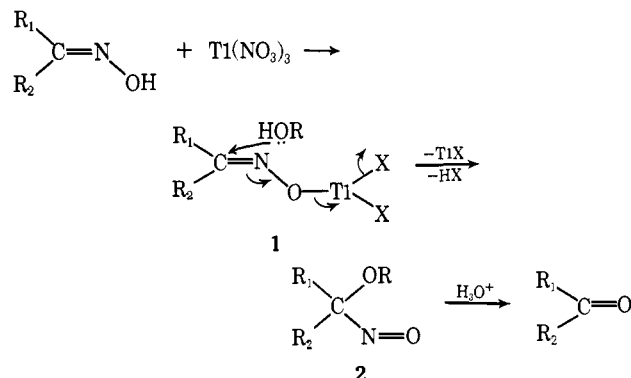


slower still; after treatment with TTN at room temperature for 1 hr the ketones were obtained in 65 and 55% yield, respectively.⁷ 2,4-Dinitrophenylhydrazone derivatives were unaffected by TTN even after several days at reflux temperature.

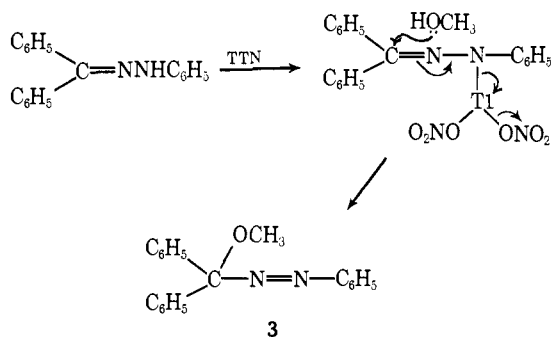
The above deoxygenation process can be explained in terms of the reactions outlined in Scheme I (X = ONO₂).

Scheme I



Compound **1** (R₁ = R₂ = X = CH₃) has been prepared⁸ by treatment of acetoxime with trimethylthallium, and shown to give acetone on hydrolysis. Compounds of the type **2** (R = H) have been proposed as intermediates in the Nef reaction;⁹ compounds of the type **2** (R = CH₃CO) have been isolated and identified as intermediates in the oxidation of oximes with lead(IV) acetate.¹⁰⁻¹² In the present study we have been unsuccessful in attempts to isolate intermediates analogous to **1** or **2**, but were able to obtain the azo ether **3**¹³ (Scheme II) in 57% yield by treatment of benzophenone

Scheme II



phenylhydrazone with TTN in anhydrous methanol. The ether **3** presumably arises, as shown, by a mechanism similar to that suggested in Scheme I for oximes.

While the reactions summarized in Scheme I appear to account adequately for the deoxygenation process, a one-electron transfer pathway may also be operative

under certain conditions. Thus, examination of the reaction of benzophenone oxime with TTN in benzene by esr spectroscopy showed clearly the formation of the corresponding iminoxy radical (triplet, $a_N = 31.6$ G, $a_H = 1.4$ G).¹⁴ Iminoxy radicals were detected similarly for a variety of oximes and it appears that, as is the case with lead(IV) acetate,^{10,11} oxidation of oximes with TTN may proceed by at least two different reaction pathways.

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Thallium in Organic Synthesis. XXVII. A Simple One-Step Conversion of Acetophenones into Methyl Phenylacetates Using Thallium(III) Nitrate (TTN)¹

Sir:

The Willgerodt-Kindler reaction is a unique transformation whereby readily accessible alkyl aryl ketones are converted into ω -arylalkanoic acid derivatives.^{2,3} 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 yields of products which are obtained in many cases.

We wish to describe in this communication a novel procedure for the direct conversion of acetophenones into methyl arylacetates using thallium(III) nitrate (TTN)⁴ in acidic methanol. Thus, 0.01 mol of the acetophenone was added to a solution of 0.011 mol of TTN in 25 ml of methanol containing 5 ml of 70% perchloric acid and the reaction mixture was stirred at room temperature for 2-18 hr. The thallium(I) nitrate which precipitated was removed by filtration, the filtrate was diluted with water, and the product was extracted with chloroform. The organic extract was washed with water, dried, concentrated, and filtered through a short column of alumina using benzene as eluent. Evaporation of the eluate followed by distillation or crystallization gave the pure methyl arylacetate. Experimental data for representative conversions are summarized in Table I.

(1) Part XXVI: A. McKillop, J. D. Hunt, R. D. Naylor, and E. C. Taylor, *J. Amer. Chem. Soc.*, **93**, 4918 (1971).

(2) M. Carmack and M. A. Spielman, *Org. React.*, **3**, 83 (1947); F. Asinger, W. Schafer, and K. Halcour, *Angew. Chem., Int. Ed. Engl.*, **3**, 19 (1964); R. Wegler, E. Kuhle, and W. Schafer, *Newer Meth. Prep. Org. Chem.*, **3**, 1 (1964).

(3) It has been reported (D. T. Manning and H. A. Stansbury, Jr., *J. Amer. Chem. Soc.*, **81**, 4885 (1961)) 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 consequently of no preparative value as a synthetic route to esters of arylacetic acids.

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

(7) Treatment of phenylhydrazone derivatives of α,β -unsaturated ketones does not result in regeneration of the parent carbonyl compound, but leads to 1-phenylpyrazoles. Thus, oxidation of chalcone phenylhydrazone with TTN in methanol gave 1,3,5-triphenylpyrazole in 40% yield.

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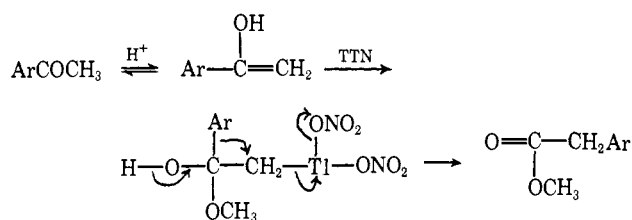
Table I. Conversion of Substituted Acetophenones into Methyl Phenylacetates

$\text{ArCOCH}_3 \longrightarrow \text{ArCH}_2\text{COOCH}_3$			
Compd	Ar =	Reaction time, hr	Yield, % ^a
1	C_6H_5	5	84
2	4- FC_6H_4	17	44
3	4- $\text{CH}_3\text{C}_6\text{H}_4$	4	86
4	2- $\text{CH}_3\text{OC}_6\text{H}_4$	12	62
5	3,4- $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$	1	88
6	3- NO_2 -4- $\text{CH}_3\text{OC}_6\text{H}_3$	15	61
7	4- HOC_6H_4	2	64 ^b
8	4- $\text{C}_6\text{H}_5\text{CONHC}_6\text{H}_4$	1 ^c	66
9	2- C_{10}H_7	2	94

^a Calculated on pure redistilled or recrystallized material.

^b Refers to 4-hydroxyphenylacetic acid, obtained by hydrolysis of the crude ester with 2 *N* sodium hydroxide. ^c Reaction carried out at 50°.

We believe that the mechanism of this transformation is best represented as shown in Scheme I. Acid-cata-

Scheme I

lyzed enolization followed by oxythallation leads to an unstable alkylthallium dinitrate. Decomposition of this intermediate proceeds *via* migration of the aryl substituent, resulting in direct formation of the methyl arylacetate and simultaneous reduction of thallium(III) to thallium(I). The essential feature of this mechanism, *viz.* 1,2-aryl migration, was readily substantiated by the simple expedient of employing acetophenone ¹⁴C as substrate. The labeled methyl phenylacetate isolated after treatment with TTN in methanol was converted into benzylamine and carbon dioxide by standard Curtius degradation of the corresponding hydrazide. All of the ¹⁴C label was located in the carbon dioxide.

From an examination of a wide range of substituted acetophenones we have been able to define the limitations of the present conversion 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 electrophile. The corresponding amides, however (*cf.* **8**, Table I), react normally. Surprisingly, *p*-hydroxyacetophenone gave a good yield of *p*-hydroxyphenylacetic acid, although some concomitant oxidation to red polymeric material also occurred. (ii) Acetophenones in which the aromatic ring is highly deactivated by electron-withdrawing substituents undergo enolization, oxythallation, and aryl migration only very slowly, and with these compounds low yields of methyl arylacetates are obtained. Within these limitations, however, the present procedure constitutes the method of

choice for the conversion of acetophenones into arylacetic acids.^{5,6}

(5) The reaction is probably not applicable to acetophenones carrying unsaturated substituents since competitive oxythallation of the olefin would be anticipated.⁴

(6) Preliminary experiments have established that the above rearrangement is general for alkyl aryl ketones, and, in contrast to the Willgerodt-Kindler reaction,² may be used for the synthesis of α -alkyl-substituted arylacetates. This extension of the present reaction was not further pursued, however, since a much superior one-step synthesis of these latter compounds has been developed which involves treatment of alkyl arylacetylenes with TTN in methanol.⁷

(7) A. McKillop, O. H. Oldenzel, B. P. Swann, E. C. Taylor, and R. L. Robey, submitted for publication.

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Competitive Bond Rotation and Bond Scission Processes in Semistabilized 1,4 Diradicals. The Thermal Fragmentation of [4.4.2]Propella-2,4-dienes

Sir:

By the mere expediency of incorporating a cyclobutane ring into a structure endowed with reduced conformational flexibility, thermal fragmentation of the strained ring will be forced to proceed nonconcertedly *via* transient 1,4 diradicals.¹ Recent extended Hückel studies of such reactive intermediates have led to the conclusion that they are twixtylic in nature, *i.e.*, they are unstable with respect to olefin pairs and consequently do not represent true energy minima.² The rather surprising implications of this analysis have not been put to sound experimental test, chiefly because cyclobutane derivatives bearing sufficient stereochemical labeling and rigidity have not been available. Also, in the great majority of cyclobutanes which have been pyrolyzed to date,³ the structural features have been such that bond rotation, ring closure, and bond scission are competitive.⁴ We now describe the stereochemical consequences attending the pyrolysis of several [4.4.2]-propella-2,4-dienes.⁵ These tricyclic molecules are ideally suited for the present purpose because: (a) they are incapable of extensive twisting; (b) the anticipated reduction in activation energies associated with initial bond homolysis (due to the developing cyclohexadienyl radical) should result in the need for lower pyrolysis temperatures; and (c) the driving force underlying the incipient aromatic character in the tetralin fragment was expected to appreciably enhance k_{scis} relative to k_{rot} . As a result, the average lifetimes of the derived twixtyls should be greatly minimized.

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(5) The synthesis of all starting materials described in this communication will be published elsewhere.