Reaction of Triazolinediones with Acetylenes. Electrophilic Addition[1]

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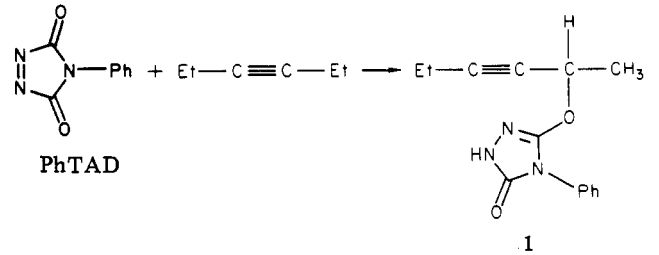
Products and rates of reaction of 4-phenyl-1,2,4-triazolinedione (PhTAD) with 3-hexyne, cyclooctyne, and several diarylacetylenes are reported. The major product from RTAD (R = phenyl or methyl) and Ar—C≡C—Ar (Ar = phenyl or 4-methoxyphenyl) is a 2:1 adduct **4a–d**, an unusual bis(azomethine imine), proven for **4b** by X-ray analysis. With PhTAD and bis(4-methoxyphenyl)acetylene, a trace (0.24%) of a 1:1 adduct was also isolated and assigned the 1,2-dihydrodiazete structure **10(Z)**. Reaction of RTAD with bis(4-methoxy-2,6-dimethylphenyl)acetylene afforded 1:1 adducts (20–26% isolated yield) assigned structures **10(X-1)** (R = phenyl) and **10(X-2)** (R = methyl). The kinetics and product data point strongly to the presence of *two* 1:1 species, **10** (isolated) and I (surmised but not directly observed), of which I is the primary precursor of the 2:1 adducts **4a–d**. Comparisons of the electrophiles PhTAD and Br_2 show that k(alkyl-substituted olefin)/k(alkyl-substituted acetylene) > 10^3, in accord with expectations for "three-center" reactions. The close parallels in relative rate of reaction of PhTAD and Br_2 with the alkyl-substituted unsaturated substrates are not observed with the aryl-substituted olefins and acetylenes.

Electrophiles react with carbon–carbon unsaturation to afford a variety of products and have received much mechanistic investigation.[2] We have been interested in the reactions of triazolinediones (RTAD) with olefins and have observed some marked similarities in the sensitivity of rate of reaction of olefins with RTAD, singlet oxygen, and bromine.[3] In this paper we report results on the reaction of triazolinediones with acetylenes.

Results

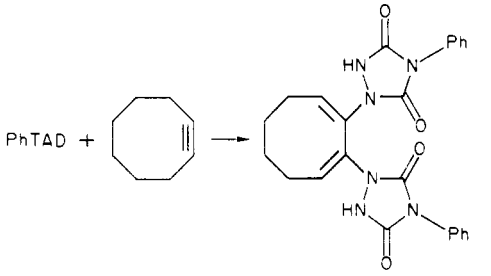
N-Phenyltriazolinedione (PhTAD) reacts with 3-hexyne slowly. When the acetylene is present in large excess (~100-fold), a product of limited stability is obtained to which is assigned structure 1 on the basis of the ^1H and ^{13}C NMR (eq 1).[4] At lower concentrations of the acetylene, the



PhTAD 1 (1)

product composition is complex and no discrete products could be obtained. Product 1 is stable to PhTAD in CH_2Cl_2.

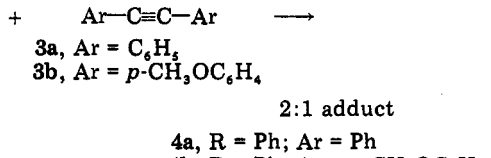
PhTAD reacts rapidly with cyclooctyne; the major product is a 2:1 adduct to which structure **2** is assigned (eq 2).[4]



(2)

2

Reaction of RTAD with a diarylacetylene in methylene chloride affords a colored product in high yield of composition 2 RTAD:1 diarylacetylene (eq 3). The NMR of

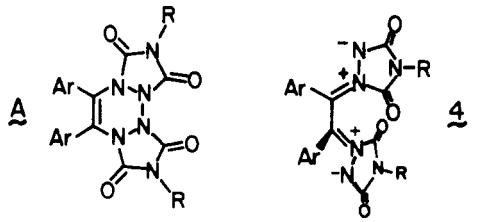


3a, Ar = C_6H_5
3b, Ar = p-$CH_3OC_6H_4$

2:1 adduct (3)

4a, R = Ph; Ar = Ph
4b, R = Ph; Ar = p-$CH_3OC_6H_4$
4c, R = CH_3; Ar = Ph
4d, R = CH_3; Ar = p-$CH_3OC_6H_4$

4 showed that the two aryl rings from **3** are intact and equivalent, the two acetylenic carbons from **3** (equivalent in the reactant) are still equivalent (though, of course, changed) in **4**, and the R groups of the two RTAD moieties in **4** are equivalent. The ^{13}C NMR shows two different carbonyl carbons and shows a chemical shift for the carbons holding the aryl groups at δ 138. These findings are consistent with A.[5] However, the color (e.g., deep red for **4b**) is not clearly associable with A.



4b, R = phenyl; Ar = p-$CH_3OC_6H_4$

The structure was shown by X-ray analysis to be the bis(azomethine imine) **4b**.[6]

(1) This work has been supported by the National Science Foundation.
(2) (a) Schmid, G. H.; Garratt, D. G. In "The Chemistry of Double-Bonded Functional Groups"; Patai, S., Ed.; Wiley: New York, 1977; Part 2, Chapter 9. (b) Freeman, F. *Chem. Rev.* **1975**, *75*, 439. (c) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 7599.
(3) Cheng, C. C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.*, preceding paper in this issue.
(4) The NMR data are summarized in the Experimental Section.
(5) Also of interest are other "tetrahydro" tetraaza analogues of benzene, dewarbenzene, benzvalene, and prismane.

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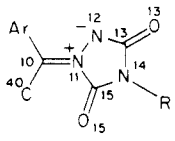
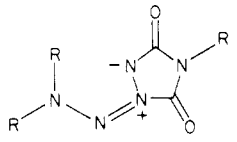
Table I. Selected Bond Lengths of Bis(azomethine imine) 4b[a]



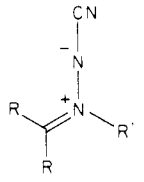
C_{10}–N_{11}	1.317	(1.346)	N_{14}–C_{15}	1.318	(1.335)
N_{11}–N_{12}	1.362	(1.362)	C_{15}–O_{15}	1.226	(1.212)
N_{12}–C_{13}	1.354	(1.350)	C_{15}–N_{11}	1.452	(1.469)
C_{13}–O_{13}	1.223	(1.199)	C_{10}–C_{40}	1.513	
C_{13}–N_{14}	1.426	(1.452)	C_{10}–Ar	1.428	(1.453)

[a] Numbers in parentheses are for the corresponding bonds in the lower half of the molecule (see structure 4).

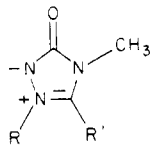
The *p*-methoxyphenyl group and the attached heterocyclic ring are close to planar, and each of these planes (the upper and lower halves of the molecule) is approximately perpendicular to each other. Bond distances of note are shown in Table I. Structures related to 4 are known, e.g., 5–8.[7,8] Structure 4 bears a close relationship to the class



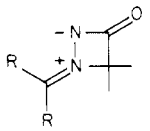
5[7b]



6[7c]



7[7d]



8[7e]

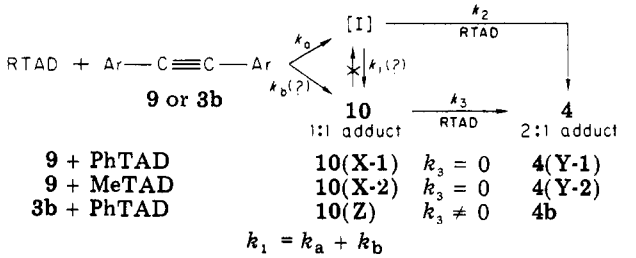
of "meso-ionic heterocycles".[9] One notes, however, that 4 is in a higher state of oxidation than the state to which the term "meso-ionic heterocycle" is now applied.[9]

Rates of reaction of PhTAD with the acetylenes **3a** and **3b** were determined in methylene chloride by following the rate of appearance of the 2:1 adduct 4. With PhTAD in excess, the reaction is cleanly first order in acetylene and first order in PhTAD (from runs at different concentrations of PhTAD), pointing to the general path of eq 4 in which k_2[C][PhTAD] > k_1[acetylene][PhTAD]. The re-

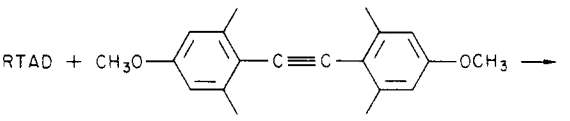
$$\text{PhTAD} + \text{Ar—C}\equiv\text{C—Ar} \xrightarrow{k_1} \underset{\text{1:1 species}}{[\text{C}]} \xrightarrow[\text{PhTAD}]{k_2} \underset{2:1}{4} \quad (4)$$

sults are summarized in the Experimental Section and in Table II (end of text).

Scheme I



In the hope of obtaining evidence on a 1:1 intermediate in the RTAD–arylacetylene reaction, the hindered acetylene **9** was investigated. PhTAD and MeTAD react with **9** in chloroform at room temperature (eq 5). The reaction



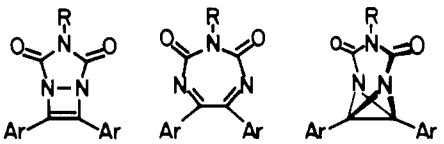
9

$$\underset{\text{1:1 adduct}}{\text{X}} + \underset{\text{"2:1 adduct"}}{\text{Y}} \quad (5)$$

R = Ph X-1 Y-1
R = CH_3 X-2 Y-2

is more complex (and slower) than with diarylacetylene **3b**. At an early point in the reaction (e.g., 25% reaction) two products, **X** and **Y**, were present in approximately equal amounts and the solution was dark red (in excess of that ascribable to RTAD). After several days the solution had lightened in color and the amount of **Y** had greatly decreased (based on NMR). Compound **X** was separated by preparative TLC.

Compounds **X-1** and **X-2** are colorless, stable 1:1 adducts of RTAD and **9**. Proton and ^{13}C NMR spectra of these adducts show unaltered aryl moieties and a high degree of symmetry.[4] Three possibilities are **10**, **11a**, and **11b**.



10 IIa IIb

10(X-1), R = Ph
10(X-2), R = CH_3

Ar = 2,6-dimethyl-4-methoxyphenyl

We assign structure **10** to **X** based on the ^{13}C NMR [one peak for the enamine carbons at 138.6 (imine carbons would be expected at lower field),[10] one peak for the carbonyl carbons at 156] and the IR [bands at 1780 (w) 1733 (vs) cm^{-1}, consistent with a triazolidinedione]. Compound **X-1** is stable at 160 °C for 30 min; at higher temperature it decomposes. Compounds **X-1** and **X-2** do not react further with PhTAD.

The second component, **Y**, from reaction of RTAD with the acetylene **9** (eq 5), was unstable and efforts to isolate it were unsuccessful. Evidence on its nature was obtained by 250-MHz NMR. After 40% reaction the solution contained MeTAD, **9**, **X-2**, and **Y-2**. Subtraction of the peaks for MeTAD, **9**, and **X-2** left four singlets at 3.74 (CH_3O-Ar, overlapping with CH_3O of **X-2**), 2.05, 3.12, and 6.49. The latter three were in the ratio 12:6:4 (ArCH_3:N-CH_3:Ar*H*) suggesting that **Y-2** is a 2:1 adduct of MeTAD and **9**. After several days the peaks for **Y-2** had disap-

(6) Compound **4a** (4, R = Ar = phenyl) is 1,1′-(1,2-diphenyl-1,2-ethanediylidene)bis[4-phenyl-3,5-dioxo-1,2,4-triazolidinium] dihydroxide, bis[inner salt]. We thank Dr. Loening at Chemical Abstracts for providing the name.

(7) (a) X-ray analyses have been reported for these compounds. (b) Weidenborner, J. E.; Fahr, E.; Richter, M. M.; Koch, K.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 236. (c) Huisgen, R.; Fleischmann, R.; Eckell, A. *Chem. Ber.* **1977**, *110*, 500. (d) LeClef, B.; Vermylen, L.; Viehe, H. G.; Meerssche, M. V.; Germain, G.; Declercq, J. P. *Tetrahedron Lett.* **1983**, *24*, 1035. (e) Calvo, C.; Ip, P.C.; Krishnamachari, N.; Warkentin, J. *Can. J. Chem.* **1974**, *52*, 2613, 3671.

(8) A structure related to 5 has been suggested for an orange product formed from PhTAD and 1,3-dimesitylbenzo[*c*]furan. Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1982**, 766.

(9) Newton, C. G.; Ramsden, C. A. *Tetrahedron* **1982**, *38*, 2965.

(10) Shamma, M.; Hindenlang, D. M. "Carbon-13 NMR Shift Assignments of Amines and Alkaloids"; Plenum Press: New York, 1979.

peared and the color of the solution had changed from red (intensity well over that attributable to MeTAD) to light yellow. These observations are consistent with assignment of the bis(azomethine imine) structure 4 (Ar = 2,6-dimethyl-4-methoxyphenyl, R = CH_3) to compound **Y-2**.

Thus, RTAD reacts with the hindered acetylene **9** to give a 1:1 adduct, **X** (**10**), and a second product, **Y**, considered to be a 2:1 adduct (**4**, R = Ph or CH_3, Ar = 2,6-dimethyl-4-methoxyphenyl). The 2:1 adduct is not formed by reaction of RTAD with the 1:1 adduct **X**, implying the presence of another intermediate, I (see Scheme I).

Might this pattern also apply to the unhindered acetylene **3b**? To maximize the possibility for an intermediate, I, to isomerize rather than to react with PhTAD, a solution of PhTAD (1 equiv) was added slowly (24 h) to a solution of acetylene **3b** (1 equiv). The major product was still the 2:1 adduct **4b**, but in addition a 0.25% yield of **Z**, a 1:1 adduct of PhTAD and **3b**, was isolated. Compound **Z** shows intact, and equivalent, aryl rings (NMR) and strong infrared absorption at 1735 cm^{-1} (similar to **X**), on which grounds it is assigned structure **10** (R = Ph, Ar = 4-$CH_3OC_6H_4$). Upon subjection to more PhTAD, **10(Z)** *is* converted to the 2:1 adduct **4b**. However, the 1:1 adduct **10(Z)** cannot be the precursor of the 2:1 adduct **4b** under the usual conditions of running the reaction (mixing of solutions of PhTAD and acetylene **3b** at "time zero") as shown by the following kinetics and product data. The rate of reaction of PhTAD and **Z** is first order in **Z** and first order in PhTAD.

$$\underset{\text{1:1 adduct}}{\mathbf{Z}} + \text{PhTAD} \xrightarrow{k_3 = 0.023 \pm 0.0008\ M^{-1}\ s^{-1}} \underset{\text{2:1 adduct}}{\mathbf{4b}} \quad (6)$$

This rate constant is comparable in magnitude to the rate constant k_1 for PhTAD and acetylene **3b** (eq 4, Table II) and is too small to serve as the major route for PhTAD and **3b** to **4b**. Consider the possibility of formation of **4b** from PhTAD and acetylene **3b** *only* by way of the 1:1 adduct **Z** (eq 7). For values of k_3 comparable to or even

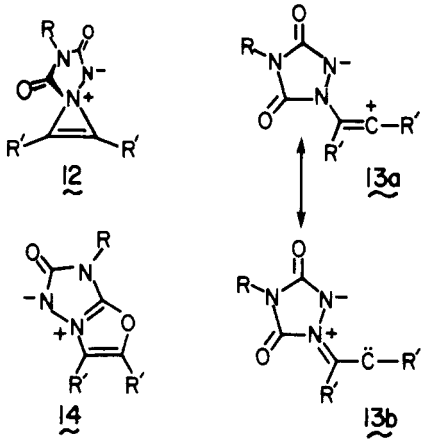
$$\text{acetylene } \mathbf{3b} + \text{PhTAD} \xrightarrow{k_1} \underset{\text{1:1 adduct}}{\mathbf{Z}} \xrightarrow[\text{PhTAD}]{k_3} \underset{\text{2:1 adduct}}{\mathbf{4b}} \quad (7)$$

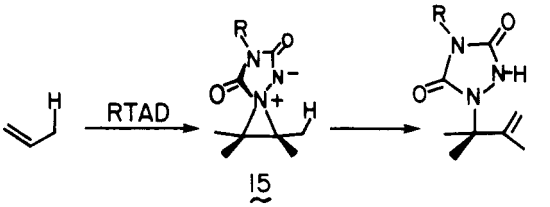
larger than k_1, substantial amounts of 1:1 adduct **Z** would build up.[11] experimentally, under the initial conditions of PhTAD/acetylene **3b** = 2, no **Z** could be detected during the reaction (and only 0.24% was obtained under the high dilution conditions described above). Thus, eq 7 is inadequate; another intermediate between reactants and **4** is needed. The results are accommodated by Scheme I.

In summary, both for the reactions of PhTAD with the hindered acetylene **9** and the unhindered acetylene **3b**, the product and kinetic data point to the presence of *two* 1:1 species, I and **10**. Species I reacts rapidly with PhTAD. For the hindered **10** (**X-1**) (derived from acetylene **9**) $k_3 \simeq 0$; for the much less hindered **10(Z)** (from acetylene **3b**), $k_3 \neq 0$. Thus, for this latter reaction the results imply there are *two different ways* to form the 2:1 adduct **4b**: k_2[I][PhTAD] and k_3[**Z**][PhTAD].[12] Also of interest is the ratio of k_2/k^1. Quantitatively, $k_2 \gg k_1$; the yield of **4b** is high (>90%, spectrophotometric) even at low initial concentrations of PhTAD and large excess of acetylene **3b**.

Some further points concern the origin and stability of the 1:1 adducts, **10**. Is an intermediate, I, the precursor of both **4b** (via k_2) and **10(Z)** (via k_i), or is **10(Z)** formed in some other way from the acetylene and RTAD (e.g., via k_b)? The extremely low yield of **10(Z)** prevents a distinction on this point at present.[13] However, **10**, once formed, is *not* converted to I (shown by the stability of the hindered 1:1 adducts, **10(X)** and **10(Y)** to the reaction conditions and by the finding that the conversion of the unhindered 1:1 adduct **10(Z)** to **4b** is first order in RTAD).

It is of interest to consider what I may be, e.g., **12**–**14** or possibly some looser 1:1 complex. Structure **12** is related to aziridinium imide **15**, an intermediate suggested for the ene reaction of RTAD with alkyl substituted olefins (eq 8).[14] Reaction of bis(4-methoxyphenyl)acetylene **3b**

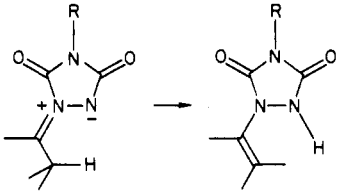




(8)

with PhTAD in acetone or acetonitrile afforded only the 2:1 adduct **4b** indicating the inability of these solvents to trap an intermediate here, at least in competition with RTAD, an apparently excellent trap for intermediate I.

The 2:1 products, **4**, of the RTAD–diarylacetylene reactions can be rationalized in many ways; the geometry of **4b** is in better accord with a precursor such as **14**[16] than with **13a,b**. The 2:1 product, **2**, from cyclooctyne may arise via a bis(azomethine imine) (related to **4**), followed by simple prototropic shifts (eq 9). The instability of **Y-1**



(9)

and **Y-2** (eq 5), considered to be of structure **4**, may also

(11) For example, for $k_3/k_1 = 2$ and $[\text{PhTAD}]_0/[\mathbf{3b}]_0 = 2$, at 50% consumption of PhTAD the yields would be **Z** (24%) and **4b** (38%), calculated from the equations in Frost, A. A.; Schwemer, W. C. *J. Am. Chem. Soc.* **1952**, *74*, 1268.

(12) Note that another possible path—**Z** to I followed by capture by PhTAD—is not in accord with the finding that the conversion of **Z** to **4b** is first order in PhTAD.

(13) The same question also arises concerning the origin of **10(X)** and **4(Y)**. The slowness of the reaction of **9** with PhTAD and the concomitant decomposition of both **Y** and PhTAD have hindered efforts to answer this important question.

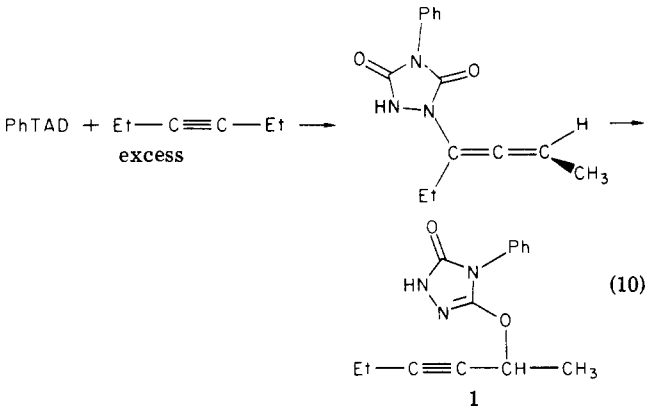
(14) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384.

(15) Reaction of PhTAD with some vinyl ethers in acetone has afforded tetrahydro-1,3,4-oxadiazene derivatives. Turner, S. R.; Guilbault, L. J.; Butler, G. B. *J. Org. Chem.* **1971**, *36*, 2838.

(16) Although **14** (R′ = 2,6-dimethyl-4-methoxyphenyl) is rather hindered, we note that PhTAD reacts rapidly with the hindered molecule 1,3-dimesitylbenzo[*c*]furan; see ref 8.

be due to prototropic rearrangement involving a neighboring benzylic hydrogen, a path not available to **4a–d**.

With 3-hexyne, the 1:1 adduct **1** was only observed when a high concentration of the acetylene was used. A possible path involves reaction of PhTAD and 3-hexyne to afford an allenylurazole followed by 3:3 rearrangement (eq 10).

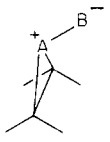


(10)

1

(We note that direct conversion of **12** to the allenyl urazole via *intra*molecular transfer of hydrogen from carbon to nitrogen seems difficult—the distance from the N to the H is approximately 3.5 Å.)[17]

Comparison of Electrophilic Reactions: RTAD and Bromine. In reactions with alkyl substituted olefins, these electrophiles (and others, e.g., singlet oxygen) show a high and similar degree of sensitivity of rate constant to olefin structure.[3] All three cases may proceed through three-center intermediates, such as **16** for RTAD[3,14] and singlet oxygen[18] and **17** for bromine. With aryl substituted



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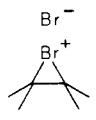

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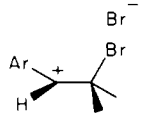

18

olefins, bromination appears to proceed through "open" ions **18**[19] (most simply shown by the nonadditive effect of substituents on the different aryl rings in the stilbene series).[19b] Reaction of RTAD with aryl-substituted olefins (stilbenes) shows a far smaller effect of *p*-methoxy, implying much less positive charge at benzylic carbon at the transition state. However, interpretation, at first sight, is complicated by the fact that the products are those of Diels–Alder addition.[20]

With acetylenes, bromination reactions follow the same pattern as with olefins: alkyl-substituted acetylenes via three-center species,[21] aryl substituted acetylenes via "open ions".[21] The data with PhTAD are rather limited but several facts stand out (Table II). Firstly, both for bromine and for RTAD, the rate of reaction with olefins exceeds the rate of reaction with acetylenes by several powers of ten. Secondly, there is a great difference between

Table II. Rates of Reaction of Alkenes and Alkynes with Phenyltriazolinedione and Bromine at 25 °C

substrate	PhTAD, CH_2Cl_2, k_1, M^{-1} s^{-1}	Br_2, CH_3OH, k_{Br_2},[a] M^{-1} s^{-1}
trans-3-hexene	0.16[b]	30 000[c]
styrene	7.5	1500[d]
trans-stilbene	0.46[e]	11[f]
trans-4-methoxystilbene	8.2[e]	26 000[f]
trans-4,4′-dimethoxystilbene	40[e]	73 000[g]
3-hexyne	~0.0001[h,i]	0.68[j]
tolan,[k] **3a**	0.0031[h]	0.0049[j]
4-methoxytolan[k]		20[j]
4,4′-dimethoxytolan,[k] **3b**	0.020[h]	
4-methyltolan[k]		0.19[j]
4,4′-dimethyltolan[k]		0.52[j]
4,4′-dimethoxy-2,2′,6,6′-tetramethyltolan,[k] **9**	~0.0004[h,i]	

[a] Note that the values tabulated are k_{Br_2}, not k_g. [b] Reference 3. [c] Calcd from k_g values (in Dubois, J. E.; Mouvier, G. *Bull. Soc. Chim. Fr.* **1968**, 1426) and k_g and k_{Br_2} values (in Kornprobst, J. M.; Dubois, J. E. *Tetrahedron Lett.* **1974**, 2203). [d] Bienvenue-Goetz, E.; Dubois, J. E. *J. Org. Chem.* **1975**, 40, 221. [e] Reference 20c. [f] Reference 19a. [g] Reference 19b. [h] This work. [i] Approximate value. [j] Reference 21. [k] Tolan is diphenylacetylene.

bromine and PhTAD in the effect of replacement of alkyl by aryl in the unsaturated (both olefinic and acetylenic) substrate. This change causes a large *decrease* in rate of reaction with bromine and a small-to-modest *increase* in rate with PhTAD (Table III).

Table III. Relative *k* Values (from Table II)

compd	Br_2	PhTAD
1,2-dialkyl olefin	60 000	0.35
1,2-diphenyl olefin	20	1.0
1,2-dialkylacetylene	1.2	~0.0002
1,2-diphenylacetylene	0.008	0.007

Thirdly, the PhTAD–aryl olefin and arylacetylene reactions are much less sensitive to substituent than are the corresponding bromination reactions, indicating that the benzylic carbon has undergone little change in charge at the transition state in these RTAD reactions. Thus, the close parallels between bromine and PhTAD in rates of reaction with alkyl substituted unsaturated systems do not carry over to the aryl substituted olefin and acetylenes. As noted above, the transition state in the bromine–aryl substituted olefin (and acetylene) reactions appears to resemble the "open" ion.[19] The simplest interpretation for the RTAD–unsaturation results is for a bridged transition state—one resembling a [2s (olefin) + 2a (RTAD)] array[3] or an aziridinium imide (like **12** or **15**).

Experimental Section

***N*-Phenyltriazolinedione (PhTAD) and *N*-methyltriazolinedione (MeTAD)** were prepared by the "Organic Syntheses" procedure.[22]

3-((1-Methylpent-2-yn-1-yl)oxy)-4-phenyl-1*H*-4,5-dihydro-1,2,4-triazol-5-one (1).[23] PhTAD (11:5 mg, 0.066 mmol) and 3-hexyne (Chemical Sample, 1.63 g, 19.9 mmol) were stirred until PhTAD was consumed (approximately 5 h). The excess 3-hexyne was evaporated under reduced pressure, affording 14 mg (82% yield) of an unstable oil: IR ($CDCl_3$, cm^{-1}) 1720 (vs), 1770 (sh); ^1H NMR (250 MHz, $CDCl_3$, Me_4Si, ppm) 1.12 (t, 3 H, J = 7.5 Hz), 1.39 (d, 3 H, J = 6.6 Hz), 2.19 (qd, 2 H, J = 7.5 Hz and 1.9 Hz), 4.71 (qt, 1 H, J = 6.6 Hz and 1.9 Hz), 7.4 (br, aryl

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(23) Attachment of the hexynyl moiety to oxygen rather than to N-1 of the 1,2,4-triazolyl ring is based on the ^{13}C chemical shift of the CH carbon at 72.4 ppm; in related nitrogen-bonded systems this carbon appears at higher field (40–45 ppm).

H's), 8.3 (br, 1 H); ^{13}C NMR (CD_2Cl_2, 1, $CH_3CH_2C{\equiv}CCH(CH_3)OR$)[23] 12.57 and 13.87 ($CH_2CH_3$), 19.72 ($CH_3$), 72.4 (CH),[23] 78.12 and 88.20 (C≡C), 126, 129, 131.27 (aryl), 154.94 (C=O). Attempted crystallization of the adduct from CH_2Cl_2 and pentane led to decomposition.

Reaction of PhTAD and 3-hexyne in CH_2Cl_2 afforded a complex mixture; the ^1H NMR showed broad absorption in the aliphatic region and strong absorption in the aromatic region (7.4).

Reaction of PhTAD and Cyclooctyne. A solution of cyclooctyne[24] (21.4 mg, 0.198 mmol) and PhTAD (69.3 mg, 0.396 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 1 h, affording a yellow solution and a white precipitate. The white precipitate (2) was obtained by filtration in 50% yield: mp 249–250 °C (methanol–water); IR (KBr, cm^{-1}) 3400 (m), 3100 (m), 2900 (m), 2840 (m), 1780 (m), 1750 (m), 1690 (vs), 1635 (m), 1490 (m), 1440 (m), 1400 (s), 1290 (m), 1140 (m), 760 (m), 700 (m), 615 (m). The ^1H NMR in Me_2SO-d_6 showed a triplet at 6.1 ppm (2 H, J = 8.0 Hz, vinyl H), a multiplet at 7.4 ppm (10 H, aryl H), and two broad bands (approximately 8 H) at 1.11 and 1.81 ppm. ^{13}C (MeSO-d_6, Me_4Si, ppm) 21.6, 26.4, 126.6, 126.7, 128.0, 128.7, 130.2, 131.5, 151.3, 152.0.

Anal. Calcd for $C_{24}H_{22}N_6O_4$ (Found): C, 62.87 (62.59); H, 4.84 (5.02); N, 18.33 (18.03).

Bis(azomethine imine) from PhTAD and Bis(4-methoxyphenyl)acetylene. 1,1'-(1,2-Bis(4-methoxyphenyl)ethanediylidene)bis(4-phenyl-3,5-dioxo-1,2,4-triazolidinium) Dihydroxide, Bis(inner salt) [4b]. A solution of 59.8 mg (0.25 mmol) of bis(4-methoxyphenyl)acetylene[25] and 87.5 mg (0.50 mmol) of PhTAD in 10 mL of chloroform was refluxed for 1 h. The solvent was evaporated under reduced pressure and the residue was recrystallized from CH_2Cl_2 and hexane, affording 136 mg of red needles (90% yield): mp 201 °C dec; IR ($CHCl_3$, cm^{-1}) 3000 (m), 1795 (m), 1700 (vs), 1595 (vs), 1380 (m), 1355 (m), 1120 (s), 800 (m); ^{1}NMR ($CDCl_3$, Me_4Si, ppm) 3.95 (s, 6 H), 7.07 (d, 4 H, J = 9.5 Hz), 7.45 (s, 10 H), 8.68 (d, 4 H, J = 9.5 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si, ppm) 56.0, 115.4, 122.5, 125.0, 128.4, 129.1, 130.7, 136.6, 138.5, 150.5, 157.8, 165.4; UV (CH_2Cl_2, nm) λ_{max} 256 (log e, 4.14), 332 (log e, 4.24), 460 (log e, 4.48).

Anal. Calcd. for $C_{32}H_{24}N_6O_6$ (Found): C, 65.30 (65.32); H, 4.11 (4.06); N, 14.28 (14.24).

X-ray Analysis of 4b. The crystals were monoclinic, space group $A2/a$, with a = 22.393 (9) Å, b = 16.117 (3) Å c = 16.614 (3) Å, β = 102.12 (3)°, and d_{calcd} = 1.334 g cm^{-3} for Z = 8 ($C_{32}H_{24}N_6O_6$, M_r = 588.58). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, $\theta - 2\theta$ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.04 × 0.04 × 0.55 mm. A total of 2752 independent reflections were measured for θ < 48°, of which 1436 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[26] and was refined by full-matrix least squares. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are R = 0.070 and w_R = 0.057 for the 1436 observed reflections. The final difference map has no peaks greater than ±0.3 e A^{-3}. The tables of atomic coordinates, bond lengths, bond angles, and final anisotropic thermal parameters are in the supplementary material.

Product Z (10, R = Phenyl, Ar = 4-Methoxyphenyl) from Reaction of Bis(4-methoxyphenyl)acetylene and PhTAD. To a solution of the acetylene (119 mg, 0.50 mmol) in1.0 mL of CH_2Cl_2 at room temperature was added PhTAD (87 mg, 0.50 mmol) in 5.0 mL of CH_2Cl_2 over a period of 24 h by means of a syringe pump. The dark red reaction mixture was subjected to preparative TLC (silica) with CH_2Cl_2 as the eluent and the compound with R_f = 0.47 was collected: 0.5 mg (0.24%) of a 1:1 adduct (**10(Z)**; mp 163–164 °C; IR ($CHCl_3$, cm^{-1}) 3040–2820 (w), 1735 (vs), 1600 (m), 1460 (m), 1375 (m), 1300 (w), 1250 (s), 1175 (m); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 3.84 (s, 6 H), 6.96 (d, 4 H, J = 8.7 Hz), 7.46 (s, 5 H), 7.77 (d, 4 H, J = 8.7 Hz); UV (CH_3CN, nm) λ_{max} 252 (log e, 4.22), 330 (log e 4.29); MS, calcd for $C_{24}H_{19}N_3O_4$ m/e 413.137, found 413.135.

Compound **Z** is converted by PhTAD in CH_2Cl_2 at 25 °C into the 2:1 adduct **4b**, established by observing the clean conversion in the ^1H NMR of the **Z** peaks to the **4b** peaks and by the strong UV band at λ 460 nm of **4b** (see "Kinetics" below).

Bis(azomethine imine) from PhTAD and Diphenylacetylene (4a).[6] The 2:1 adduct (obtained by the procedure for **4b** after refluxing overnight) was recrystallized from methylene chloride and hexane, affording 198 mg of brown crystals (75% yield): mp 175 °C dec; IR ($CHCl_3$, cm^{-1}) 3000 (m), 1805 (m), 1710 (vs), 1590 (m), 1485 (m), 1380 (s), 1350 (m), 1115 (s), 900 (m); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 7.33 (s, 10 H), 7.50 (m, 6 H), 8.60 (m, 4 H); UV (CH_2Cl_2, nm) λ_{max} 294 (log e 3.65), 427 (log e 3.72).

Anal. Calcd for $C_{30}H_{20}N_6O_4$ (Found): C, 68.17, (68.19); H, 3.81 (3.82); N, 15.91 (15.81).

Bis(azomethine imine) from MeTAD and Bis(4-methoxyphenyl)acetylene (4d). The 2:1 adduct (obtained by the above procedure) was stable in solution, but the solid decomposed upon standing: mp 200 °C; IR ($CHCl_3$, cm^{-1}) 3000 (s),1810 (m), 1700 (vs), 1595 (s), 1500 (s), 1400 (m), 1180 (vs), 1110 (s), 1020 (m), 920 (m); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 3.10 (s, 6 H), 3.90 (s, 6 H), 6.94 (d, 4 H, J = 9.4 Hz), 8.62 (d, 4 H, J = 9.4 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si, ppm) 26.2, 55.9, 115.3, 122.5, 136.3, 137.8, 151.7, 159.7, 165.1; UV (CH_2Cl_2, nm) λ_{max} 258, 333, 445.

Bis(azomethine imine) from MeTAD and Diphenylacetylene (4c). The yellow crystalline 2:1 adduct (obtained by the above procedure) had the following characteristic data: 202–203 °C; IR ($CHCl_3$, cm^{-1}) 1820 (m), 1715 (vs), 1590 (w), 1440 (w), 1380 (m), 1347 (w), 1250 (w), 1110 (s), 960 (w); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 3.13 (s, 6 H), 7.61 (m, 6 H), 8.45 (m, 4 H); UV (CH_2Cl_2, nm) λ_{max} 247, 293, 425. The purity of this new compound was not high enough to get correct combustion analysis.

Bis(2,6-dimethyl-4-methoxyphenyl)acetylene (9).[27] To a Grignard reagent solution at 0 °C, prepared from 1.2 g (0.050 mol) of Mg, 10 g (0.046 mol) of 4-bromo-3,5-dimethylanisole,[28] and 100 mL of THF, was added 0.1 g of $CoCl_2$ and 6.5 g (0.049 mol) of trichloroethylene under nitrogen atmosphere. The mixture was refluxed for 1 h. The solution was cooled, poured into cold water, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure, affording 4 g (60%) of dark oil. The oil was chromatographed on silica gel with hexane:methylene chloride (8:3) as eluent (R_f = 0.28). The crude acetylene (0.5 g) was recrystallized from acetic acid 3–4 times, affording 250 mg (4%) of colorless crystals: mp 202.5 °C; IR ($CHCl_3$, cm^{-1}) 3000 (m), 2980 (m), 2840 (m), 1600 (vs), 1323 (vs), 1278 (m), 1150 (vs), 1050 (m); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 2.55 (s, 12 H), 3.87 (s, 6 H), 6.72 (s, 4 H).

Anal. Calcd for $C_{20}H_{22}O_2$ (Found): C, 81.59 (81.33); H, 7.53 (7.60).

Reaction of Bis(2,6-dimethyl-4-methoxyphenyl)acetylene (9) with MeTAD. MeTAD (17.7 mg, 0.16 mmol) and starting acetylene (20.5 mg, 0.07 mmol) were dissolved in 2 mL of $CDCl_3$. The progress of the reaction was checked by NMR. After 4 days, the reaction mixture was separated by TLC with CH_2Cl_2 as the eluent (R_f = 0.46), affording 6.0 mg (21%) of **10(X-2)**: mp 199–200 °C (hexane); IR ($CHCl_3$, cm^{-1}) 3000–2800 (w), 1790 (w), 1725 (vs), 1600 (s), 1432 (s), 1322 (s), 1312 (s), 1190 (s), 1150 (s), 1065 (m); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 2.31 (s, 12 H), 3.16 (s, 3 H), 3.76 (s, 6 H), 6.57 (s, 4 H); UV (CH_3CN) λ_{max} 270 nm (log e, 4.06).

Anal. Calcd for $C_{23}H_{25}N_3O_4$ (Found) C, 67.79 (67.86); H, 6.18 (5.96); N, 10.31 (10.13).

Evidence for Y-1 from Bis(2,6-dimethyl-4-methoxyphenyl)acetylene with MeTAD. A solution of 10 mg (0.034 mmol) of the starting acetylene and 4.7 mg (0.042 mmol) of MeTAD in 0.8 mL of $CDCl_3$ was allowed to stand overnight and analyzed by 250-MHz ^1H NMR. The NMR spectrum showed peaks for reactants [acetylene **9** gave three singlets at 2.50 ($ArCH_3$), 3.78 (CH_3O), and 6.63 (aryl-*H*) in the ratio of 12:6:4 and MeTAD gave a peak at 3.2] and for two products (**X-2**: four singlets at 2.29 [$ArCH_3$], 3.14 [NCH_3], 3.74 [CH_3O, overlapping with a peak

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for **Y-2**], and 6.54 [aryl H] in the ratio of 12:3:6[29]:4; **Y-2**, assigned structure 4 [R = CH_3, Ar = 2,6-dimethyl-4-methoxyphenyl]: four singlets at 2.05 [$ArCH_3$], 3.12 [NCH_3], 3.74 [CH_3O, overlapping with a band for **X-2**], and 6.49 [aryl H] in the ratio 12:6:6[29]:4.) The ratio of acetylene **9**, MeTAD, **X-2**, and **Y-2** was 42:34:12:12.

Reaction of Bis(2,6-dimethyl-4-methoxyphenyl)acetylene with PhTAD. To a solution of 20.5 mg (0.07 mmol) of bis-(2,6-dimethyl-4-methoxyphenyl)acetylene in 4 mL of CH_2Cl_2 was added 26.8 mg (0.153 mmol) of PhTAD in 4 mL of CH_2Cl_2. The solution turned dark red. After stirring for 5 days at room temperature, the dark red solution was directly applied to a preparative TLC plate with CH_2Cl_2 as eluent (R_f = 0.58), affording 8.4 mg (26%) of urazole **10(X-1)**: mp 153.5 °C (hexane); IR (CHCl3, cm^{-1}) 3000–2820 (m), 1780 (w), 1733 (vs), 1600 (s), 1325 (m), 1315 (m), 1220 (m), 1192 (m), 1140 (s), 1068 (w); ^1H NMR ($CDCl_3$, Me_4Si, ppm) 2.37 (s, 12 He, 3.77 (s, 6 H), 6.59 (s, 4 H), 7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si, ppm) 21.22, 55.07. 113.75, 118.82, 125.37, 128.79, 129.27, 131.61, 138.63, 140.88, 156.01, 160.73; UV (CH_3CN, nm) λ_{max} 267 (log e, 4.16).

Anal. Calcd for $C_{28}H_{27}N_3O_4$ (Found): C, 71.62 (71.35); H, 5.80 (6.02); N, 8.95 (8.77).

Compound **X-1** was unchanged upon heating at 160 °C for 30 min; at higher temperature it decomposed. Compound **X-1** does not undergo further reaction with PhTAD.

Examination of the original reaction solution by NMR showed bands for urazole **X-1** (described above) and bands at 2.17 (s, $ArCH_3$), 3.76 (s, $ArOCH_3$), 6.50 (s, ArH), product **Y-1**. The peaks of *N*-phenyl group overlapped with those of PhTAD and urazole **X-1**. Efforts to isolate this second compound were unsuccessful.

(29) Overlapping peak, estimated number. (*Note*: This is the only overlapping peak in this spectrum of 12 possible [11 observed] peaks, all singlets.)

Into an NMR tube were placed 6.5 mg (0.22 mmol) of bis-(2,6-dimethyl-4-methoxyphenyl)acetylene, 3.9 mg (0.023 mmol) of PhTAD, and 0.5 mL of CD_2Cl_2. After 6 h the ^1H NMR spectrum of the reaction mixture showed three singlets for the $ArCH_3$ protons of starting acetylene, urazole **X-1**, and the second product, **Y-1**, in a ratio of 21:2:4, corresponding to 3.3×10^{-3} mmol of **Y-1**. The solution was diluted with CH_2Cl_2; λ_{max} of **Y-1** 472.5 nm (log e 3.96).

Kinetics. Rates of reaction of PhTAD with the acetylene were measured in CH_2Cl_2 at 25 °C under pseudo-first-order conditions (PhTAD in excess), following the appearance of the bis(azomethine imine), **4a** or **4b**.

4b: Initial concentrations of PhTAD $\times 10^3$, bis(4-methoxyphenyl)acetylene $\times 10^4$, k_1 in M^{-1} s^{-1}; 9.95, 3.85, 0.0203; 10.3, 1.96, 0.0207; 10.2, 0.99, 0.0202; 4.87, 1.96, 0.0198; 6.74, 1.96, 0.0207 (average k_1 for the five runs, 0.0200 ± 0.0003 M^{-1} s^{-1}). **4a**: PhTAD $\times 10^3$, diphenylacetylene $\times 10^4$, k_1 in M^{-1} s^{-1}; 9.77, 5.91, 0.00315; 9.58, 5.91, 0.0303 (average k_1 = 0.00309 ± 0.00006 M^{-1} s^{-1}). **4b from the 1:1 adduct Z**: PhTAD $\times 10^2$, compound **Z** $\times 10^5$, k_3 in M^{-1} s^{-1}; 1.84, 2.54, 0.0232; 0.68, 3.11, 0.0244; 1.10, 2.64, 0.0220 (average k_3 for the three runs, 0.0232 ± 0.0008 M^{-1} s^{-1}).

Registry No. 1, 90461-05-5; **2**, 90461-06-6; **3b**, 2132-62-9; **4b**, 90461-07-7; **4c**, 90461-10-2; **4d**, 90461-09-9; **9**, 90461-11-3; **10(X-1)**, 90461-13-5; **10(X-2)**, 90461-12-4; **10(Z)**, 90461-08-8; PhTAD, 4233-33-4; MeTAD, 13274-43-6; 3-hexyne, 928-49-4; cyclooctyne, 1781-78-8.

Supplementary Material Available: X-ray data for **4b** (tables of atomic coordinates, final anisotropic thermal parameters, bond lengths, bond angles, dihedral angles); ^{13}C NMR assignments for **2**, **4b**, **4d**, **10(X-1)**: UV spectra for **3b** and **4b**; kinetics data for **3b** with PhTAD (10 pages). Ordering information is on any current masthead page.

Stable Carbocations. 255.[1] α-Ethylenehaloarenium Ions

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Ionization of a series of *p*-halogen-substituted phenylethyl chlorides **1a–c** under stable ion conditions gave via phenyl participation the corresponding 4-halo-α-ethylenebenzenium ions **2a–c**. The stability of ions **2a–c** is affected by the halogen atoms through their "back donation". Similarly, ionization of 9-(2-fluoroethyl)-10-bromoanthracene (**7**) gave 9-(α-ethylene)-10-bromoanthracenium ion **6** by similar anthryl group participation. Ionization of 1-(2-haloethyl)-4-bromonaphthalenes **11a,b**, however, even at −110 °C gave only the rearranged benzylic ion **12** without any detectable 4-bromo-α-ethylenenaphthalenium ion **10**.

Extensive study of the solvolysis of 2-arylethyl systems, notably by Cram, suggested involvement of aryl participation forming α-ethylenebenzenium ions ("phenonium ions") as the reaction intermediates.[2] These ions subsequently have been observed under long-lived stable ion conditions.[3] The degree of phenyl participation in the solvolytic reactions has been shown to be dependent on the substituents in the phenyl ring. Electron-releasing groups in the para position such as methoxy and methyl have been shown to enhance phenyl participation whereas electron-withdrawing groups such as NO_2, CF_3, etc., diminish such participation.[2] The influence of para substitution by halogen atoms on the phenyl ring is of particular interest in view of the opposing inductive and conjugative effects. Solvolysis of 2-(*p*-chlorophenyl)ethyl esters has been shown to involve some phenyl participation, as indicated by Hammett plots of log K_t against the σ value of the substituent.[4] Deviation from the straight-line plots was taken as a measure of phenyl participation. Halogens are considered to be electron-withdrawing groups due to their electronegativity but at the same time they also have nonbonded electron pairs, which are well-known for their stabilizing ability of carbenium ion centers through their "back donation" ability, especially in the case of fluorine. The degree of "back donation" was found to be dependent on the electronegativity of halogen atoms.[5]

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