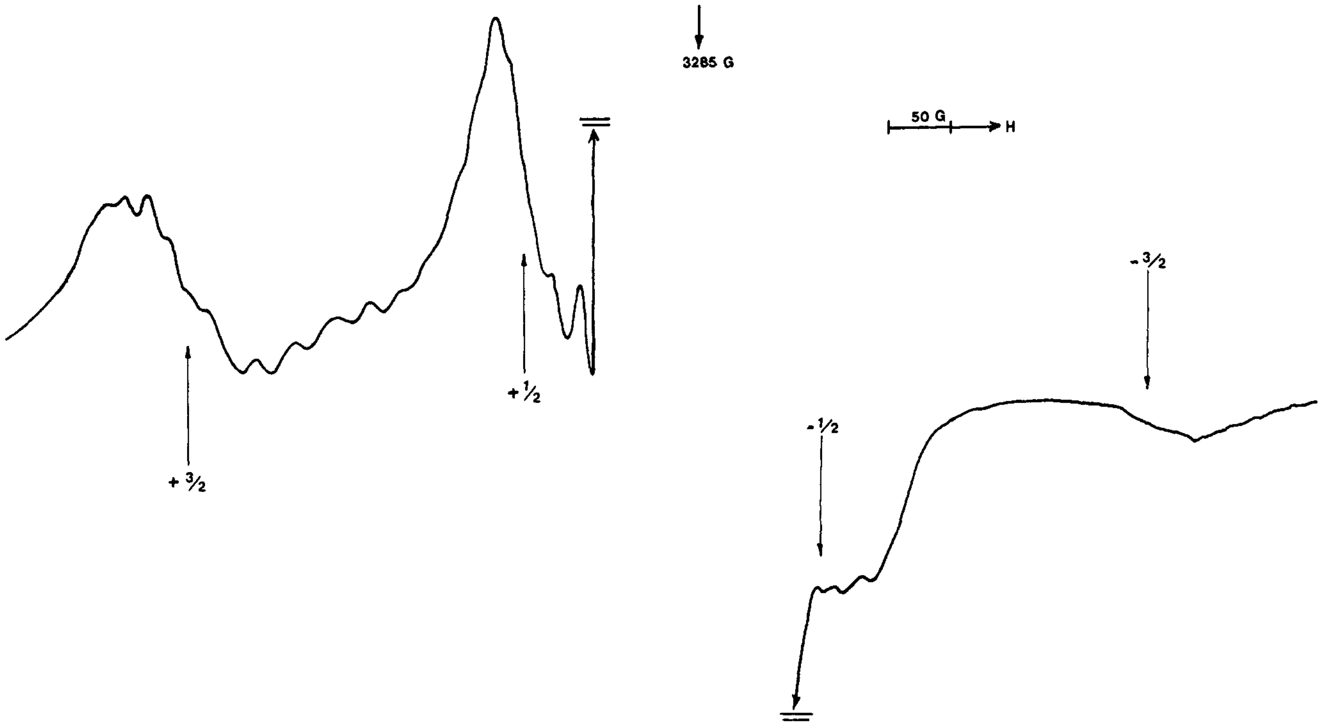

Figure 1. Esr spectrum for *n*-butyl bromide after exposure to γ rays at 77°K, showing hyperfine features assigned to the radical $CH_3CH_2\dot{C}HCH_2Br$. Central features from other species are omitted for clarity.

anisotropies detected, though small, correspond to about three times as much valence p character, which strongly suggests that it is the C–X σ bonds which are involved in the delocalization mechanism, as is implied by the preferred conformation and required by the theory of hyperconjugation.

The s character on halogen increases steadily from chlorine to iodine. This probably reflects the increasing availability of the valence s orbitals for bonding in this sequence. We stress that hyperfine interaction to β-fluorine atoms, which has received a great deal of recent attention,[4,5] is negligibly small when compared with the present phenomena. Furthermore, it seems most likely that a different mechanism is involved.[4]

The results for the group IV compounds have close links with the very interesting studies of Traylor and his coworkers,[6] who have shown that the electrophilic reactivity of aromatic compounds containing $-CH_2X$ substituents is greatly enhanced, provided that the X group is free to adopt conformations comparable with I. Similarly, our present results shed light upon the problem of the stereochemistry of halogen addition to olefins. Clearly, if structure I is strongly favored energetically, further addition is likely to be trans to the group X.

The results for *tert*-butyl bromide, whose spectra were relatively well resolved, rule out the anticipated structure $H_2\dot{C}C(Me)_2Br$, which would only be expected to have two strongly interacting protons. The structure is probably $Me_2\dot{C}CH_2Br$, with eight almost equivalent protons, but, if this is the case, the methyl proton coupling is smaller than usual. This could be taken to indicate a more symmetrical bridged structure.[7]

The best results for the chloro compounds were obtained with $(CD_3)_3CCl$ (Table I). Again, the number of lines obtained on each main feature (≥ 13) requires us to postulate a 1,2 migration of the chlorine atom.[8]

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[4] M. Iwasaki, *Mol. Phys.*, 20, 503 (1971).

[5] G. R. Underwood, V. L. Vogel, and I. Krefting, *J. Amer. Chem. Soc.*, **92**, 5019 (1970).

[6] W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 7476 (1970).

[7] It seems probable that the unidentified species in irradiated butyl bromide mentioned by M. L. Bonin, M. A. Bonin, and F. Williams [*J. Chem. Phys.*, **54**, 2641 (1971)] is the radical $CH_3CH_2\dot{C}HCH_2Br$.

[8] A referee has drawn our attention to recent work of A. J. Bowles, A. Hudson, and R. A. Jackson [*Chem. Phys. Lett.*, **5**, 552 (1970)] who detected the radical H_2CCH_2Cl in fluid solution. Their results show clearly that the structure is asymmetric and that the chlorine atom is locked in the position indicated in I. Their isotropic coupling to ^{35}Cl (17.4 G) is, however, considerably smaller than ours for the $(CD_3)_2\dot{C}CD_2Cl$ radical. This difference arises partly because the coupling is strongly temperature dependent, decreasing on warming above 77°K, and possibly because there is a large error in our measurement which arises because the tensor components in the solid-state spectra overlap considerably.

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Thallium in Organic Synthesis. XXVIII. Selective Oxidation of Acetylenes to Carboxylic Acids, Acyloins, Benzils, and Arylacetic Acids with Thallium(III) Nitrate[1,2]

Sir:

Although one of the classic reactions of acetylene chemistry is mercury(II) salt catalyzed hydration of the C≡C bond, there is only one report on the analogous reaction of acetylenes with isoelectronic thallium(III) salts.[3] In view of the marked differences in the reac-

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[1] Part XXVII: A. McKillop, B. P. Swann, and E. C. Taylor, *J. Amer. Chem. Soc.*, **93**, 4919 (1971).

[2] We gratefully acknowledge partial financial support of this work by Eli Lilly and Co., Indianapolis, Ind.

[3] S. Uemura, R. Kitoh, K. Fujita, and K. Ichikawa, *Bull. Chem. Soc. Jap.*, **40**, 1499 (1967).

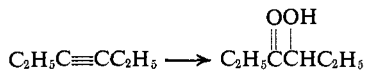
tions of olefins with mercury(II) and thallium(III) salts, and in particular thallium(III) nitrate (TTN),[4] we have investigated the reaction of this reagent with a variety of acetylenes. We have found that TTN effects not hydration but *oxidation* of the triple bond, where the nature of the product is strikingly dependent on the structure of the acetylene. Our results, which are summarized below, constitute a substantial extension of the utility of acetylenes as intermediates in organic synthesis.

Monoalkylacetylenes. These compounds reacted exothermically with 2 equiv of TTN in aqueous acidic glyme and underwent smooth degradation in high yield (70–90%) to carboxylic acids *containing one carbon atom less than the starting material.* For example, 1-octyne was converted into heptanoic acid in 80% yield (eq 1).[5]

$$C_6H_{13}C{\equiv}CH \longrightarrow C_6H_{13}COOH \qquad (1)$$

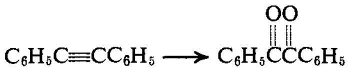
General Procedure. The terminal acetylene (0.01 mol) was added to a stirred solution of 0.02 mol of TTN in 25 ml of glyme, 15 ml of water, and 8 ml of 70% perchloric acid, and, after the initial vigorous reaction had subsided, the yellow reaction mixture was stirred at room temperature for a further hour. Complete removal of all of the thallium(I) salt was ensured by addition of 15 ml of 2 *N* potassium iodide solution, followed by stirring for a further 20 min. The inorganic salts were removed by filtration, and the filtrate was diluted with water and extracted with benzene. The extracts were dried (Na_2SO_4) and evaporated, and the residual oil was esterified by heating at 50° for 2 hr with 40 ml of methanol containing 5 ml of 70% perchloric acid. The cooled reaction mixture was diluted with water and extracted with benzene, and the extracts were concentrated and distilled to give the ester.

Dialkylacetylenes. Under the same reaction conditions, dialkylacetylenes were converted into acyloins in high yield (60–85%) on treatment with 1 equiv of TTN. For example, 3-hexyne was converted into 4-hydroxy-3-hexanone in 85% yield (eq 2).



$$C_2H_5C{\equiv}CC_2H_5 \longrightarrow C_2H_5\overset{\overset{O}{\|}}{C}\overset{\overset{OH}{|}}{C}HC_2H_5 \qquad (2)$$

Diarylacetylenes. Oxidation of diarylacetylenes with 1 equiv of TTN, again in aqueous acidic glyme, gave a 50:50 mixture of the benzil and unchanged starting material, but use of 2 equiv of TTN resulted in smooth conversion into benzils. For example, diphenylacetylene was converted into benzil in 85% yield (eq 3).[6]



$$C_6H_5C{\equiv}CC_6H_5 \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}C_6H_5 \qquad (3)$$

Yield data for representative conversions are given in Table I.

The experimental conditions for this conversion were the same as those specified above for effecting eq 1 and 2 except that the reaction mixture was heated under reflux for 2–7 hr prior to work-up.

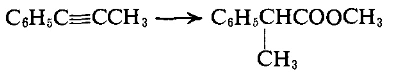
Table I. Oxidation of Diarylacetylenes to Benzils with $TTN–H_3O^+$

$$ArC{\equiv}CAr' \longrightarrow ArCOCOAr'$$

Ar	Ar'	Yield, %[a]
C_6H_5	C_6H_5	85
	$4\text{-}CH_3C_6H_4$	85
	$4\text{-}CH_3OC_6H_4$	75
	$2\text{-}NO_2C_6H_4$	65
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	97
	$4\text{-}CH_3OC_6H_4$	90
	$4\text{-}NO_2C_6H_4$	60
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	88

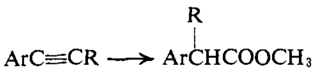
[a] Yields refer to pure recrystallized material.

Alkylarylacetylenes. Treatment of alkylarylacetylenes with TTN in aqueous acidic glyme gave mixtures of products arising from reactions similar to those outlined in eq 2 and 3. Thus, oxidation of methylphenylacetylene gave a mixture of unchanged starting material, methyl phenyl diketone, methyl benzyl ketone, and ethyl phenyl ketone.[7] When oxidation was carried out in methanol solution, however, smooth oxidative rearrangement occurred to give methyl arylacetates. For example, methylphenylacetylene was converted into methyl α-methylphenylacetate in 85% yield (eq 4). Yield data for representative conversions are given in Table II.



$$C_6H_5C{\equiv}CCH_3 \longrightarrow C_6H_5\underset{\underset{CH_3}{|}}{C}HCOOCH_3 \qquad (4)$$

Table II. Oxidative Rearrangement of Alkylarylacetylenes with $TTN–CH_3OH$



$$ArC{\equiv}CR \longrightarrow Ar\overset{\overset{R}{|}}{C}HCOOCH_3$$

Ar	R	Yield, %[a]
C_6H_5	CH_3	95
	C_2H_5	95
	$n\text{-}C_3H_7$	97
	$n\text{-}C_4H_9$	98
	CH_2CH_2Cl	95
	$CH_2C_6H_5$	92

[a] Yields were determined by glpc.

General Procedure. The alkyne (0.01 mol) was added to a stirred solution of 4.88 g (0.011 mol) of TTN in 25 ml of methanol and the mixture was heated under reflux for 2 hr. Thallium(I) nitrate was removed from the cooled reaction mixture by filtration, and the filtrate was extracted with ether or chloroform. The extracts were washed with water and 5% aqueous sodium bicarbonate solution and dried (Na_2SO_4). The solution was then filtered through a short column of Florisil (10 g) using chloroform as eluent; evaporation of the eluate gave the methyl α-alkylarylacetate which, in every case, was shown to be pure at this stage by glpc.

The remarkable specificity in these oxidations can be explained in terms of the probable mechanisms of the reactions. We suggest that oxidation of all types

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

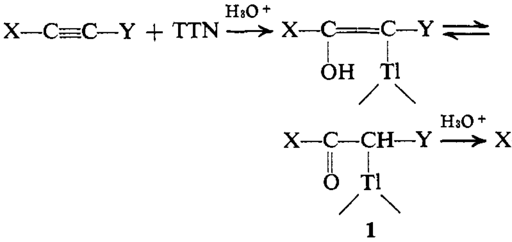
(5) H. Gopal and A. J. Gordon (*Tetrahedron Lett.*, 2941 (1971)) report the conversion of phenylacetylene and *tert*-butylacetylene to benzoic (66%) and pivalic acid (60%), respectively, with ruthenium tetroxide.

(6) An analogous conversion has recently been effected by ruthenium tetroxide (see ref 5).

(7) Examination of the ir spectrum of the crude reaction product indicated the presence of acyloins, but a quantitative analysis by glpc was not possible; acyloins are known to disproportionate under glpc conditions (D. L. Bunbury and M. S. Osyany, *J. Chromatogr.*, 14, 98 (1964)).

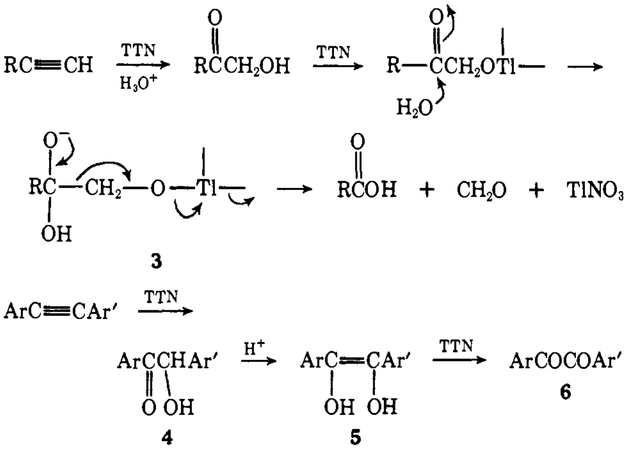
of acetylenes with 1 equiv of TTN in aqueous solution proceeds, as shown in Scheme I, to give initially the corresponding α-hydroxy ketone (**2**). The solvolytic instability of organothallium(III) derivatives of the type **1** is well documented[8] and hence the conversion **1** → **2** is unexceptional. This reaction sequence thus accounts for the formation of acyloins from dialkylacetylenes, and independent studies have established that acyloins are only slowly oxidized to the corresponding α-diketones with TTN. With both monoalkylacetylenes and diarylacetylenes, however, a second oxidation step occurs relatively rapidly, and hence 2 equiv of oxidant were required for completion of reaction. The mechanisms of these further oxidations are shown in Scheme II. Thallium(III) salts are known to undergo rapid ligand exchange with primary alcohols;[9] the intermediate **3** thus formed in the case of monoalkylacetylenes can then fragment to the observed carboxylic acid as shown. With diarylacetylenes the initial oxidation product is the corresponding benzoin **4**; subsequent oxidation of **4** to the benzil **6** *via* the enediol tautomer **5** has been shown to occur smoothly and in high yield under identical reaction conditions.[10,11]

Scheme I[a]



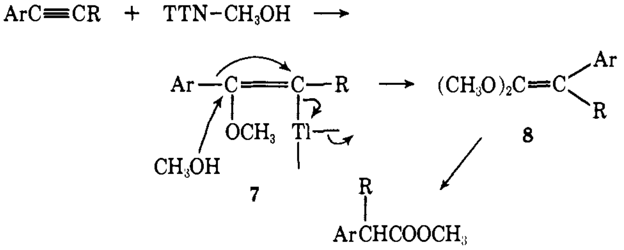
[a] X = Y = H, alkyl, aryl.

Scheme II



In none of the reactions summarized in eq 1–3 (*i.e.*, under aqueous conditions) was any product isolated which was derived from oxidative rearrangement of the initial oxythallation intermediate. This result is entirely in accordance with the reactions shown in Scheme I. Thus, 1,2-alkyl or -aryl migration in **1** would necessitate preliminary heterolysis of the C–Tl bond and formation of a carbonium ion α to an already electron-deficient carbon. Consequently, the preferred pathway in aqueous solution is S_N2 type solvolysis of the thallium substituent. Smooth oxidative rearrangement of alkylarylacetylenes to methyl α-alkylarylacetates was observed, however, in methanol solution (see eq 4 and Table II); the probable course of this conversion is represented in Scheme III, where the assumed initial methoxythallation product **7** is now (in contrast to **1**) ideally disposed for aryl migration. Attempts to isolate intermediates of the type **7** or **8** have so far proved unsuccessful, but the reaction sequence shown explains in a qualitative sense the relative ease of rearrangement with differently substituted aromatic groups. Thus, for the conversions $4\text{-}XC_6H_4C{\equiv}CH \rightarrow 4\text{-}XC_6H_4CH_2CO\text{-}OCH_3$ the yields of esters for X = NO_2, H, and CH_3O were 0, 17, and 61%, respectively, consistent with the relative migratory aptitudes of the aromatic groups.

Scheme III



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[8] W. Kitching, *Rev. Pure Appl. Chem.*, **19**, 1 (1969).

[9] R. Criegee, L. Kraft, and B. Rank, *Justus Liebigs Ann. Chem.*, **507**, 159 (1933).

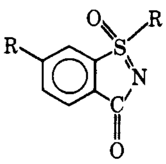
[10] A. McKillop, B. P. Swann, and E. C. Taylor, *Tetrahedron Lett.*, 5281 (1970).

[11] A. McKillop, M. E. Ford, B. P. Swann, and E. C. Taylor, to be published.

New Ring Systems of Carbon, Nitrogen, and Chiral Sulfur[1]

Sir:

In connection with our interest in compounds chiral at sulfur, we have prepared six new heterocyclic systems in which the sulfur, nitrogen, and carbon of the sulfoximide function are part of the ring system (**1–6**), one of them (**3**) in an optically active state. The first two heterocyclic systems (**7**[2] and **8**[3]) based on this function were announced when all new systems but **3** were in hand. Inspired by the report of **7**, we prepared **9** and confirmed the stability of the ring system.



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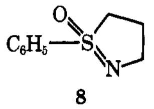

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Our syntheses[4] are outlined in Charts I, II, and III.

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[1] This investigation was supported by the U. S. Public Health Service, Research Grant No. GM 12540-07 from the Department of Health, Education, and Welfare.

[2] P. Stoss and G. Satzinger, *Angew. Chem., Int. Ed. Engl.*, **10**, 79 (1971).

[3] C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *J. Amer. Chem. Soc.*, **93**, 3771 (1971).

[4] All new compounds gave carbon and hydrogen analyses within