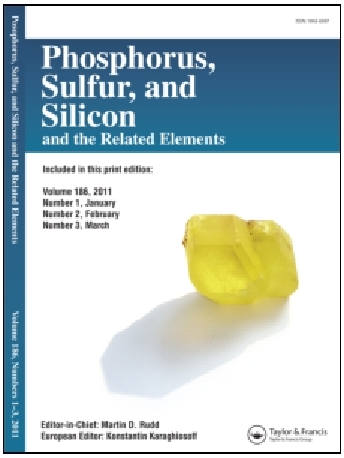

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NEW SYNTHETIC REACTIONS USING ARENETELLURINIC ANHYDRIDES

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NEW SYNTHETIC REACTIONS USING ARENETELLURINIC ANHYDRIDES

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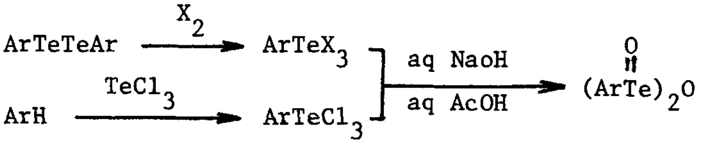
Abstract New synthetic reactions utilizing arenetellurinic acid anhydrides are described. The anhydrides proved to be very useful reagents for the transformation of various functional groups. Furthermore they induced various intramolecular cyclofunctionalizations to yield many oxygen and nitrogen heterocycles.

INTRODUCTION

Organotellurinic acids and their anhydrides have been known for many years. However their chemical properties have been little investigated.[1] They should be expected to be useful as oxidizing agents like organotelluroxides and tellurones due to the presence of labile Te-O bonds.[2] Arenetellurinic acid anhydrides are readily accessible by alkline hydrolysis of arenetellurium trihalides followed by acidification.[1] Arenetellurium trihalides are easily obtained by treatment of diaryl ditellurides with halogens or by the reaction of reactive arenes with tellurium tetrachloride (equation 1).[1] They are insoluble in common solvents, except acetic acid, but as oxidation proceeds, they are reduced to readily soluble bis(aryl) ditellurides. Recently we[3] and Barton[4] reported that aryltellurinic acid anhydrides act as mild oxidizing agent towards various kinds of organic compounds.



$$\left.\begin{array}{l} \text{ArTeTeAr} \xrightarrow{X_2} \text{ArTeX}_3 \\ \text{ArH} \xrightarrow{\text{TeCl}_3} \text{ArTeCl}_3 \end{array}\right] \xrightarrow[\text{aq AcOH}]{\text{aq NaoH}} (\text{Ar}\overset{\text{O}}{\overset{\|}{\text{Te}}})_2\text{O} \qquad (1)$$

RESULTS AND DISCUSSION

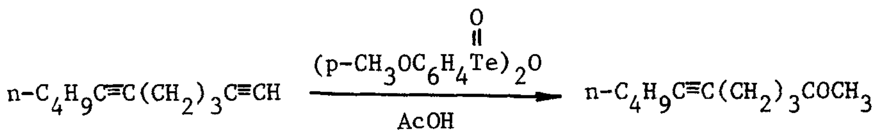
We have used benzene-, p-methoxybenzene-, and β-naphthalenetellurinic acid anhydrides as reagents throughout the course of this research.

Oxidation Reaction

p-Methoxybenzenetellurinic acid anhydride reacts with thiols, phenols, phosphines, thioamides, thionesters, and N,N'-diphenylthiourea to yield disulfides, quinones, phosphine oxides, nitriles, esters, and N,N'-diphenyl carbodiimide.[3,4] In addition, the anhydride effects the oxidation of benzyl type alcohols and methyl lactate to the corresponding carbonyl compounds.[3]

Hydration of Terminal Alkynes

We have discovered another useful reaction of these reagents towards alkynes. Tellurinic anhydrides are usually inert to nonterminal alkynes except for the conversion of diphenylacetylene into benzil with the aid of sulfuric acid. On the other hand, they catalyzed the hydration of terminal alkynes in refluxing acetic acid in good yields.[3] It should be especially noted that 1,6-undecadiyne suffered the selective hydration of only the terminal acetylene bond as shown below.

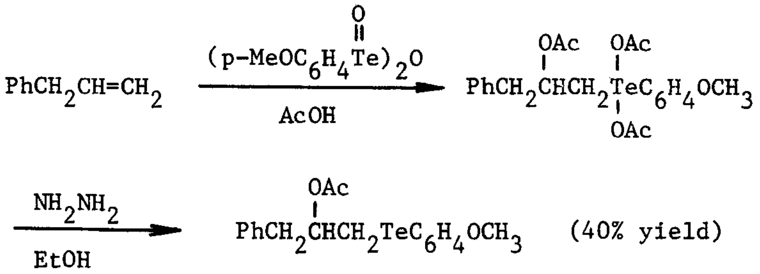


$$n\text{-}C_4H_9C{\equiv}C(CH_2)_3C{\equiv}CH \xrightarrow[\text{AcOH}]{(p\text{-}CH_3OC_6H_4\overset{\overset{O}{\|}}{Te})_2O} n\text{-}C_4H_9C{\equiv}C(CH_2)_3COCH_3$$

Thus, the present method nicely complements the conventional hydration method using a mercuric salt catalyst which is applicable to both terminal and internal acetylenes. A reasonable mechanism for this hydration has been proposed.

Oxytellurinylation and Related Reactions

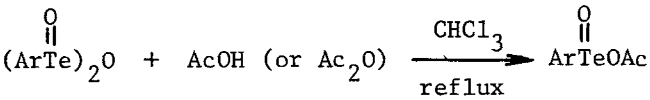
Next we have investigated the reaction with olefins. Sonoda and his coworkers reported that benzenetellurinic anhydride oxidizes olefins in refluxing acetic acid to yield vic-diacetates. This reaction was accelerated by the presence of a catalytic amount of sulfuric acid.[5] The acetoxylation probably proceeds through acetoxytellurenylation of the olefin with benzenetellurenyl acetate (PhTeOAc) generated from benzene-tellurinic anhydride, followed by acetolysis of phenyltelluro group. The postulated active species, a benzenetellurenic acid derivative, is produced by reduction of the tellurinic acid anhydride. However, we have found that p-methoxybenzenetellurinic anhydride reacts with allylbenzene in acetic acid at reflux for 15 h to give, together with some recovered starting material, tetravalent tellurium triacetate rather than vic-diacetate.[6] Since the telluroxide function is readily convertible into tellurium diacetate in acetic acid, we assume that p-methoxybenzenetellurinyl acetate is the reactive species and undergoes acetoxytellurinylation with allylbenzene. The mixed anhydride is also postulated as the real catalyst for the selective hydration of terminal alkynes.[3] Because of hygroscopic and intractable nature of the product triacetate, the corresponding telluride was isolated after reduction with hydrazine hydrate in ethanol.



$$PhCH_2CH{=}CH_2 \xrightarrow[AcOH]{(p\text{-}MeOC_6H_4\overset{\overset{O}{\|}}{Te})_2O} PhCH_2\overset{OAc}{CH}CH_2\underset{OAc}{\overset{OAc}{Te}}C_6H_4OCH_3$$

$$\xrightarrow[EtOH]{NH_2NH_2} PhCH_2\overset{OAc}{CH}CH_2TeC_6H_4OCH_3 \quad (40\%\ \text{yield})$$

The formation of the tellurinyl acetate was actually confirmed in a separate experiment which involved heating of the tellurinic anhydrides in acetic acid or anhydride. Tellurinyl acetates are very hygroscopic oil materials and show the indicated spectral



$$(\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Te}}})_2\mathrm{O} + \mathrm{AcOH}\ (\mathrm{or}\ \mathrm{Ac_2O}) \xrightarrow[\mathrm{reflux}]{\mathrm{CHCl_3}} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Te}}}\mathrm{OAc}$$

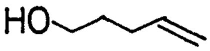
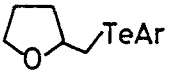
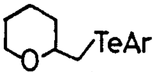
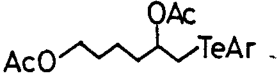
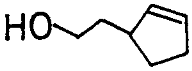
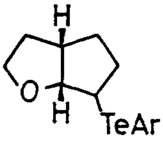
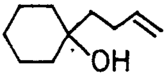
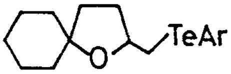
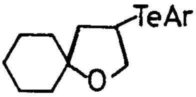
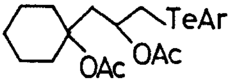
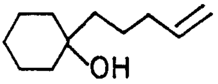
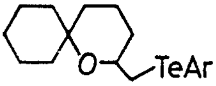
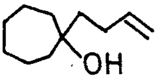
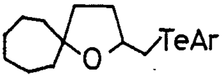
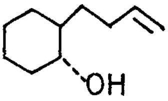
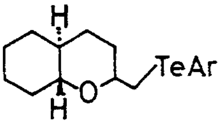
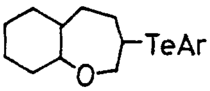
properties (Table I). The tellurinyl trifluoroacetates can be prepared easily by a similar procedure.

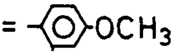
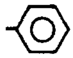
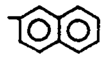
TABLE I Spectral data of aryltellurinyl acetates.

Ar	IR (neat) $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$, δ)
Ph	1715	1.90(s, 3H, OAc), 7.0-7.5(m, 3H, ArH) 7.6-8.0(m, 2H, ArH)
p-Anisyl	1712	1.90(s, 3H, OAc), 3.78(s, 3H, OMe) 6.86(ABd, 2H, ArH), 7.76(ABd, 2H, ArH)

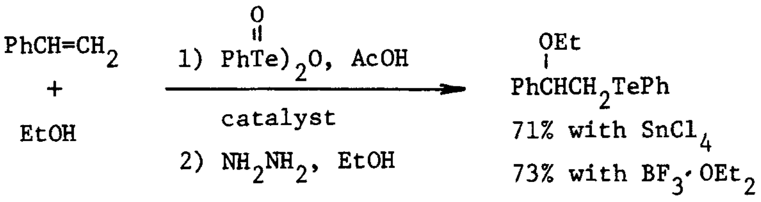
It was reasoned that if a strong nucleophile were present in the reaction mixture or present as a substituent at a suitable position in the olefinic molecule, S_N2 reaction with it or an intramolecular cyclization instead of acetoxylation might occur. In fact, treatment of hydroxyolefins with tellurinic anhydrides in acetic acid at reflux temperature for 15 h afforded cyclic ethers bearing an aryltellurium group. Because of their hygroscopic and intractable nature, the cyclized products were isolated as the corresponding tellurides after reduction with hydrazine hydrate in ethanol.[6] Table II exhibits features of this oxytellurinylation. The addition is highly regioselective, obeying Markovnikov's rule, and stereoselective anti on the basis of the stereochemistry of the bicyclic product (Run 3). The five-membered cyclic ether is generally easier to form than the other size rings. The example of Run 5 illustrates that five-membered ring formation is favorable over the four-membered one in spite of anti-Markovnikov addition. An attempted formation of three- or

TABLE II Intramolecular oxytellurinylation

Run	Substrate	Product	Yield/%
1			80[a], 77[b], 73[c]
2			38[a], 26[c]
			26[a], 23[c]
3			42[a], 53[c]
4			86[a]
5			15[a]
			29[a]
6			90[a]
7			94[a]
8			45[a]
			22[a]

a: Ar =  b: Ar =  c: Ar = 

four-membered ring from allyl alcohol was unsuccessful. Sluggish cyclization often competes with acetoxylation (Run 2 and 5). Intermolecular ether formation was also actually observed as shown below.



$$\mathrm{PhCH{=}CH_2} + \mathrm{EtOH} \xrightarrow[\text{catalyst; 2) } \mathrm{NH_2NH_2}\text{, EtOH}]{\text{1) } \overset{\overset{O}{\|}}{\mathrm{PhTe}})_2\mathrm{O}\text{, AcOH}} \overset{\overset{OEt}{|}}{\mathrm{PhCH}}\mathrm{CH_2TePh}$$

71% with $SnCl_4$

73% with $BF_3 \cdot OEt_2$

All of the aryltellurinic anhydrides used showed nearly equal reactivity for the oxytellurinylation. For example, benzene-, p-methoxybenzene-, and β-naphthalene-tellurinic anhydrides converted o-allylphenol and 2-allyl-6-methylphenol to 2,3-dihydro-2-(aryltelluro)methylbenzofuran and 2,3-dihydro-7-methyl-2-(aryltelluro)methylbenzofuran in 80, 94, 92 and 91, 90, 89% yields, respectively. The catalytic activities of several Lewis acids to this reaction were further studied. The cyclization of o-allylphenol was examined as an example. As shown in Table III, stannic chloride, boron trifluoride etherate, and ferric chloride were very effective catalysts. Zinc iodide was also effective, but the activity was low.

Aminotellurinylation and Related Reactions

Here we wish to report the first aminotelluration of olefins induced by benzenetellurinyl acetate-ethyl carbamate and its extension to cyclofunctionalization of olefinic carbamates into nitrogen heterocycles. We have recently found that benzenetellurinyl acetate reacts with olefins in the presence of BF_3OEt_2 and excess ethyl carbamate to give (2-phenyltellurinyl)alkyl carbamates in preference to the acetoxytellurinylation product.[7] This reaction also worked well with benzyl carbamate. When boron trifluoride etherate was omitted, no reaction occurred. Benzenetellurinyl

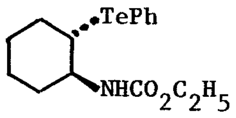
TABLE III Catalytic activities of Lewis acids in the oxytellurinylation reaction.

Catalyst[a]	Reaction Time (h)	Yield (%)
$SnCl_4$	0.5	96[b]
$BF_3\cdot OEt_2$	0.5	91
$BF_3\cdot OEt_2$[c]	15	88
$FeCl_3$	2	88
ZnI_2	12	94
$AlCl_3$	0.5	ca 20
$TiCl_4$	1	26
$Zn(OAc)_2\cdot H_2O$	12	0

a) 1.2 eq. b) RT c) 20 mol%

trifluoroacetate was a more effective reagent and gave highly improved yields. Because of difficulty in the purification of the products, they were isolated as tellurides after reduction with hydrazine hydrate in ethanol. Typical results are shown in Table IV. In the case of terminal olefins the reaction proceeds with high Markovnikov regioselectivity, where the tellurium species act as the electrophiles. However, increasing the bulkiness of the substituent tends to promote the formation of the anti- Markovnikov adduct. The reactivity of internal olefins is considerably effected by both the electronic and steric factors of the substituents. Thus, dialkyl substitution electronically promotes the reaction, so that cyclohexene reacts even in refluxing dichloromethane. On the other hand, norbornene and β-methylstyrene are inert owing to steric hindrance. The stereochemistry of the adduct from cyclohexene clearly supports anti-addition with nucleophilic attack on an epitelluronium intermediate by ethyl

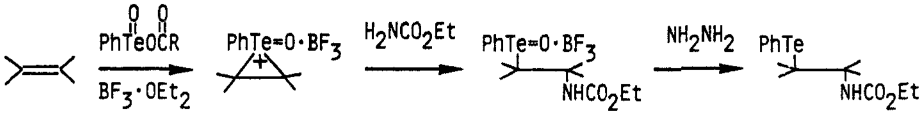
TABLE IV Aminotellurinylation of olefins

Run	Olefin	Reagent	Product	Yield (%)[a]
1	$PhCH=CH_2$	$Ph\underset{\underset{O}{\parallel}}{Te}O\underset{\underset{O}{\parallel}}{C}CH_3$	$Ph\underset{\underset{NHCO_2C_2H_5}{\vert}}{C}HCH_2TePh$	97
2	$PhCH_2CH=CH_2$	$Ph\underset{\underset{O}{\parallel}}{Te}O\underset{\underset{O}{\parallel}}{C}CH_3$	$PhCH_2\underset{\underset{NHCO_2C_2H_5}{\vert}}{C}HCH_2TePh + PhCH_2\underset{\underset{TePh}{\vert}}{C}HCH_2NHCO_2C_2H_5$	45 (62 : 38)[b]
3	$PhCH_2CH=CH_2$	$Ph\underset{\underset{O}{\parallel}}{Te}O\underset{\underset{O}{\parallel}}{C}CF_3$		83 (61 : 39)
4	$Ph\underset{\underset{CH_3}{\vert}}{C}=CH_2$	$Ph\underset{\underset{O}{\parallel}}{Te}O\underset{\underset{O}{\parallel}}{C}CF_3$	$Ph\underset{\underset{NHCO_2C_2H_5}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}CH_2TePh$	78
5	$n\text{-}C_4H_9CH=CH_2$	$Ph\underset{\underset{O}{\parallel}}{Te}O\underset{\underset{O}{\parallel}}{C}CF_3$	$n\text{-}C_4H_9\underset{\underset{NHCO_2C_2H_5}{\vert}}{C}HCH_2TePh + n\text{-}C_4H_9\underset{\underset{TePh}{\vert}}{C}HCH_2NHCO_2C_2H_5$	73 (90 : 10)
6	$n\text{-}C_{14}H_{29}CH=CH_2$	$Ph\underset{\underset{O}{\parallel}}{Te}O\underset{\underset{O}{\parallel}}{C}CF_3$	$n\text{-}C_{14}H_{29}\underset{\underset{NHCO_2C_2H_5}{\vert}}{C}HCH_2TePh + n\text{-}C_{14}H_{29}\underset{\underset{TePh}{\vert}}{C}HCH_2NHCO_2C_2H_5$	86 (86 : 14)
7	Cyclohexene	$Ph\underset{\underset{O}{\parallel}}{Te}O\underset{\underset{O}{\parallel}}{C}CF_3$		86

a) With $BF_3 \cdot OEt_2$ (1.2 eq.) and $NH_2CO_2C_2H_5$ (20 eq.) in refluxing $CHCl_3$ for 20 h.

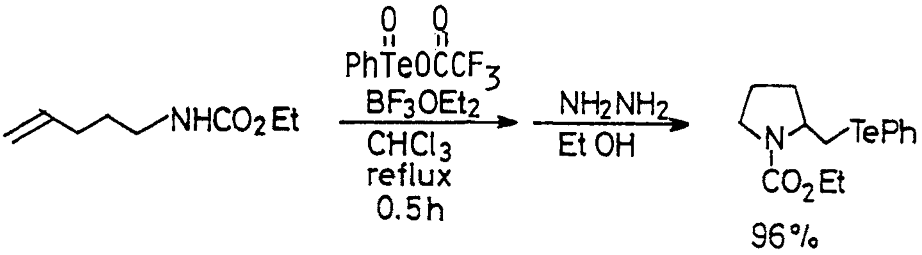
b) Isomer ratio.

carbamate. This fact was confirmed by comparison with the authentic trans form prepared in an independent experiment.



We have studied the catalytic effect of some Lewis acids on the aminotellurinylation. As shown in Table V, boron trifluoride etherate was very effective. The other Lewis acids such as zinc iodide and aluminum chloride were ineffective, though stannic chloride somewhat accelerated the reaction.

Next we report on intramolecular aminotelluration. When a carbamate group was introduced at a suitable position of an olefinic molecule, an intramolecular cyclization occurred to give a nitrogen heterocycle bearing an aryltelluromethyl as exemplified below.[7]



Such cyclofunctionalization is very valuable because of its synthetic application to natural products and related compounds. The cyclization is complete within 30 min and is much faster than the above intermolecular one.

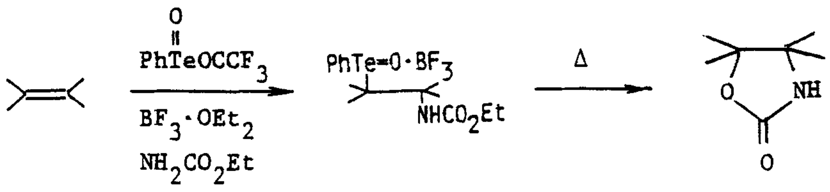
Finally, we wish to report further extension of the aminotellurinylation reaction to 2-oxazolidinone synthesis. When the reaction was carried out at a higher temperature in refluxing 1,2-dichloroethane, a tellurium free product, 2-oxazolidinone, was obtained in high yield as shown below.[8] Diphenylditelluride was isolated as a byproduct.

TABLE V Catalytic activities of some Lewis acids in aminotellurinylation.

Run	Olefin	Reagent	Catalyst	Product	Yield (%)
1	$\mathrm{PhCH{=}CH_2}$	$\mathrm{Ph\underset{\overset{\|}{O}}{Te}O\underset{\overset{\|}{O}}{C}CH_3}$	$\mathrm{BF_3{\cdot}O(C_2H_5)_2}$	$\mathrm{Ph\underset{\underset{NHCO_2C_2H_5}{\vert}}{C}HCH_2TePh}$	97
2	$\mathrm{PhCH{=}CH_2}$	$\mathrm{Ph\underset{\overset{\|}{O}}{Te}O\underset{\overset{\|}{O}}{C}CH_3}$	$\mathrm{SnCl_4}$		51
3	$\mathrm{PhCH_2CH{=}CH_2}$	$\mathrm{Ph\underset{\overset{\|}{O}}{Te}O\underset{\overset{\|}{O}}{C}CH_3}$	$\mathrm{BF_3{\cdot}O(C_2H_5)_2}$	$\mathrm{PhCH_2\underset{\underset{NHCO_2C_2H_5}{\vert}}{C}HCH_2TePh}^{a}$ + $\mathrm{PhCH_2\underset{\underset{TePh}{\vert}}{C}HCH_2NHCO_2C_2H_5}^{a}$	45^{b}
4	$\mathrm{PhCH_2CH{=}CH_2}$	$\mathrm{Ph\underset{\overset{\|}{O}}{Te}O\underset{\overset{\|}{O}}{C}CH_3}$	$\mathrm{SnCl_4}$		10^{b}
5	$\mathrm{PhCH_2CH{=}CH_2}$	$\mathrm{Ph\underset{\overset{\|}{O}}{Te}O\underset{\overset{\|}{O}}{C}CH_3}$	$\mathrm{AlCl_3}$		trace^{b}
6	$\mathrm{PhCH_2CH{=}CH_2}$	$\mathrm{Ph\underset{\overset{\|}{O}}{Te}O\underset{\overset{\|}{O}}{C}CH_3}$	$\mathrm{ZnI_2}$		0
7	$\mathrm{PhCH_2CH{=}CH_2}$	$\mathrm{Ph\underset{\overset{\|}{O}}{Te}O\underset{\overset{\|}{O}}{C}CF_3}$	$\mathrm{BF_3{\cdot}O(C_2H_5)_2}$	(52 : 38)	82

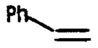
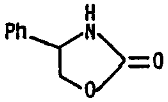
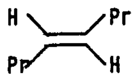
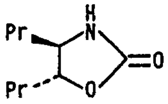
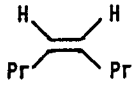
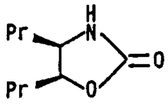
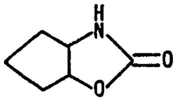
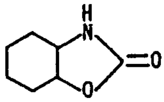
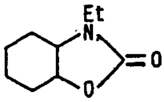
a) Isomer ratios in Runs 3-5 were not determined.

b) Total yield.



As demonstrated in Table VI, the reaction affords highly regio- and stereoselective products. We reasonably assume that the reaction proceeds initially with high Markovnikov regio- as well as trans-selectivity to yield an aminotellurinylated adduct, which is then converted to 2-oxazolidinone by S_N2 type backside attack of carbonyl oxygen on the carbon carrying the benzenetellurinyl group. Consequently high net cis stereoselectivity is realized.

TABLE VI 2-Oxazolidinone synthesis from olefins.

Run	Substrate	Product	Yield/%
1			91
2			53
3			84
4			92
5			86
6			76a)

a) Ethyl N-ethyl carbamate was used.

Because effective deprotection methods are known, the present reaction constitutes a useful approach to β-functionalized amines from olefins.

CONCLUDING REMARK

This paper describes many new reactions of arenetellurinic acid anhydrides. Since there have been developed a number of chemical modifications of aryltelluro groups such as reductive detelluration, oxidative elimination, halogenolysis, and methanolysis,[9] we believe the present reactions provide useful new synthetic means to a variety of interesting compounds.

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