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

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(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.

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(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, $C_6H_5COCH[Tl(OOC\text{-}i\text{-}Pr)_2]_2$.

Table I. Oxidative Rearrangement of Acetophenones to Methyl Arylacetates

$$ArCOCH_3 \longrightarrow ArCH_2COOCH_3$$

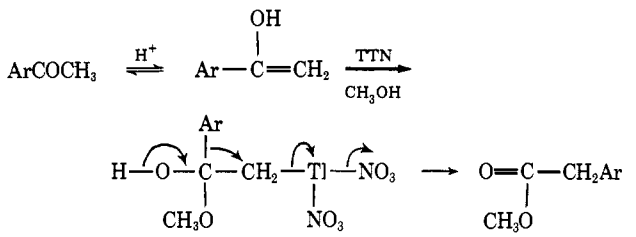
Compd no.	Acetophenone	Time, hr	Yield, %[a]	Mp, °C	Lit. mp or bp (mm), °C
1	Acetophenone	5	84	bp 96–98 (6 mm)	131–132 (50)[b]
2	4-Bromoacetophenone	15	35[c]	113–114	114[d]
3	4-Fluoroacetophenone	17	44[c]	83–84	84–85[e]
4	4-Methylacetophenone	4	86	bp 108–112 (9 mm)	73–74 (0.2)[f]
5	2,4,6-Trimethylacetophenone	24	81[c]	163–165	166–168[g]
6	4-Hydroxyacetophenone	2	64[c]	149	148[h]
7	2-Methoxyacetophenone	12	62[c]	119–120	121–122[i]
8	3-Methoxyacetophenone	12	68	bp 132–136 (9 mm)	107–108 (2)[j]
9	4-Methoxyacetophenone	1	89	bp 122–125 (6 mm)	134–135 (12)[k]
10	3,4-Dimethoxyacetophenone	1	88	bp 162–166 (10 mm)	176–178 (16)[l]
11	4-Methoxy-3-nitroacetophenone	15	59	95–97	102[m]
12	4-Benzoylaminoacetophenone	0.5[n]	66	159–160	*o*
13	1-Acetylnaphthalene	2	91	bp 162–165 (11 mm)	170–171 (20)[f]
14	2-Acetylnaphthalene	2	89	138–140	142[p]

[a] Based on pure redistilled or recrystallized material. [b] M. Rising and J. Stieglitz, *J. Amer. Chem. Soc.*, **40**, 723 (1918). [c] Product isolated as the free acid after alkaline hydrolysis. [d] P. P. Bedson, *J. Chem. Soc.*, **37**, 90 (1880). [e] R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph, and E. M. Smith, *ibid.*, 3247 (1961). [f] N. Acton and E. Berliner, *J. Amer. Chem. Soc.*, **86**, 3312 (1964). [g] V. Meyer and W. Molz, *Chem. Ber.*, **30**, 1270 (1897). [h] E. Salkowski and H. Salkowski, *ibid.*, **12**, 650 (1897). [i] S. K. Arora, A. C. Jain, and T. R. Seshadri, *Tetrahedron*, **18**, 559 (1962). [j] W. C. Lumma, Jr., and G. A. Berchtold, *J. Amer. Chem. Soc.*, **91**, 1566 (1969). [k] P. Pschorr, O. Wolfes, and W. Buckow, *Chem. Ber.*, **33**, 162 (1900). [l] H. R. Snyder, J. S. Buck, and W. S. Ide, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 333. [m] H. W. Bersch, *Arch. Pharm.*, **277**, 271 (1939). [n] Reaction conducted at 50°. [o] *Anal.* Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.57; N, 5.20. Found: C, 70.99; H, 5.62; N, 5.00. [p] O. Blank, *Chem. Ber.*, **29**, 2374 (1896).

acetate in 84% yield. The generality of this transformation was then investigated by examination of the reactions of a wide variety of acetophenones with TTN under similar conditions. Methyl arylacetates were obtained in yields varying from moderate to excellent; experimental details for representative conversions are summarized in Table I.

The mechanism of the above transformation can be represented as shown in Scheme I, that is, acid-catalyzed enolization of the ketone, oxythallation of the C=C bond thus formed, and oxidative rearrangement by 1,2-aryl migration with simultaneous reduction of thallium(III) to thallium(I). The yields of rearrangement products and the relative rates of oxidation (see Table I) can then be readily explained on the basis of the relative migratory aptitudes of the variously substituted aromatic rings. The essential feature of this mechanism, *viz.* 1,2-aryl migration, was readily substantiated by employing acetophenone-^{14}CO as substrate; the results obtained are summarized in Scheme II. The labeled methyl phenylacetate isolated after treatment of the acetophenone with TTN was converted into benzylamine and carbon dioxide by standard Curtius degradation of the corresponding hydrazide. All of the ^{14}C label was located in the carbon dioxide.

Scheme I



Scheme II

$$C_6H_6 + CH_3\overset{*}{C}OO^-Na^+ \xrightarrow{AlCl_3} C_6H_5\overset{*}{C}OCH_3 \xrightarrow[CH_3OH]{TTN}$$

$$C_6H_5CH_2\overset{*}{C}OOCH_3 \xrightarrow{N_2H_4} C_6H_5CH_2\overset{*}{C}ONHNH_2 \xrightarrow[H^+]{NaNO_2}$$

$$C_6H_5CH_2\overset{*}{C}ON_3 \xrightarrow{HCl} C_6H_5CH_2NH_2\cdot HCl + \overset{*}{C}O_2$$

From an examination of the reactions of a wide variety of substituted acetophenones, we have been able to define the scope and limitations of the present synthesis as follows. (i) The reaction is unsuccessful when applied to compounds containing amino substituents due to preferential complexation of the amino group with the thallium reagent. The corresponding amides, however, react normally (see compd **12**, Table I). (ii) Acetophenones in which the aromatic ring is highly deactivated by electron-withdrawing groups undergo enolization, oxythallation, and aryl migration only very slowly, and with these compounds low yields of methyl arylacetates are obtained. Even with these limitations, however, the present procedure constitutes the method of choice for the conversion of acetophenones into methyl arylacetates.[7]

Preliminary experiments have also established that the above rearrangement is general for alkyl aryl ketones, and, in contrast to the Willgerodt–Kindler reaction, may be used for the preparation of α-alkyl-substituted arylacetates. Thus, oxidation of propiophenone with TTN in acidic methanol gave a mixture of products, among which was the expected product of rearrangement, methyl α-methylphenylacetate (45%). The other major product was readily identified as α-methoxypropiophenone. The results obtained with acetophenone and propiophenone are summarized in eq 1 and 2; the increased amount of methoxylated derivative formed in the case of propiophenone can

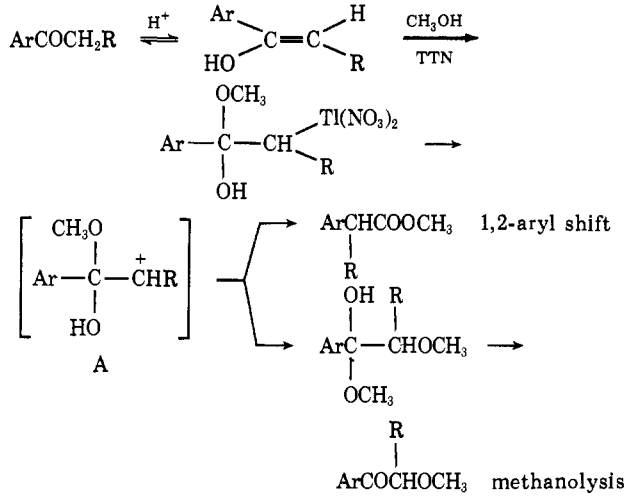
$$C_6H_5COCH_3 \longrightarrow \underset{94\%}{C_6H_5CH_2COOCH_3} + \underset{6\%}{C_6H_5COCH_2OCH_3} \quad (1)$$

$$C_6H_5COCH_2CH_3 \longrightarrow \underset{\underset{45\%}{CH_3}}{C_6H_5\overset{|}{C}HCOOCH_3} + \underset{\underset{32\%}{OCH_3}}{C_6H_5COCH\overset{|}{C}H_3} \quad (2)$$

(7) The reaction is probably not applicable to acetophenones in which there are unsaturated substituents, as competitive oxythallation of the olefin would be anticipated.[1a,5]

easily be explained as shown in Scheme III. Formation of similar mixtures of products has been observed previously in the oxidation of simple olefins with TTN.[1a,5] Moreover, it follows from Scheme III that increased amounts of solvolysis products should be formed from intermediates of type A in which R is a substituent group capable of stabilizing the carbonium ion. This is the case with propiophenone as compared with acetophenone, *i.e.*, a secondary *vs.* a primary carbonium ion. Further evidence to substantiate this point was obtained by treatment of ω-methoxyacetophenone with TTN in methanol–perchloric acid; reaction proceeded slowly, and phenylglyoxal dimethyl acetal was isolated in 82% yield. No product of rearrangement was formed, presumably because of stabilization of the intermediate carbonium ion (A, R = OCH_3) by the adjacent methoxy group.

Scheme III



Extension of the present reaction to the synthesis of other methyl α-alkylarylacetic esters was not pursued further, however, since a much superior one-step synthesis of these latter compounds has been developed which involves treatment of alkylarylacetylenes with TTN in methanol.[8]

Experimental Section[9]

Starting Materials. Compounds **1–4**, **6–9**, **13**, **14**, and ω-methoxyacetophenone were commercially available and were purified prior to use. The following compounds were synthesized by literature procedures: **5**,[10] **10**,[11] **11**,[12] and **12**.[13]

General Procedure for the Oxidation of Acetophenones with TTN. The acetophenone (0.01 mol) was added to a solution of 0.01 mol of TTN in 25 ml of methanol containing 5 ml of 70% perchloric acid, and the mixture was stirred at room temperature for the appropriate period (see Table I). The thallium(I) nitrate which precipitated was removed by filtration; the filtrate was diluted with water, extracted with chloroform (2 × 25 ml), dried (Na_2SO_4), concentrated, and chromatographed on acid-washed alumina using benzene as eluent. The product obtained on concentration of the eluate was distilled to give the pure methyl arylacetate. Where mixtures of products were obtained (as shown by either nmr or glpc), the mixture obtained after chromatography was heated under reflux with 2 *N* sodium hydroxide solution for 2 hr. Decantation of the aqueous phase followed by acidification with concentrated hydrochloric acid gave the crude arylacetic acid as a colorless solid which was purified by crystallization from ethanol or water.

Table II. ^{14}C Labeling Results

Sample	Cpm	% activity relative to acetophenone
Background	57	
Acetophenone-^{14}CO	230,451	100
Methyl phenylacetate-^{14}CO	204,800	89.5
Methyl phenylacetate-^{14}CO + Hyamine hydroxide	90,612	89.5
Benzylamine hydrochloride + Hyamine hydroxide	455	0.45

Oxidation of Propiophenone with TTN. A mixture of 2.68 g (0.02 mol) of propiophenone and 9.0 g (0.02 mol) of TTN in 20 ml of methanol containing 5 ml of 70% perchloric acid was stirred at room temperature for 24 hr. Isolation of the products was carried out as described above and gave an oil whose nmr spectrum showed three different methyl singlets. Chromatography on acid-washed alumina using benzene as eluent gave 1.03 g (31%) of pure methyl α-methylphenylacetate: bp 92–96° (9 mm) (lit.[14] bp 119°, 22 mm); nmr τ 2.80 (s, 5 H), 6.40 (q, 1 H), 6.49 (s, 3 H), 8.59 (d, 3 H). Integration of the initial reaction product showed that this compound accounted for 45% of the total mixture. α-Methoxypropiophenone similarly was found to account for 32% of the total product; nmr τ 1.8–2.8 (m, 5 H), 5.60 (q, 1 H), 6.77 (s, 3 H), 8.61 (d, 3 H).

Oxidation of ω-Methoxyacetophenone with TTN. A mixture of 1.5 g (0.01 mol) of ω-methoxyacetophenone and 4.44 g (0.01 mol) of TTN in 20 ml of methanol containing 5 ml of 70% perchloric acid was stirred at room temperature for 16 hr. Isolation of the product as described above gave 1.43 g (82%) of a colorless liquid identified as phenylglyoxal dimethyl acetal by its nmr spectrum: τ 1.7–2.8 (m, 5 H); 5.06 (s, 1 H); 6.60 (s, 6 H).

Carbon-14 Labeling Experiments. Acetophenone-^{14}CO was prepared in 55% yield by the method of Speer and Jeanes[15] from sodium acetate (8.2 g) containing 25 μCi of sodium acetate-*1*-^{14}C, 39.1 g of benzene, and 55 g of aluminum chloride.

Oxidation of the acetophenone-^{14}CO with TTN was carried out as described above; 4.50 g of the resulting methyl phenylacetate was then heated under reflux for 6 hr with 3 ml of 98% hydrazine in 10 ml of ethanol. The phenylacethydrazide which precipitated from the cooled reaction mixture was removed by filtration and used without further purification.

Phenylacethydrazide (1.0 g, 0.0066 mol) was suspended in 15 ml of water and 7 ml of 6 *N* hydrochloric acid added at 0°. Ether (25 ml) was then added followed by a solution of sodium nitrite (2.5 g, 0.036 mol) in 15 ml of water, and the mixture was shaken at 0° for 10 min. The ethereal layer was separated and the aqueous layer extracted with ether. The combined extracts were washed with aqueous sodium bicarbonate solution followed by water and then dried (Na_2SO_4). Benzene (50 ml) was added and the ether removed by distillation on a water bath. Concentrated hydrochloric acid was then added and the mixture heated under reflux for 2 hr to complete decomposition of the azide. The aqueous layer was separated and the benzene layer washed with water. Concentration of the aqueous extracts gave 0.35 g (37%) of benzylamine hydrochloride which was collected by filtration, washed with benzene, and dried under vacuum.

Samples for counting were prepared by dissolving each labeled compound (0.001 mol) in a solution prepared from toluene (250 ml),

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PPO (2,5-diphenyloxazole, 1.0 g), and dimethyl-POPOP (1,4-di[2-(4-methyl-5-phenyloxazolyl)]benzene, 0.01 g). All samples except benzylamine hydrochloride were soluble in this medium. Benzylamine hydrochloride was solubilized using Hyamine hydroxide (*p*-[diisobutylcresoxyethoxyethyl]dimethylbenzylammonium hydroxide) by addition of 3 ml to the above solution. The quenching of the scintillation caused by this latter component was monitored by counting a sample of methyl phenylacetate both with and without the equivalent amount of Hyamine hydroxide. Each sample was counted for 1 min, and the results are shown in Table II.

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Mechanism of Ozonolysis. A New Route to Ozonides[1]

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Abstract: The photooxidation of diaryl diazo compounds in the presence of aldehydes leads to the formation of ozonides. In the case of 1-(1-naphthyl)-1-phenyl-1-propene the photooxidation method gives an ozonide cis/trans ratio which is the same as that obtained from the trans olefin and different from that obtained from the cis olefin. Ozonolysis of *cis*- and *trans*-1-(1-naphthyl)-1-phenyl-1-propene leads to stereospecific formation of the corresponding epoxides as the major products.

Several observations in apparent conflict with the Criegee[2] mechanism of ozonolysis have led to additional suggestions for the mechanism.[3-9] Most of these additional suggestions have been concerned with the stereochemical consequences of the reaction, that is, the ability of the olefin stereochemistry to somehow affect the amounts and stereochemistry of the ozonide products. An important element of one of these proposals is that the Criegee zwitterion–carbonyl recombination pathway to ozonide formation can be accompanied by varying amounts of one or more additional pathways also leading to ozonide.[3-7] The amount and nature of these additional pathways would then be dependent upon such factors as olefin steric requirements, concentration and geometry, solvent, and other parameters.

Because the olefin–ozonide stereochemical dependence plays such an important role in interpreting the mechanism, it seemed to us that it would be useful to try and determine, by some independent pathway, the ozonide stereochemistry produced in a pure zwitterion plus carbonyl compound reaction pathway. Such an approach requires a nonozone production of the zwitterion in an environment where ozonide might be expected to form. We report here the results of some work in which we have found such a route to ozonide, as well as determined, in some cases, the ozonide stereoisomer ratio and related it to the mechanism problem.

Results and Discussion

The suggestion that the photooxidation of diphenyldiazomethane proceeds through the intermediacy of a carbonyl oxide was first made by Kirmse, Horner, and Hoffman.[10] The suggestion later received support from two groups. Bartlett and Traylor reported[11] that such photooxidations lead to the formation of benzophenone diperoxide, a product which they concluded arose from dimerization of the carbonyl oxide. Hamilton and Giacin, on the other hand, found that an intermediate present in the photooxidation of diphenyldiazomethane was capable of oxidizing the hydrocarbon solvent used.[12] They concluded that the intermediate was the carbonyl oxide in its diradical form as opposed to the dipolar form postulated by Bartlett and Traylor.

If these reactions are proceeding through the Criegee carbonyl oxide or zwitterion then they could provide independent evidence for the involvement of the zwitterion in ozonide formation. Using a photooxidation apparatus similar to one described in the literature,[13] we have photolyzed diazo compounds in the presence of oxygen and aldehydes hoping to form ozonides *via* the Criegee pathway. When diphenyldiazomethane was photolyzed in chlorobenzene alone the product was benzophenone diperoxide thus confirming the results of Bartlett and Traylor.[11] When the photooxidation was carried out in the presence of acetaldehyde, propionaldehyde, or benzaldehyde as solvent then the

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