gives 100% addition with benzophenone also gives the smallest pseudo-first-order rate constants at comparable Grignard reagent concentrations.

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Chromium Atoms in Organometallic Synthesis

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Abstract: Cocondensation of atomic chromium vapor with organic substrates at $-196°$ at pressures below 10^{-4} Torr yields organochromium complexes. It is possible to synthesize not only bis(cyclopentadienyl)chromium, but also bis(arene)chromium compounds in which the arenes contain highly electronegative substituents. Chromium atoms trimerize acetylenes to benzenes, isomerize 1-butene to a mixture of 2-butenes, and also form complexes with 1,3-butadiene and with propene. The mode of complexation in the latter two cases has been investigated by deuterolysis studies.

The use of high-temperature species as synthetic reagents has been developed over the past decade,[1] and some areas within this field have been reviewed.[2,3] The use of transition metal atoms is of much more recent vintage and has allowed the direct synthesis of a number of organometallic complexes, previous routes to which were cumbersome.[4,5] Furthermore, it has proved possible to isolate at low temperatures several interesting and unstable compounds whose existence had only been inferred through mechanistic studies.[6,7]

Chromium vapor, generated from a resistively heated crucible in an evacuated apparatus similar to that used for the reactions of carbon vapor,[1] is predominantly monoatomic. The chromium atoms thus produced, when cocondensed with a variety of unsaturated hydrocarbons at $-196°$, react to yield isolable organochromium complexes.

Sandwich Compounds. Cocondensation of chromium atoms with an excess of cyclopentadiene monomer yields, after removal of the excess substrate, volatile red crystals of chromocene, which was identified by its mass spectrum and melting point.

Arenes react with chromium atoms to give good yields of bis(arene)chromium complexes. Bis(benzene)chromium had previously been synthesized directly in this manner,[4] but the scope of the reaction has now been extended to include not only bis(alkylbenzene)chromium but also bis(halobenzene)chromium compounds. Conventional methods of making bis(arene)chromium complexes fail when the arene possesses a strongly electron-withdrawing substituent, presumably attributable to the low π-electron density of the aromatic ring.[8] Nevertheless, using the cocondensation procedure chlorobenzene, fluorobenzene, and even *p*-difluorobenzene successfully formed bis(arene)chromium compounds. Tetrafluorobenzene failed to yield a compound thermally stable at room temperature.

The bis(alkylbenzene)chromium compounds are sufficiently volatile to be pumped out of the reaction flask over a several-hour period and collected directly for spectroscopic analysis. The bis(halobenzene)chromium complexes are also volatile but possess sufficient air stability to allow their extraction using benzene or toluene. Yields quoted are of pure isolated complex and vary from 12 to 60% depending on the substituents.

The ^1H nmr spectra of these complexes are rationalizable in terms of increased shielding since the ring current is drastically reduced on complexation to a transition metal; thus the peaks are shifted upfield with respect to those exhibited by the free ligand (see Table I). The mass spectra of these compounds exhibit moderate to strong parent ions, and the major fragmentation pattern appears to involve stepwise loss of the intact aromatic rings as shown in Table II.

Preliminary experiments with cycloheptatriene indicate the formation of the extremely air- and temperature-sensitive chromium sandwich compound, but the identification is based solely on mass spectral data and must remain tentative until a more definitive nmr spectrum is available. Treatment of the low temperature reaction matrix with PF_3 failed to produce the expected $(C_7H_8)Cr(PF_3)_3$ analogous to the known $(C_7H_8)Cr(CO)_3$.[9]

Acetylenes. The trimerization of acetylenes by metal atoms has previously been reported for nickel,[6] and it has now been demonstrated using chromium atoms. 2-Butyne is trimerized to hexamethylbenzene, and terminal acetylenes such as 1-butyne (or 1-pentyne) yield isomeric mixtures of 1,2,4- and 1,3,5-triethyl- (or tripropyl-) benzenes. The yields, however, are not catalytic, and dark green involatile residues remain in the reaction flask after sublimation or solvent extraction of the benzenes. Nmr investigations of these residues

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(2) P. L. Timms, *Endeavour*, **27**, 133 (1968).

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(6) P. S. Skell, J. J. Havel, D. L. Williams-Smith, and M. J. McGlinchey, *J. Chem. Soc., Chem. Commun.*, 1098 (1972).

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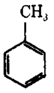
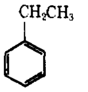
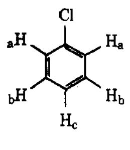
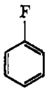
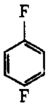
Table I. ^{1}H Nmr Data for Ar_2Cr Complexes[a]

Ar	Chemical shift, τ[b]	Peak multiplicity	Coupling constants, Hz
	5.66	Singlet	
	5.7 7.4	Singlet (5 H) Singlet (3 H)	
	5.77 7.5 8.2	Singlet (5 H) Quartet (2 H) Triplet (3 H)	 $J_{H-H} = 7$
	5.25 5.65	Doublet of doublets (2 H) Multiplet (3 H)	$J_{H_a-H_b} = 5$ $J_{H_a-H_c} = 1$ $J_{H_b-H_c} < 1$
	5.4	Multiplet	
	5.3	Singlet	

[a] All spectra recorded at 60 MHz in C_6D_{12}, using TMS as internal reference. [b] H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, "Benzenoid-Metal Complexes," Ronald Press, New York, N. Y., 1966, p 36.

Table II. Mass Spectra of Bis(arene)chromium Complexes

m/e	Assignment	Rel intensity	m/e	Assignment	Rel intensity
Bis(toluene)chromium (70 eV, 90°)			Bis(ethylbenzene)chromium (70 eV, 90°)		
236	$C_{14}H_{16}Cr^+$	29	264	$C_{16}H_{20}Cr^+$	7
144	$C_7H_8Cr^+$	48	158	$C_8H_{10}Cr^+$	11
92	$C_7H_8^+$	*100*	106	$C_8H_{10}^+$	36
91	$C_7H_7^+$	95	91	$C_7H_7^+$	*100*
77	$C_6H_5^+$	18	77	$C_6H_5^+$	9
Bis(chlorobenzene)chromium (70 eV, 120°)					
276/278/280	$C_{12}H_{10}Cl_2Cr^+$	19	154	$C_{12}H_{10}^+$	57
241/243	$C_{12}H_{10}ClCr^+$	8	129	$C_6H_5Cr^+$	59
206	$C_{12}H_{10}Cr^+$	1	112/114	$C_6H_5Cl^+$	*100*
188/190	$C_{12}H_9Cl^+$	16	77	$C_6H_5^+$	84
164/166	$C_6H_5ClCr^+$	31			
Bis(fluorobenzene)chromium (70 eV, 140°)			Bis(*p*-difluorobenzene)chromium (70 eV, 190°)		
244	$C_{12}H_{10}F_2Cr^+$	39	280	$C_{12}H_8F_4Cr^+$	61
225	$C_{12}H_{10}FCr^+$	0.5	185	$C_6H_4F_3Cr^+$	0.4
167	$C_6H_5F_2Cr^+$	3	166	$C_6H_4F_2Cr^+$	26
148	$C_6H_5FCr^+$	38	147	$C_6H_4FCr^+$	3
96	$C_6H_5F^+$	*100*	114	$C_6H_4F_2^+$	*100*
77	$C_6H_5^+$	16	95	$C_6H_4F^+$	8
			76	$C_6H_4^+$	23

gave no evidence of the presence of bis(arene)chromium complexes which might be postulated as intermediates in these metal promoted trimerizations, perhaps implying that no more than one arene ring is bonded to the chromium at any time.

Dienes. The cocondensation of Cr atoms and 1,3-butadiene yielded no volatile organochromium compounds on warm-up but, after removal of excess butadiene and addition of D_2O, a number of C_4 hydrocarbons were released as shown in Table III.

Table III. C_4 Hydrocarbons Released by D_2O Treatment of the Residue from the Reaction of Cr Atoms with 1,3-Butadiene

	μmol of product/mmol of Cr vaporized	Deuterium distribution (%)				
		D_4	D_3	D_2	D_1	D_0
n-Butane	7.4					
1-Butene	157.2	8.2	8.2	54.9	26.6	2.1
trans-2-Butene	29.8	3.4	5.5	46.3	34.9	9.9
cis-2-Butene	42.0	7.6	6.6	53.2	27.0	5.6
1,3-Butadiene	1.9					

The predominance of dideuterated butenes indicates a certain degree of σ-bonding whereby each metal–carbon bond has been marked with a deuterium. The formation of dideuterated butenes upon deuterolysis has also been observed in the reactions of aluminum atoms with 1,3-butadiene,[10] except that the reaction appears to be much more specific with Al. In contrast, D_2O treatment of the residue from 1,3-butadiene and nickel atoms[6] releases undeuterated butadiene indicating solely π-bonding between the diene and the metal. It would appear that there is a gradual change from σ to π character in the bonding of olefins with metals as one moves from left to right across the Periodic Table, and Al (σ) and Ni (π) are extreme cases. A possibility which cannot be distinguished at present is that bonding is similar for these metal complexes, but that the details of hydrolysis are different at the extremities of the period. Infrared examination of the complexes prior to hydrolysis is presently under investigation and will be helpful in making this distinction.

The involatile residue from Cr and 1,3-butadiene may contain bridging butadiene ligands as previously postulated for Ni[6] and Fe.[11] Consequently, it was hoped that treatment of this residue with strongly π-accepting ligands such as CO or PF_3 might lead to the formation of stable monomeric complexes. This technique had been used successfully with the residue from Fe atoms and 1,3-butadiene to produce (diene)$_2$FeL, where L = CO, PF_3.[11] Furthermore, 1,3-butadienetetracarbonylchromium(0), a compound of known thermal instability, has been made using a similar technique.[12] Although addition of PF_3 to the chromium–diene residue, after removal of the excess diene, did not lead directly to the desired product, it was found possible to prepare (diene)Cr(PF_3)$_4$ if chromium atoms were cocondensed simultaneously with both butadiene and PF_3. This volatile, yellow-brown complex, which decomposes even *in vacuo* after several days at room temperature, was identified by its nmr and mass spectra.

We have postulated a gradual change in the σ to π character of bonding in metal–olefin complexes as one crosses the Periodic Table. In keeping with this concept, D_2O treatment of the involatile residues from the reactions of metal atoms with propene yields products which are most informative. Thus, aluminum yields

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(10) P. S. Skell and L. R. Wolf, unpublished observations.

(11) D. L. Williams-Smith, L. R. Wolf, and P. S. Skell, *J. Amer. Chem. Soc.*, 94, 4042 (1972).

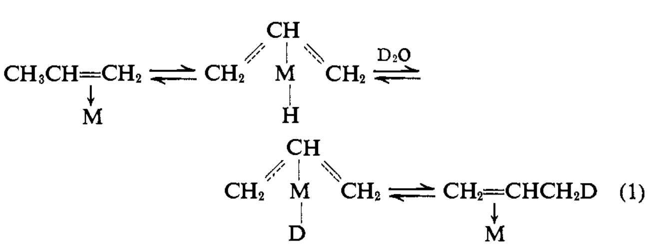
(12) E. K. von Gustorf, O. Jaenicke, and O. E. Polansky, *Angew. Chem., Int. Ed. Engl.*, 11, 532 (1972).

mostly dideuterated propane and hexanes,[10] whereas nickel yields undeuterated propene.[6] Chromium, however, is not so specific in its behavior as either Al or Ni and the deuterium distribution in the products is shown in Table IV.

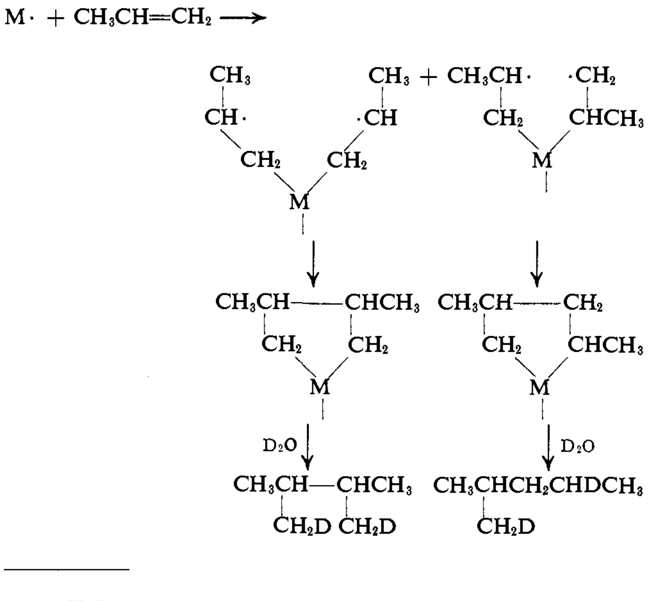
Table IV. C_3 and C_6 Hydrocarbons Released by D_2O Treatment of the Residue from the Reaction of Cr Atoms with Propene

	μmol of product/mmol of Cr vaporized	Deuterium distribution (%) D_3	D_2	D_1	D_0
Propane	333.8	8	31	51	10
Propene	147.8			46	54
2,3-Dimethylbutane	55.6	3	72	16	9
2-Methylpentane	13.7	8	49	18	25

We have previously postulated[6] that the cocondensate from propene and nickel atoms gives hydrolysis products explicable on the basis of a π-allyl hydride intermediate, whereby deuterolysis leads to both undeuterated and monodeuterated propene (eq 1). The π-allyl hydride mechanism is also supported by the fact that chromium atoms have been shown to isomerize 1-butene to a mixture of *cis*- and *trans*-2-butenes at −78°; this process requires a 1,3-hydrogen shift and such a 1,3-shift process has been elegantly demonstrated by Boennemann[13] to involve a π-allyl nickel hydride. The formation of propane and the isomeric hexanes (which are predominantly dideuterated) possibly occurs by a mechanism analogous to that proposed for the aluminum–propene reaction (Scheme I).[10] It is difficult to explain the entire mechanism of the chromium reactions with olefins by analogy to either Al or Ni since the deuterium distributions indicate that the behavior of Cr lies somewhere between that of the two extreme cases.


(1)

Scheme I



Experimental Section

Chromium vapor was produced by electrical heating (8 V, 42 A) of Cr chips in a conical tungsten spiral coated with alundum cement; this was mounted between two water-cooled stainless steel electrode supports in an apparatus similar to that used for the reaction of carbon vapor.[1] Substrate vapor was led into the system through an inlet tube with holes suitably positioned such that the substrate and metal vapor cocondensed in the same region on the cold (−196°) walls of the reaction flask. Since 20% of the metal vaporized fails to reach the walls, being intercepted by the electrode supports and the substrate inlet ring, the weight of chromium available for reaction is only 80% of the weight loss of the crucible.

Bis(cyclopentadienyl)chromium. Freshly distilled cyclopentadiene (9.96 g, 151 mmol) was cocondensed with chromium vapor (126 mg, 2.42 mmol) over a 35-min period. Hydrogen (6.49 mmol) was collected during the course of the reaction. After the reaction flask was warmed to −78°, the products were fractionated *in vacuo* to yield, at −196°, unchanged cyclopentadiene and also cyclopentene (0.32 mmol) and, at −30°, volatile dark red crystals of chromocene (23 mg, 0.126 mmol, 5.2%), mp 172° (lit.[14] mp 173°). The mass spectrum (70 eV, 70°) exhibited peaks at *m/e* 182 (100%), 117 (36%), and 52 (48%) assignable to $C_{10}H_{10}Cr^+$, $C_5H_5Cr^+$, and Cr^+, respectively, which possessed the correct isotope abundance pattern for Cr. This spectrum compares well with the published data.[15]

Bis(toluene)chromium. Atomic chromium vapor was cocondensed with excess toluene at −196°, and the unreacted substrate was removed by pumping at room temperature. The reaction flask was surrounded by a hot water bath and a waxy green solid collected in a −196° trap. This green solid was identified by its mass and nmr spectra as bis(toluene)chromium (52 mg, 60%), subl 47°.

Bis(ethylbenzene)chromium (49 mg, 52%), subl 61°, was similarly isolated as a waxy green solid and identified by its mass and nmr spectra.

Bis(chlorobenzene)chromium (71 mg, 47%) was obtained as air-stable olive green plates, mp 89–90°, which sublimed to the upper part of the reactor flask when it was heated with hot water.

Bis(fluorobenzene)chromium (38 mg, 15%) was obtained as a yellow solid, mp 96–98°, which was sufficiently volatile to be pumped out of the system, or which was soluble in toluene and could thus be extracted from the flask residue.

Bis(*p*-difluorobenzene)chromium was obtained as a bight yellow solid (47 mg, 12%), mp 95° dec, by prolonged pumping of the heated reactor flask, and identified by its mass and nmr spectra.

Bis(cycloheptatriene)chromium. Cycloheptatriene (9.94 g, 108 mmol) was cocondensed with chromium vapor (101 mg, 1.95 mmol) at −196°. The excess triene was removed at −78°; the reaction flask was warmed to room temperature, and 50 ml of dry pentane was added to the residue forming a dark red solution of very low thermal and air stability which was siphoned out, filtered, and evaporated. The ^1H nmr (in toluene-d_8) showed primarily a broad singlet at τ 4.75. The mass spectrum (70 eV, 140°) showed peaks at *m/e* 236 (20%), 144 (12%), 92 (50%), and 91 (100%), which are assignable to $C_{14}H_{16}Cr^+$, $C_7H_8Cr^+$, $C_7H_8^+$, and $C_7H_7^+$, respectively.

Acetylene Trimerizations. 2-Butyne (10.0 g, 185.2 mmol) was cocondensed with chromium vapor (384 mg, 7.38 mmol) at −196°. The reaction flask was warmed to −25° and the contents were stirred, using a magnetic stirrer, for 1 hr. The volatiles were pumped off *via* traps at −78 and −196° to remove unreacted 2-butyne. A small amount of isomerization was shown by the isolation of 6.39 mmol of 1-butyne. Further pumping, combined with evaporation of the hexane extract of the reaction flask, produced hexamethylbenzene (70 mg, 0.43 mmol). An nmr examination of the C_6D_6 extract of the residue did not reveal the presence of bis(hexamethylbenzene)chromium.

By a similar procedure, 1-butyne (4.7 g, 75.2 mmol) and chromium vapor (31.7 mg, 0.61 mmol) yielded a mixture of 1,2,4-tri-

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(13) H. Boennemann, *Angew. Chem., Int. Ed. Engl.*, **9**, 736 (1970).

(14) G. Wilkinson, *J. Amer. Chem. Soc.*, **76**, 209 (1954).

(15) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Amer. Chem. Soc.*, **77**, 3689 (1955).

ethylbenzene (54 mg, 0.33 mmol) and 1,3,5-triethylbenzene (46 mg, 0.28 mmol). Again no bis(arene)chromium complex could be isolated.

1-Pentyne (7.22 g, 106.2 mmol) and chromium vapor (328 mg, 6.31 mmol) were cocondensed at −196°, held at −18° for 21 hr, and then fractionated to recover the unreacted substrate. The benzene extract of the flask residue yielded 1,2,4-tripropylbenzene (157 mg, 0.77 mmol) and 1,3,5-tripropylbenzene (63 mg, 0.31 mmol).

Butadiene. 1,3-Butadiene (5.16 g, 95.7 mmol) was cocondensed with chromium vapor (239 mg, 4.61 mmol) at −196°, and then the reaction flask was maintained at −78° for 1 hr. The excess butadiene was removed *in vacuo* and the flask allowed to attain room temperature, but no volatile organometallics could be pumped off. D_2O (10 g) was condensed into the reaction flask to hydrolyze the residue, and the volatile products, which were analyzed by gas chromatography and mass spectrometry, are presented in Table III.

1,3-Butadienetetrakis(trifluorophosphine)chromium(0). Cocondensation of chromium vapor and 1,3-butadiene at −196° followed by addition of PF_3 to the cold matrix yields no volatile organometallics. However, simultaneous cocondensation of butadiene (4.87 g, 90.2 mmol), trifluorophosphine (3.26 g, 37.1 mmol), and chromium vapor (140 mg, 2.7 mmol) produced a multicolored matrix whose color disappeared rapidly on warming. The contents of the reaction flask were stirred magnetically at −78° for 1 hr, and then were fractionated through traps at −25 and −196°. The −25° trap contained 16 mg (3%) of a yellowish-brown crystalline solid, mp 205–210° dec, which showed prominent mass spectral peaks at *m/e* 458, 370, and 282 assigned to $C_4H_6Cr(PF_3)_4^+$, $C_4H_6Cr(PF_3)_3^+$, and $C_4H_6Cr(PF_3)_2^+$, respectively, and also peaks due to $Cr(PF_3)_6$. The ^1H nmr spectrum (in 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane) shows three multiplets of equal area at τ 5.4, 8.3, and 9.2.

Propene. Chromium vapor (106 mg, 2.05 mmol) was cocondensed with propene (3.16 g, 75.2 mmol) at −196°. The flask was maintained at −78° for 1 hr, and then the excess propene was removed *in vacuo*. D_2O (10 g) was condensed onto the residue and the flask was allowed to attain room temperature. The volatile products were analyzed by gas chromatography and mass spectrometry and are presented in Table IV.

1-Butene. Chromium vapor (40 mg, 0.77 mmol) was cocondensed with 1-butene (0.535 g, 95.5 mmol) at −196°. The flask was warmed to −78° and left at this temperature for 35 min, and the volatiles were removed *in vacuo*. Gas chromatographic analysis of the volatiles showed the presence in the 1-butene of 11.3 mmol of 2-butene (30.5% trans, 69.5% cis).

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Thallium in Organic Synthesis. XXXIII. A One-Step Synthesis of Methyl Arylacetates from Acetophenones Using Thallium(III) Nitrate (TTN)[1]

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Received August 9, 1972

Abstract: Treatment of acetophenones with thallium(III) nitrate in acidic methanol is shown to result in smooth oxidative rearrangement to give methyl arylacetates in moderate to excellent yields. The scope and limitations of the synthesis have been defined and the mechanism of the transformation studied by labeling techniques.

Arylacetic acids and their derivatives are important synthetic intermediates which are normally prepared either by classical multistage syntheses or by the Willgerodt–Kindler reaction.[3] The latter process is a unique transformation whereby alkyl aryl ketones are transformed into ω-arylalkanoic acid derivatives.[4] The synthetic utility of the reaction is, however, limited by (a) the conditions of high temperature and, frequently, high pressure under which the reaction is conducted; (b) a tedious and rather complicated isolation technique; and (c) the modest and variable yields of products which are obtained in many cases. We describe in this paper a simple, one-step procedure for the preparation of methyl arylacetates by oxidative rearrangement of acetophenones with thallium(III) nitrate (TTN).[1b,5,6]

Treatment of acetophenone at room temperature with 1 equiv of TTN in methanol containing a small amount of perchloric acid resulted in smooth reduction of the TTN to thallium(I) nitrate; precipitation of the inorganic salt was complete after 5 hr. Filtration and evaporation of the filtrate gave an oil which, by glpc, consisted of two components in the ratio of 16:1. These were readily identified as methyl phenylacetate (94%) and ω-methoxyacetophenone (6%), and distillation of the mixture gave pure methyl phenyl-

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(1) (a) Part XXXII: A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, in press. (b) Preliminary communication: A. McKillop, B. P. Swann, and E. C. Taylor, *ibid.*, **93**, 4919 (1971).

(2) (a) University of East Anglia; (b) Princeton University.

(3) (a) M. Carmack and M. A. Spielman, *Org. React.*, **3**, 83 (1947); (b) F. Asinger, W. Schafer, and K. Halcour, *Angew. Chem., Int. Ed. Engl.*, **3**, 19 (1964); (c) R. Wegler, E. Kuhle, and W. Schafer, "Newer Methods of Preparative Organic Chemistry," Vol. 3, Academic Press, New York, N. Y., 1964, p 1.

(4) It has been reported (D. T. Manning and H. A. Stansbury, Jr., *J. Amer. Chem. Soc.*, **81**, 4885 (1959)) that treatment of acetophenone with nitrosyl chloride in ethanol–pyridine gives a complex mixture of products from which ethyl phenylacetate was isolated in 8.4% yield. This reaction is of no preparative value as a synthetic route to esters of arylacetic acids.

(5) A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Lett.*, 5275 (1970).

(6) There is only one previous report on the reaction of an alkyl aryl ketone with a thallium(III) salt: V. P. Glushkova and K. A. Kocheshkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1186 (1957); *Chem. Abstr.*, **52**, 6238 (1958). Treatment of acetophenone with thallium(III) isobutyrate was reported to give phenacylidenedithallium tetraisobutyrate, $C_6H_5COCH[Tl(OOC\text{-}i\text{-}Pr)_2]_2$.