testing. The only distinctive, gross signs of toxicity in cockerels were a general listlessness followed either by eventual improvement (250 mg/kg, oral) or ataxia and death (375 mg/kg, oral). Austin elicited no effects in etiolated *Triticum* coleoptiles.

Acknowledgments. We thank Dr. Dorothy I. Fennell, NRRL for accession and identification of the fungus. Mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

Supplementary Material Available: Fractional coordinates (Table I), bond distances (Table II), bond angles (Table III), observed and calculated structure factors (Table IV) and ir, ^1H NMR, and ^{13}C NMR spectra (17 pages). Ordering information is given on any current masthead page.

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Thallium in Organic Synthesis. 44. Oxidative Rearrangements via Oxythallation with Thallium(III) Nitrate Supported on Clay[1,2]

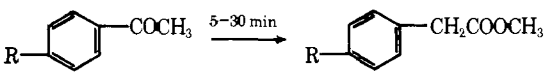
Sir:

Considerable recent use has been made of the concept of utilizing reagents or reactants adsorbed on insoluble inorganic supports for organic synthesis. Silver carbonate deposited on Celite is a highly selective and very effective reagent for the oxidation of alcohols to carbonyl compounds;[3] alcohols, thiols, and acetic acid adsorbed on dehydrated alumina effect various SN2 displacement reactions and epoxide ring openings under very mild conditions;[4] isopropyl alcohol adsorbed on dehydrated alumina can be used for the selective reduction of an aldehyde in the presence of a ketone;[5] and both Collins' reagent supported on Celite,[6] and chromic acid intercalated in graphite,[7] possess distinct advantages (greater selectivity, manipulative convenience) over solutions of the same reagents. Moreover, simple addition of certain supports to a reaction mixture can have a dramatic effect on reaction rate.[8] The effectiveness of the inorganic support in these reactions appears to be due to a combination of factors—an increase in the effective surface area for reaction; the presence of pores which constrain both substrate and reactant and thus lower the entropy of activation of reaction; and a synergism (for displacement reactions) resulting from bringing electrophile and nucleophile into proximity, while at the same time enhancing the nucleophilicity (and basicity) of the latter.[4]

We now report that thallium(III) nitrate (TTN) adsorbed on K-10, a readily available and inexpensive acidic montmorillonite clay,[9] is a remarkably effective reagent for the rapid, selective, high yield, room temperature oxidation of a variety of unsaturated organic substrates.

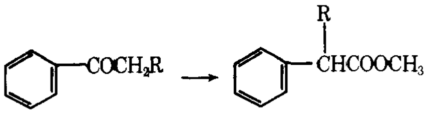
The TTN/K-10 reagent is readily prepared by stirring K-10 with a solution of TTN in a mixture of methanol and trimethyl orthoformate followed by evaporation to dryness.[10] The resulting colorless, free-flowing powder can be stored in well-capped bottles for months without any appreciable loss in activity. All of the oxidations described below were carried out by stirring a suspension of the TTN/K-10 reagent with a solution of the substrate in an inert solvent (heptane, methylene chloride, carbon tetrachloride, toluene, dioxane) until a starch iodide test for thallium(III) was negative. Products were isolated by removal of the spent reagent system by filtration, washing of the filtrate with aqueous sodium bicarbonate, then water, drying, evaporation of the solvent, and recrystallization or distillation of the crude product.

Oxidative rearrangement of alkyl aryl ketones is a particularly smooth reaction. Acetophenones, for instance, are rapidly converted into methyl arylacetates, and yields are excellent (eq 1).[11] Propiophenone and butyrophenone are converted into methyl α-methyl- and α-ethyl phenylacetate, respectively, under the same reaction conditions (eq 2). These



(1)

$R = H, 86\%$
$R = CH_3, 84\%$
$R = CH_3O, 92\%$
$R = F, 88\%$ (cf. 44% in CH_3OH)[12]
$R = Br, 89\%$ (cf. 35% in CH_3OH)[12]



(2)

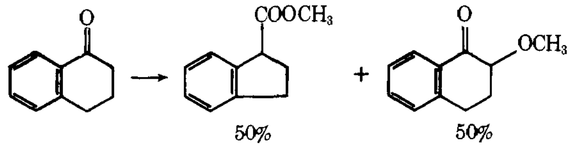
$R = CH_3, 98\%$
$R = C_2H_5, 98\%$

results contrast sharply with those obtained using TTN in refluxing acidic methanol; under the latter conditions, for example, propiophenone gives a mixture of methyl α-methylphenylacetate (45%) and α-methoxypropiophenone (32%).[12] Oxidations of benzo-fused cycloalkanones with TTN/K-10 also proceed more cleanly than with TTN in methanol. 1-Tetralone is converted to a mixture of more than ten products by TTN in methanol, but with TTN/K-10 a 1:1 mixture of methyl indane-1-carboxylate and 2-methoxy-1-tetralone is formed (eq 3).

Table I. Comparative Effectiveness of Various Supports for the TTN-Mediated Rearrangement of Acetophenone to Methyl Phenylacetate

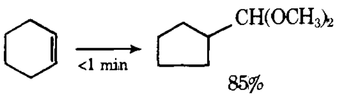
		Product distribution		
Support	Reaction time[a]	Unreacted $PhCOCH_3$	$PhCH_2COOCH_3$	b
AERO 8020 silica-alumina	1 min	60	20	20
Alcoa F-1 alumina	2 min	50	50	0
K-10 montmorillonite clay	5 min	<1	>99	0
K-306 montmorillonite clay	5 min	10	70	20
Florisil	5 min	40	30	30
Southern bentonite	10 min	20	80	0
Graphite	30 min	25	75	0
Davison 135 neutral silica-alumina	90 min	15	85	0
Amberlyst 15	8 h	50	50	0

[a] Time required for complete utilization of Tl(III) as determined by starch iodide paper. [b] Indicates other products are also formed.



(3)

Oxidative rearrangement of simple olefins such as cyclohexene (eq 4), styrene (eq 5), and 1-phenyl-1-propene (eq 6) is extremely rapid. Although oxidation of cinnamaldehyde and substituted cinnamaldehydes with TTN in methanol gives complex mixtures of products and is of no synthetic utility, the use of TTN/K-10 results in rapid, clean oxidative rearrangement and formation of arylmalondialdehyde tetramethylacetals in excellent yield (eq 7).



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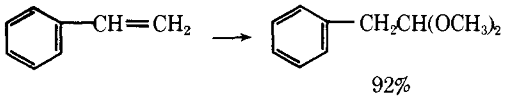
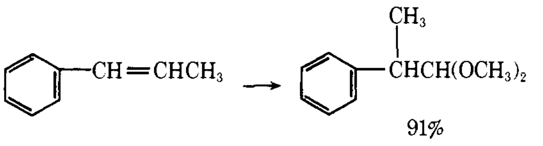
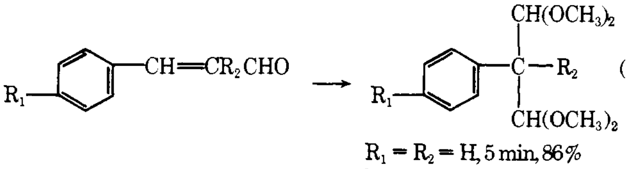


(5)



(6)

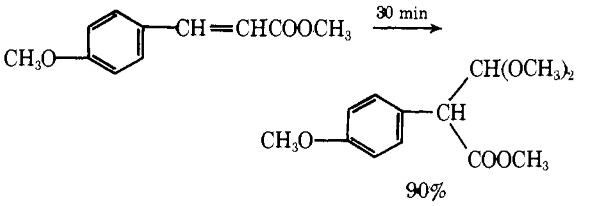


(7)

$R_1 = R_2 = H$, 5 min, 86%
$R_1 = CH_3O$, $R_2 = H$, 5 min, 86%
$R_1 = H$, $R_2 = CH_3$, 15 min, 83%

Cinnamic esters, which are unaffected by hot solutions of TTN in methanol, are smoothly oxidized by TTN/K-10 at room temperature (eq 8).

The above conversions clearly demonstrate the relative superiority of TTN/K-10 over TTN/methanol for these oxythallation processes, and while the precise reasons for the effectiveness of K-10 in these reactions remain unclear, it appears that supports with a laminar structure, and in particular acidic ones such as K-10, are much more effective than nonacidic sponge-like supports. Moreover, systematic examination of more than 20 different TTN support systems has established that TTN/K-10 is by far the most effective with respect to ease of preparation, rate of reaction, selectivity of oxidation, and general experimental simplicity. Data for the conversion of acetophenone into methyl phenylacetate using TTN deposited on a variety of inorganic and organic supports are listed in Table I, and clearly show that TTN/K-10 is the reagent of choice for this transformation.



(8)

We have no clear understanding as yet of the exact physical nature of the TTN/K-10 support system. Reaction of TTN (which is a trihydrate, $Tl(ONO_2)_3{\cdot}3H_2O$) with trimethyl orthoformate is known to result in removal of the water of hydration from the coordination sphere of the thallium,[8] and the TTN/K-10 reagent appears to consist of nonhydrated thallium(III) nitrate and methanol adsorbed on the surface of the acidic clay. Thus, the dried reagent corresponds approximately by weight to $Tl(ONO_2)_3/3CH_3OH/K$-10, and the clay can be washed free of both thallium(III) nitrate and methanol by treatment with polar solvents such as acetonitrile. One particularly important point about the TTN/K-10 reagent, however, is that under the standard reaction conditions (nonpolar, inert solvents) both the thallium(III) nitrate on the support and the thallium(I) nitrate which is generated during the reaction are tightly bound to the support throughout the whole of the reaction. Consequently, there is no detectable level (atomic absorption) of contamination of either solvent or product by thallium.[13]

References and Notes

(1) (a) For the previous paper in this series, see E. C. Taylor, R. L. Robey, K.-T. Liu, B. Favre, H. T. Bozimo, R. A. Conley, C.-S. Chiang, A. McKillop, and M. E. Ford, *J. Am. Chem. Soc.*, **98**, 3037 (1976). (b) We are indebted to the National Science Foundation (Grant No. MPS72-00427) for partial support of this work.

(2) The term "oxythallation" refers to electrophilic attack (usually on a C=C bond), by Tl(III), accompanied by capture of the resulting carbonium (or thallinium) ion by a nucleophile (gegenion or solvent). The resulting "oxythallated" intermediate is usually extremely unstable and breaks down spontaneously to product(s). Both mechanistic and synthetic aspects of oxythallation have been discussed in detail in previous papers in this series.

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(8) Unpublished observations by E. C. Taylor, C.-S. Chiang, and A. McKillop.

(9) Girdler Catalyst K-10, Girdler Chemicals, Inc., Louisville, Ky.

(10) Detailed directions for the preparation of the TTN/K-10 reagent are as follows: A 500-ml, round-bottomed flask equipped with a magnetic stirring bar is charged with 125 ml of trimethyl orthoformate and 100 ml of methanol. The mixture is stirred and 49 g (0.11 mol) of $TTN{\cdot}3H_2O$ is added in one portion. Stirring is continued until all of the thallium salt has dissolved (approximately 2 min), and then 110 g of K-10 clay is introduced in one portion through a powder funnel. The reaction is slightly exothermic. The powder funnel is rinsed with 25 ml of methanol and the mixture is stirred for a further 5 min. The flask is then transferred to a rotary evaporator and the excess solvents are removed by distillation under reduced pressure (bath temperature 60–70 °C (15–25 mm)). This is complete in 1.5 h, and 170 g of TTN/K-10 is obtained as a dry, free-flowing, pale yellow powder. Various batches of the K-10 support material were used, but identical results were obtained in all cases.

(11) Crude yields of chromatographically pure products were uniformly quantitative; the yields reported in this paper are for distilled or recrystallized products. All of the reactions reported herein have been carried out many times with completely reproducible results.
(12) A. McKillop, B. P. Swann, and E. C. Taylor, *J. Am. Chem. Soc.*, **95**, 3340 (1973).
(13) This is true both for 0.1 and 1.0 molar scale reactions.

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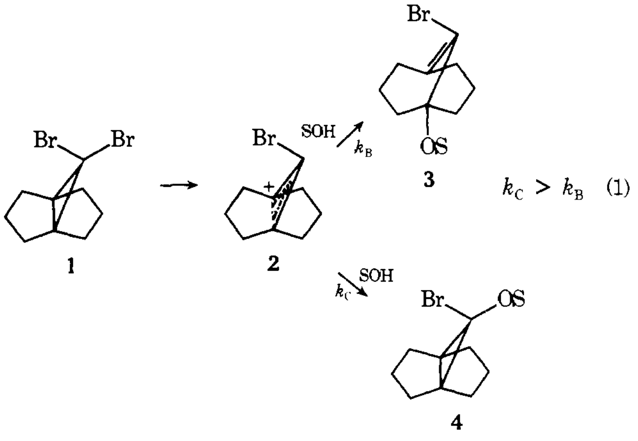
Propellanes. 12. A Bridgehead Olefin Transoid in a Six-Membered Ring. Formation of a Stable Cyclopropanone

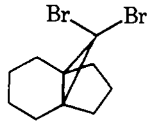
Sir:

A surge of interest[1] in the production and fate of bridgehead olefins has followed Wiseman's demonstration that these olefins are similar in strain energy and reactivity to their corresponding trans cycloolefins.[2] As expected, most work has been limited to cases where the bridgehead double bond is transoid in a ring of ≥ 7 carbons. While effort has been expended on the synthesis of examples of bridgehead double bonds transoid in six-membered rings,[3] no energy comparisons have been possible. We now report data which allow some perspective on the energetics of bridgehead olefin formation.

Our approach[4] to bridgehead olefins has been through the solvolysis of tricyclic cyclopropyl halides (i.e., propellanes); others have also utilized this route.[5] An obvious potential precursor for a bridgehead olefin transoid in a six-membered ring is 9,9-dibromo[3.3.1]propellane (9,9-dibromotricyclo[3.3.1.0^{1,5}]nonane, **1**),[6] although one would expect relatively more cyclopropyl product than in the earlier cases we reported[4b,c] (eq 1).



Solvolysis of **1** (HOAc, 0.012 M NaOAc, 125 °C) proceeded with a rate constant of 3.1×10^{-7} s^{-1}, some 6200 times slower than acetolysis of **5**. Unfortunately, however, 2 mol of acid was produced, indicating that both bromines had been lost. We pursued this no further, since our experience with **6a** indicated we were probably seeing HOAc addition to the cyclopropane ring followed by solvolysis; with **6a**, addition took place six times faster than the solvolysis of **1**.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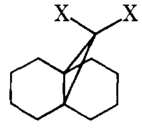
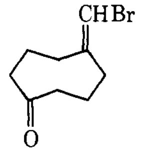

6a, X = Br
b, X = Cl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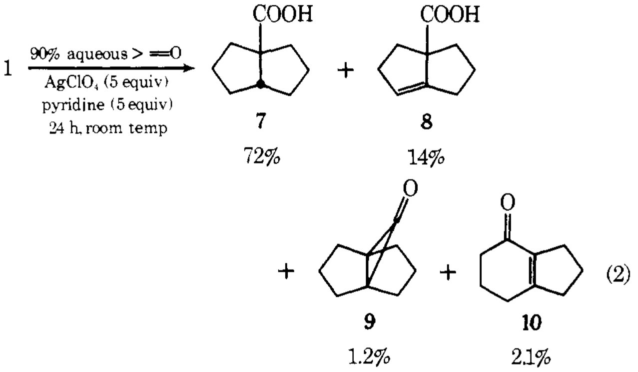
Silver assisted hydrolysis of **1** in aqueous acetone proved more fruitful. In 90% aqueous acetone, **1** reacted eight-ten times slower than **6a**, but two-three times faster than **6b**. The products isolated from hydrolysis (buffered to allow isolation of **9**) are shown in eq 2.



Thus the acid mixture of **7** and **8** was the major product. Catalytic hydrogenation (Pd/C, EtOH) gave pure **7**.[7] The olefinic resonance of **8** indicated its presence; the ^{13}C NMR of the mixture showed nine peaks not attributable to **7**, including two olefinic carbons (δ 151.9, 122.2). The diazomethane-derived esters showed separate resonances at δ 3.62 (**7**-OCH$_3$) and δ 3.67 (**8**-OCH$_3$). Cyclopropanone **9**, which led to primarily **7** when treated under unbuffered hydrolysis conditions or when shaken with aqueous base, was identified

Scheme I