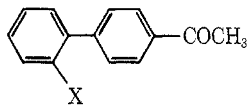

IIa, X = Cl
b, X = Br

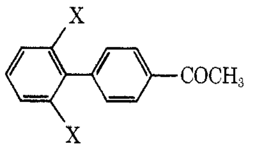

IIIa, X = Cl
b, X = Br


IV


Va, X = Cl
b, X = Br


VIa, X = Cl
b, X = Br


VIIa, X = Cl
b, X = Br


VIIIa, X = Cl
b, X = Br

In any case, many of these are new compounds and it is advisable to have experimental data for the neutral molecules with which the mass spectral data can be compared. We report here the carbonyl stretching frequencies in the infrared spectra of I-VIII and ultraviolet data as measures of the behavior of the neutral molecules.

Some of the compounds were prepared by Friedel-Crafts acetylation of substituted biphenyls. The others had to be prepared by a longer route usually involving an unsymmetrical Ullmann coupling of a *p*-halobenzoate ester and a halobenzene with nitro groups adjacent to halogens, conversion of nitro groups to halogens, and conversion of the methoxycarbonyl group to the acetyl group.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Satisfactory combustion analyses were obtained for all new compounds (Va, Vb, VIa, VIIa, VIIb, VIIIa, VIIIb, IX, X, XII, XIII, XIV, XVI, XVII, XVIII, XX) except VIb, whose high- and low-resolution mass spectra indicated no impurities.

Spectra. Infrared carbonyl stretching frequencies were measured on a Perkin-Elmer 267 grating spectrophotometer and calibrated against polystyrene. A matched set of 1.0-mm NaCl cells was used; the solvent was CCl_4. Ultraviolet spectra were obtained on a Cary 14 instrument with hexane as solvent in 1-cm cells. Proton magnetic resonance spectra (for confirmation of substitution patterns) were obtained on a JEOLCO C-60 HL spectrometer with tetramethylsilane as standard. Low-resolution mass spectra were obtained on a Hitachi RMU-6E single-focusing instrument using 75-eV electrons (emission current 80 μA). The source pressure was always in the range 5–10 × 10^{-7} Torr; the source temperature was 185 ± 5°. Four replicate determinations gave a reproducibility of at least 3%; day-to-day variation was <5%. High-resolution mass spectra (for analysis of composition and inspection for interfering fragment ions) were obtained on an MS902 instrument at the Research Triangle Center for Mass Spectrometry, supported by a grant from the Biotechnology Resources Branch of the Division of Research of the National Institutes of Health (RR-330).

Purification. Gas–liquid chromatography was performed on a Perkin-Elmer 900 gas chromatograph using a 4 ft × 0.25 in. stainless steel column packed with 3.8% OV-17 on AWS Chromosorb W support at temperatures from 140 to 220°. Collected peaks were chromatographed on Mallinckrodt ChromAR sheet 500 and ChromAR sheet 1000 with hexane as eluting solvent, using long- and short-wavelength ultraviolet lamps for detection. Peaks deemed singular were submitted for high-resolution mass spectral analysis.

Synthesis. 2-Chloro-4′-acetylbiphenyl (VIIa). This compound was prepared by a Friedel–Crafts reaction of acetyl chloride (3.1 g, 40 mmol) and 2-chlorobiphenyl (7.4 g, 40 mmol) in the presence of $AlCl_3$ (5.8 g, 44 mmol) in 100 ml of CS_2. After 2 hr most solvent was distilled and the mixture was poured on ice–concentrated HCl (100 g/10 g); this mixture and washing were extracted with benzene and the benzene solution was washed with H_2O, 10% NaOH, and H_2O, dried, and treated with charcoal, yield 6.5 g (72%), mp (from MeOH) 48–51°.

Anal. Calcd for $C_{14}H_{11}ClO$: monoisotopic mol wt, 230.0498. Found: 230.0503.

2-Bromo-4′-acetylbiphenyl (VIIb). This was prepared similarly to VIIa in 69% yield, mp (from MeOH) 92–95°.

Anal. Calcd for $C_{14}H_{11}BrO$: monoisotopic mol wt, 273.9993. Found: 273.9996.

Methyl 3-Nitro-4-phenylbenzoate (IX). A reaction mixture of methyl 3-nitro-4-bromobenzoate (5.18 g, 20 mmol), iodobenzene (9.8 g, 20 mmol), and copper bronze (2.4 g) was heated under a slight positive pressure of Ar at 190–195° for 7 hr, and the excess iodobenzene was distilled. The residue was extracted with benzene and the extract was chromatographed on activity I alumina with benzene; the combined yellow eluate yielded 5.03 g (98%) of product, mp 91–92°.

Anal. Calcd for $C_{14}H_{11}NO_4$: monoisotopic mol wt, 257.0688. Found: 257.0683.

Methyl 3-Chloro-4-phenylbenzoate (X). The reduction of IX (2.57 g, 10 mmol) with 10% Pd/C (0.2 g) in ethyl acetate–acetic acid (20 ml/15 ml) under 55–60 psi H_2 in a Parr apparatus for 8 hr gave 2.27 g of oily methyl 3-amino-4-phenylbenzoate (XI) after filtering, extraction of Pd/C with benzene, washing with $NaHCO_3$, drying, and evaporation. The amine (1.13 g, 5 mmol) was used directly in 60 ml of HCl (6 *N*) to generate the diazonium ion with $NaNO_2$ (0.35 g in 5 ml of water). After addition of CuCl (0.8 g) in HCl (concentrated, 5 ml) the mixture was vigorously stirred for 1 hr, warmed to 60° on the steam bath, poured into 100 ml of ice water, and stirred for 1 hr. The precipitate was filtered, washed, dried *in vacuo*, dissolved in benzene, and treated with charcoal to give product (57%).

2-Chloro-4-acetylbiphenyl (Va). This was prepared from X by the method of Corey and Durst[10] using the dianion of methanesulfin-*p*-toluidide at −78°. After decomposition with water, the sample was extracted with ether and washed with HCl, $NaHCO_3$, and NaCl solution. Drying over $MgSO_4$ and evaporation yielded an uncrystallizable oil purified by tlc, then glc.

Anal. Calcd for $C_{14}H_{11}ClO$: monoisotopic mol wt, 230.0498. Found: 230.0501.

Methyl 3-Bromo-4-phenylbenzoate (XII). A solution of XI (1.13 g, 5 mmol) in 24% HBr (30 ml) was diazotized at 0–5° by slow addition of $NaNO_2$ (0.35 g in 5 ml of water), and CuBr (1.15 g in 5 ml of 48% HBr) was added. The mixture was stirred for 1 hr, heated to 60°, poured into ice water, and stirred for 1 hr; the solid was filtered, washed with water, dried, dissolved in benzene, and treated with charcoal to give product (0.76 g).

2-Bromo-4-acetylbiphenyl (Vb). This was prepared from XII by the method of Corey and Durst[10] and worked up as in the preparation of Va; the product before chromatographic purification was treated with Girard T reagent to remove a small amount of unreacted XII. An uncrystallizable oil was finally obtained and purified by tlc, then glc.

Anal. Calcd for $C_{14}H_{11}BrO$: monoisotopic mol wt, 273.9993. Found: 273.9996.

Methyl *p*-(2,6-Dinitrophenyl)benzoate (XIII). Under a slight positive pressure of Ar, 2,6-dinitrochlorobenzene (2.02 g, 10 mmol), methyl *p*-iodobenzoate (2.88 g, 11 mmol), and copper bronze (5 g) were heated with stirring for 4 hr at 195–200°. After cooling and extracting with hot benzene, the solution was concentrated and chromatographed on activity I alumina with benzene until the eluent was no longer yellow. Evaporation and recrystallization from methanol gave 2.05 g (68%) of product, mp 127–128°.

Anal. Calcd for $C_{14}H_{10}N_2O_6$: monoisotopic mol wt, 302.0538. Found: 302.0532.

Methyl *p*-(2,6-Dichlorophenyl)benzoate (XIV). The reduction of XIII (4.06 g, 13.4 mmol) with 10% Pd/C (0.4 g) in ethyl acetate–acetic acid (40 ml/20 ml) under 55–60 psi H_2 for 20 hr in a Parr apparatus gave crude methyl *p*-(2,6-diaminophenyl)benzoate (XV), which was isolated by addition of 100 ml of benzene, filtering, washing three times with $NaHCO_3$, drying over $MgSO_4$, and flash evaporation. The oil (3.24 g, 100%) was used directly in further steps; 1.27 g (5.25 mmol) of the oil in acetic acid (25 ml) was added to $NaNO_2$ (0.85 g) in H_2SO_4 (8.5 ml). The temperature was kept below 30° during and for 1 hr after addition. The solution was poured slowly into a stirred solution of CuCl (1.08 g, 10.8 mmol) in HCl (concentrated, 10 ml) and stirred for 1 hr. After pouring on ice and letting stand for 2 hr, the solid was filtered, washed, dried, dissolved in benzene, treated with charcoal, and recovered by stripping solvent to give an uncrystallizable product (0.98 g, 67% theory).

Anal. Calcd for $C_{14}H_{10}Cl_2O_2$: monoisotopic mol wt, 280.0058. Found: 280.0064.

2′,6′-Dichloro-4-acetylbiphenyl (VIIIa). This was prepared from XIV by a procedure similar to that for preparing Vb; Girard T treatment was again used, and the final product was purified by tlc and glc, mp 48–51°.

Anal. Calcd for $C_{14}H_{10}Cl_2O$: monoisotopic mol wt, 264.0109. Found: 264.0109.

Methyl *p*-(2,6-Dibromophenyl)benzoate (XVI). This material was prepared from XV (3.2 g, 13 mmol) by a procedure similar to that for the preparation of XIV. Chromatography of the product on activity I alumina with benzene gave 0.73 g (15%) of product as an oil which could not be crystallized.

Anal. Calcd for $C_{14}H_{10}Br_2O_2$: monoisotopic mol wt, 367.9049. Found: 367.9045.

2′,6′-Dibromo-4-acetylbiphenyl (VIIIb). This was prepared from XVI by a procedure similar to that for preparing Vb; Girard T treatment was again used. The final product was purified by glc to give a colorless oil.

Anal. Calcd for $C_{14}H_{10}Br_2O$: monoisotopic mol wt, 351.9097. Found: 351.9094.

Methyl 3,5-Dinitro-4-phenylbenzoate (XVII). After flushing with Ar, methyl 3,5-dinitro-4-bromobenzoate (13.0 g, 50 mmol), iodobenzene (28.7 g, 140 mmol), and copper bronze (10 g) were heated at 195–200° for 5 hr. Excess iodobenzene was vacuum distilled and the residue was extracted with hot benzene; this benzene solution was filtered, treated with charcoal, and chromatographed on activity I alumina with benzene until the eluate was no longer yellow, yield 14.9 g (98%), mp 149–150° (from methanol).

Anal. Calcd for $C_{14}H_{10}N_2O_6$: monoisotopic mol wt, 302.0538. Found: 302.0535.

Methyl 3,5-Dichloro-4-phenylbenzoate (XVIII). The reduction of XVII (15.1 g, 50 mmol) with 10% Pd/C (0.57 g) in ethyl acetate–acetic acid (70 ml/35 ml) under 35–40 psi H_2 for 8 hr in a Parr apparatus gave crude methyl 3,5-diamino-4-phenylbenzoate (XIX), which was purified as XV was. This reaction was exothermic to the extent that the hydrogenation was stopped after the first 20 min for 1 hr, then resumed. The product (12.0 g, 99%) was an oil used directly in following steps. The preparation of XVIII from XIX was similar to that of XIV, yield 15%, mp 134–135°.

Anal. Calcd for $C_{14}H_{10}Cl_2O_2$: monoisotopic mol wt, 280.0058. Found: 280.0061.

2,6-Dichloro-4-acetylbiphenyl (VIa). This was prepared from XVIII by a procedure similar to that for preparing Va. A yellow oil was obtained, which was purified by glc, yield 54%.

Anal. Calcd for $C_{14}H_{10}Cl_2O$: monoisotopic mol wt, 264.0109. Found: 264.0111.

Methyl 3,5-Dibromo-4-phenylbenzoate (XX). The preparation of XX was similar to that of XIV, using a solution of CuBr in 48% HBr, yield 19%, mp 108–109°.

Anal. Calcd for $C_{14}H_{10}Br_2O_2$: monoisotopic mol wt, 367.9049.

Table I
Infrared, Ultraviolet, and Mass Spectral Data for Substituted p-Arylacetophenones and Related Compounds

Compd[a]	ν_{CO}, cm^{-1}	λ_{max}, nm[b]	ϵ_{max}	$[CH_3CO^+]/[M\cdot^+]$[c]	Log Z/Z_0
I	1692	278	1100	0.36	0
IIa (m-Cl)	1694	288	1.2×10^3	0.63	+0.24
IIb (m-Br)	1694	288	8.8×10^2	0.69	+0.28
IIIa (3,5-Cl_2)	1699, 1703	296	7.9×10^2	0.88	+0.34
IIIb (3,5-Br_2)	1698	297	1.8×10^3	1.10	+0.49
IV (p-Ph)	1689	276	2.3×10^4	0.18	−0.30
Va (3-Cl-4-Ph)	1694	268	2.0×10^4	0.35	−0.02
Vb (3-Br-4-Ph)	1692	266	1.2×10^4	0.43	+0.07
VIa (3,5-Cl_2-4-Ph)	1698	257	7.9×10^3	0.47	+0.11
VIb (3,5-Br_2-4-Ph)	1699	256	6.0×10^3	0.51	+0.15
VIIa [p-(2-ClPh)]	1691	261	1.6×10^4	0.28	−0.11
VIIb [p-(2-BrPh)]	1691	261	1.6×10^4	0.45	+0.09
VIIIa [p-(2,6-Cl_2Ph)]	1692	250	1.2×10^4	0.56	+0.19
VIIb [p-(2,6-Br_2Ph)]	1692	249	1.7×10^4	0.62	+0.23

[a] Numbered as a derivative of acetophenone for easy comparison. [b] For the longest wavelength transition. [c] $[CH_3CO^+]/[M\cdot^+] = Z$ for this study.

Found: 367.9054.

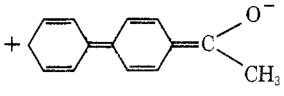
2,6-Dibromo-4-acetylbiphenyl (VIb). This was prepared from XX by a procedure similar to that for preparing Vb, using Girard T reagent, tlc and glc to yield an oil (64%).

Anal. Calcd for $C_{14}H_{10}Br_2O$: monoisotopic mol wt, 351.9097. Found: 351.9094.

Observed Halogen Exchange between Methyl 3-Nitro-4-bromobenzoate and Iodobenzene under Ullmann Conditions. A mixture of methyl 3-nitro-4-bromobenzoate (15.5 g, 60 mmol), iodobenzene (31.7 g, 156 mmol), and copper bronze (5.0 g) was heated under a slight positive pressure of Ar at 190–195° for 6 hr, at which time a large m/e 307 peak was observed in the mass spectrum of the crude reaction mixture; heating for an additional 3 hr increased the intensity of this peak relative to that of the starting materials' parent ions. On addition of 5.0 g more of copper bronze and heating at 190–195° for 6 hr, the peak at m/e 307 disappeared from the spectrum of the crude product, and on work-up a sample of IX (95% yield) was obtained whose mixture melting point with a sample of IX prepared by the previous route was undepressed.

Results and Discussion

The spectral data for compounds I–VIII are given in Table I. For the most part, the infrared stretching frequencies of the carbonyl group exhibit the trends expected within this series. For the exceptions, the errors are just outside the reproducibility of the data. A correlation is known[11] to exist between the carbonyl stretching frequencies of aromatic ketones and Hammett σ constants, and the data for compounds I, II, and IV bear out this correlation (for m-Cl, $\sigma = +0.37$; for m-Br, $\sigma = +0.39$; for p-Ph, $\sigma = -0.01$ and $\sigma^+ = -0.17$). Beyond this, a further shift to greater frequency is seen in the doubly substituted compounds IIIa and IIIb. If we compare the effect of the steric blocking of phenyl by adjacent halogen, and take as our basis the shift between IV and I, then we should compare the shift between V and II and the shift between VI and III. While the shift between IV and I is only 3 cm^{-1}, there is essentially no shift between V and II or VI and III, overall. This observation seems consistent with the interpretation of the shift in IV as a result of interactions of the type



which would be decreased by twisting of the biphenyl system when there are blocking groups in the ortho positions. In such cases, the effect of the phenyl group becomes small, so that the major electronic influence on the carbonyl frequency is that of the electron-withdrawing halogens.

There is no obvious model for gauging the interactions in the compounds with substituents in the far rings, VII and VIII. Since disubstitution (VIII) produces only a small shift from monosubstitution (VII), we may estimate that this increase is additive and a measure of the effect of going from no to one as well as from one to two halogens. We can calculate, then, that the hypothetical frequency of a nonresonating phenyl group is $\nu_{VII} - (\nu_{VIII} - \nu_{VII})$, or 1691 − 1, or 1690 cm^{-1}. More significantly, we have a gauge of the effect of substitution in the distant phenyl ring. Comparison of the shifts in VII and V, and of the shifts in VIII and VI, from the frequency of I shows that the interaction of the halogen with the carbonyl group in VII and VIII is very much damped. Assuming that the greatest portion of this interaction is inductive because of the twisting between rings which removes resonance interaction, we note that the damping is consonant with damping off of inductive effects through bonds as one moves further from the reactive center.

The ultraviolet data also exhibit a trend supporting the intervention of steric inhibition by blocking halogen atoms. As an example, let us assume that the dihedral angle between the rings in solution is the same as that found for biphenyl in heptane solution, 23°.[12] Examination of the ultraviolet spectra of II, III, chlorobenzene, bromobenzene, m-dichlorobenzene, and m-dibromobenzene shows no significant absorption (*i.e.*, no more than 3% of ϵ_{max}) at λ_{max} of the appropriate compound in Table I for which it would serve as a model of a locally excited state. Hence, the absorption at λ_{max} is due entirely or essentially entirely to the transition involving a molecule-encompassing orbital. Further evidence for this is given by the comparison of the spectra of I and IV. Finally, the influence of halogen on ϵ_{max} is small in compounds II, compared to I, and we extrapolate to hypothesize that the important effect of halogen on ϵ_{max} in compounds V–VIII is its influence on the dihedral angle θ, where it influences the absorptivity by the relation[13]

$$\cos^2 \theta = \epsilon/\epsilon_0 \qquad (3)$$

where ϵ_0 is the molar absorptivity of hypothetical planar reference compound, taken here as planar IV. Taking this reference as the reference compound for all members of the series IV–VIII for the reasons cited above, we may calculate the dihedral angle θ in each compound. These values are given in Table II. For the most part, the data follow a trend of increasing angle with increasing steric interference, as expected. Deviations from the trend proba-

Table II
Values of the Dihedral Angle θ between the Aryl Rings of Substituted *p*-Arylacetophenones

Compd[a]	θ, deg
IV (*p*-Ph)	23
Va (3-Cl-4-Ph)	31
Vb (3-Br-4-Ph)	48
VIa (3,5-Cl_2-4-Ph)	57
VIb (3,5-Br_2-4-Ph)	62
VIIa [*p*-(2-ClPh)]	40
VIIb [*p*-(2-BrPh)]	40
VIIIa [*p*-(2,6-Cl_2Ph)]	48
VIIIb (*p*-(2,6-Br_2Ph)]	38

[a] Numbered as a derivative of acetophenone for easy comparison.

bly reflect the poorness of the assumptions and seem to be greater for the compounds substituted in the further ring.

The energy of the transition also increases in a steady fashion as the bulk of the blocking substituents increases, as inspection of the values of λ_{max} in Table I shows. This is less amenable to simple quantitative interpretation, but points to decreased interaction between rings in the blocked compounds as well.

Thus, both the infrared and the ultraviolet spectra of these compounds in solution point to steric inhibition of resonance by bulky substituents at the position adjacent to the bond between the rings.

The Z/Z_0 values from the mass spectra of the multiply substituted acetophenones (Table I) are estimated remarkably well by Z/Z_0 values calculated on the basis of additive effects of individual substituents. Thus, the value for Va, -0.02, is close to the value calculated from IIa and IV, -0.06; that for Vb, $+0.07$, is fairly close to the calculated value based on IIb and IV, -0.02. For the disubstituted compounds, VIa and VIb, the observed values of Z/Z_0 are $+0.11$ and $+0.15$, and the calculated values are $+0.04$ and $+0.19$. We estimate that removal of the resonance interaction would have reduced the value of the *p*-phenyl constituent of Z/Z_0 to $\rho\sigma = -0.01$, where ρ is taken from the earlier correlations of singly and multiply substituted compounds[1,9] and σ is taken from solution data for the *p*-phenyl substituent (it is the Hammett σ constant). Therefore, a set of calculated values nearly the same as the Z/Z_0 values of II and III would be predicted by the model in which interaction is similar to that in solution. This is clearly not the case. The data are much closer to the model in which effects are additive, and in fact we cannot distinguish between the experimental results and this model on the basis of the expected error level.[9]

There are no suitable models for the compounds substituted in the further ring, VII and VIII. The effects of substituents in VII and VIII generally appear to be similar to those in V and VI when the compounds are examined as a class.

The additivity of substituent effects in V and VI suggests that there are no important substituent interactions in these compounds. Thus, in the ion, hydrogen-chlorine and hydrogen-bromine interactions are not sufficient to remove the usual resonance effect of the *p*-phenyl group, and even more bulky blocking groups must be sought if one wishes to find evidence for twisting of the aryl rings.

While these results are unusual, they are not totally unexpected. Molecular orbital calculations indicate a reduced energy barrier to rotation in the *p*-arylacetophenone system when the molecule is ionized.[6] One previous study of hindrance of the *p*-dimethylamino group in acylbenzene ions also led to results indistinguishable from those calculated on the basis of additivity.[14] It is not clear why this latter functional group can be blocked by adjacent halogen in the nitrobenzene molecular ion,[7,8] and further studies of this class of compounds is underway.

It is appropriate now to add a few remarks derived from a deeper consideration of substituent effects.[2] Suppose, first, that the halogen substituent led to decreased interaction between the rings. The number of free rotors will be less in the ion. However, in the activated complex for acetyl ion formation, there will be less demand on the substituent for planarity with the reactive center, and the number of free rotors will increase. The *increase* for the substituted, hindered case will be less than the increase for the unhindered case. Then $k(E)$ will rise more abruptly with internal energy, producing a larger fragment ion current than a model ignoring this effect would predict. We do not observe an excess of fragment ion in the substituted compounds; so this model can be rejected as an influence or intensity. If we suppose that the halogen has no influence on the number of free rotors, as we do when we claim no change in interaction between substituents in the halogenated *p*-arylacetophenones, then the rate of rise of $k(E)$ in the halogenated and the model compound is similar and ion intensities may be correlated by the rule we observe to draw conclusions about the onset potential difference (activation energy).

Consider also the effect of a halogen substituent on the shape of the energy distribution in molecular ions. In many aromatic systems a band is found at 11.2 or 11.7 eV corresponding to ionization of lone-pair electrons of bromine or chlorine, respectively.[15] However, the appearance potential of $C_6H_5CO^+$ in acetophenone is 10.45 eV,[16] and the appearance potential of CH_3CO^+ is higher. Therefore, if contributions to ion intensity from the lone-pair band have an appreciable effect, they will raise $[CH_3CO^+]$, or the intensity of some other fragment, but not the intensity of the molecular ion; Z/Z_0 can be raised but not lowered. Again, since we do not observe an excess of fragment ion, this effect cannot be important.

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Registry No.—I, 98-86-2; IIa, 99-02-5; IIb, 2142-63-4; IIIa, 14401-72-0; IIIb, 14401-73-1; IV, 92-91-1; Va, 6908-81-2; Vb, 50987-24-1; VIa, 50987-25-2; VIb, 50987-26-3; VIIa, 3808-89-7; VIIb, 3808-91-1; VIIIa, 50987-27-4; VIIIb, 50987-28-5; IX, 39180-36-4; X, 50987-29-6; XI, 39180-37-5; XII, 50987-30-9; XIII, 50987-31-0; XIV, 50987-32-1; XV, 50987-33-2; XVI, 50987-34-3; XVII, 50987-35-4; XVIII, 50987-36-5; XX, 50987-37-6; acetyl chloride, 75-36-5; 2-chlorobiphenyl, 2051-60-7; methyl 3-nitro-4-bromobenzoate, 2363-16-8; iodobenzene, 591-50-4; 2,6-dinitrochlorobenzene, 606-21-3; methyl *p*-iodobenzoate, 619-44-3; methyl 3,5-dinitro-4-bromobenzoate, 23938-86-5.

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Infrared Studies of Anion Radicals. IV. Diketones[1a]

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The reduction of *o*-dibenzoylbenzene (II), *o*-dipentamethylbenzene (III), and benzil (IV) by sodium in THF were studied by ir in NaCl cavity cells. Two reduction stages were observed in each, the first containing an unreduced and apparently unchelated ketone; the second showed ketyl-like absorptions near 1520–1590 cm^{-1} [as compared with benzophenone (I) ketyl]. The latter are probably chelated species. Fully reduced III showed a characteristic C=C stretch at 1610 cm^{-1}.

Recent progress in the development of methods of studying anion radicals by infrared spectroscopy has provided a probe by which considerable information may be obtained concerning the nature of anion radicals.[1] This report is concerned with the infrared shifts observed in some diketones upon metal reduction. The advantage of ir in this area is the ability to observe some structure regardless of the diamagnetic or paramagnetic species formed. In addition, some correlation can be made with results from epr and other structural analyses in determining the species under observation.

The shifts observed are those of ketone and aryl absorptions in the 1800–1500-cm^{-1} range. With each compound in this work we find at least two absorptions occurring in this region, and, since these tend to shift about somewhat irregularly, we will not be concerned with their exact assignment, but rather with the general aspects of the spectra.

Reduction to the weakly ion-paired ketyl has been shown to have two effects in this region of the ir. First, weakening of the carbonyl bond to something more like a bond and a half lowers the normal ketone frequency about 100 cm^{-1} to around 1550 cm^{-1} (*e.g.*, see benzophenone, Figure 1[2] and Table I). Second, the aromatic 1600 cm^{-1} region vibrations are also "loosened" by the presence of the antibonding electron of the anion (or dianion) and are thrown down to approximately the same region, *i.e.*, the 1500's (see paper II of this series).

Experimental Section

Reductions were performed in sealed tubes by sodium metal mirrors in THF or DME solvent, by standard methods previously described.[1a] Perkin-Elmer 621 and 21 ir instruments were used for measurements, and concentrations required were about 5 ± 5 × 10^{-2} *M*. For low-temperature observations, a cold box was constructed of polystyrene foam using double KBr windows for insulation and pure solvent reference cells. Heat removal was effected by use of a coil of copper tubing into which was pulled liquid nitrogen (by means of an air pump) until the internal temperature desired was reached. Temperatures were measured by a thermocouple. Spectra tracings and apparatus diagrams are available in the microfilm edition. See paragraph at end of paper regarding supplementary material.

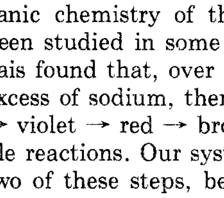
Results and Discussion

Benzophenone (I). This ketone was used as standard for comparison of the ir shift in the 1500–1900-cm^{-1} region as a known ketone → ketyl reaction. The ir shifts of the diketones upon reduction are shown in Table I. The reduction stages were followed by prominent changes in color. These changes are noted and generally conform to previously observed species, though not always structurally known ones. Several of the absorptions recorded did not lend themselves to interpretation, largely because at this stage of our knowledge of the ir of anion radicals we simply do not have enough data on charge-bearing species.

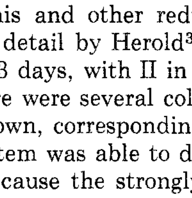
***o*-Dibenzoylbenzene (II).** The first conspicuous color change was to orange in the Na–DME reduction. The organic chemistry of this and other reduction species has been studied in some detail by Herold[3] and Novais.[4] Novais found that, over 3 days, with II in the presence of an excess of sodium, there were several color changes, orange → violet → red → brown, corresponding to several probable reactions. Our system was able to detect only the first two of these steps, because the strongly alkaline solution tends to erode both the salt cell and the epoxy glue fixing it to the Pyrex tube.

The first observable reduction stage of II gives several absorptions in the 1500–1900-cm^{-1} range which are attributed to at least one unreduced carbonyl group. This group is under considerable electron withdrawal resulting in absorptions (1805 and 1735 cm^{-1}) which are not characteristic of known ketyls like benzophenone. One possible structure for this species could be that of the singly reduced IIa, probably not chelated.

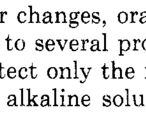
The second stage of reduction exhibits ir absorptions which are almost exactly those of benzophenone ketyl. For this reason the species may possibly be that of the chelate IIb or the intermediate IIc proposed by Novais.[4] With the present information we are not in a position to distinguish between these two possibilities; however, it is certain that there is no unreduced carbonyl present.



IIa



IIb



IIc

***o*-Dipentamethylbenzoylbenzene (III).** The highly sterically hindered structure of III forces it to undergo a somewhat different route from II in its reduction stages. Epr studies conducted on this diketone[5] show the color changes to be yellow (no epr spectra made) → brown (paramagnetic) → orange (diamagnetic). The final reduc-