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Tellurium-Mediated Halogen Transfer from Polyhaloalkanes to Diyne Acceptors

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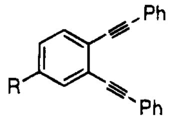
Elemental tellurium catalyzes transfer of halogen from $(CHCl_2)_2$, from C_2HCl_5 and from $(CHBr_2)_2$, to the phenylated diynes **1**−**3**, **17**, **20**, and **24**, in which the alkyne moieties are in close proximity. The process is associated with cyclorearrangement reactions by which halogenated polycycles are formed. In boiling C_2HCl_5, derivatives of 1,2-bis(phenylethynyl)benzenes afford 5-halogenated indeno[2,1-*a*]indenes, 1,8-bis(phenylethynyl)naphthalene gives a chlorinated benzo[*k*]fluoranthene derivative, and 2,2′-bis(phenylethynyl)[1,1′-biphenyl] forms 9-chloro-14-phenylbenz[*a,c*]anthracene. Diynes **25** and **26** in which the ethynyl functions are further removed from each other fail to yield halogenated products. Diyne **25** undergoes oxidative cyclization by which 1,3-diphenyldibenzo[3,4:6,7]cyclohepta[1,2-*c*]furan (**29**) is formed. Compound **26** is transformed to hydrocarbon **32**, which involves a phenyl ring walk and elimination of H_2Te.

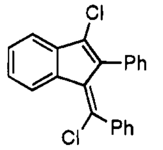
Recently[1] we reported that elemental sulfur in polyhalogenated alkanes adds to 1,2-bis(phenylethynyl)benzene (**1**) and to similar phenylated diynes to give sulfur heterocycles as well as organic sulfides and disulfides. In some cases these addition processes could be catalyzed by the rhodium chloride−tricaprylmethylammonium chloride ion pair.[2] We expected, therefore, that substitution of the sulfur by tellurium would furnish analogous organotellurium compounds. In fact, this did not happen. Instead we obtained tellurium-free halogenated products. In this paper we show that this new tellurium-mediated halogen transfer reaction is a useful catalytic process for the preparation of a variety of halogenated polycyclics.

Results and Discussion

Prolonged heating (1−2 weeks) of diyne **1** in boiling 1,1,2,2-tetrachloroethane (TCE) resulted in the formation of traces of (*Z*)-3-(chlorophenylmethylene)-2-phenyl-1-chloroindene (**4**) that was characterized by X-ray diffraction analysis.[3] This halogen transfer from the solvent to the diyne acceptor could be dramatically enhanced by elemental tellurium. When, for example, 1 mmol of **1** was heated for 24 h with 1 mmol of Te in 2 mL of TCE at 140 °C, 51% of **4** was isolated. In boiling pentachloroethane (PCE) (156 °C, 24 h) the main product (61%) was the known 5-chloro-10-phenylindeno[2,1-*a*]indene (**7**)[4] contaminated with only 12% of **4**. The amount of Te could be reduced by a factor of 5 without affecting the composition of the product mixture, although a longer reaction period was required. In the absence of Te, however, no compound **7** was formed.



1: R = H
2: R = CH_3
3: R = Cl



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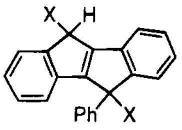

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Application of 1,1,2,2-tetrabromoethane as solvent (170 °C, 2 h) led to the conversion of **1** into 6% of 5-bromo-10-phenylindeno[2,1-*a*]indene (**8**) (which proved to be identical with an authentic sample prepared from 5-phenylindeno[2,1-*a*]indene and Br_2).[4] In this experiment the reacted solvent was transformed to 1,2-dibromoethene.

Although **4** was found to be the only chlorinated product of **1** at 140 °C, and the formation of **7** was shown to prevail at 156 °C, **4** could not be converted into **7** upon treatment with Te in boiling PCE. Thus, we conclude that **4** is not an intermediate in the formation of **7**. Neither can indeno[2,1-*a*]indene (**6**) be regarded as the precursor of **7** and **8** in the transfer halogenation reactions: the halogen-free parent compound **6**[5] is not affected at all under our experimental conditions.

Both halogen-transfer reactions were shown to proceed equally well under inert and ambient atmosphere. They were neither stimulated by benzoyl peroxide nor by UV irradiation. The rate of formation of **4** proved, however, to increase by addition of small amounts of water and to decrease by careful elimination of traces of moisture. Addition of the diradical scavenger 1,4-cyclohexadiene,[6,7] was found to significantly inhibit the accumulation of **7**, but does not affect the generation of **4**. It should be noted

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

[1] Blum, J.; Badrieh, Y.; Shaaya, O.; Meltser, L.; Schumann, H. *Phosphorus, Sulfur, Silicon,* **1993**, *79*, 87.

[2] Badrieh, Y.; Greenwald, A.; Schumann, H.; Blum, J. *Chem. Ber.* **1992**, *125*, 667.

[3] Complete crystallographic data, including tables of positional and thermal parameters, tables of least squares planes, bond lengths, bond angles, and ORTEP and stereoscopic drawings have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[4] Müller, E.; Munk, K.; Fritz, H.-G; Suerbier, M. *Justus Liebigs Ann. Chem.* **1969**, *723*, 76.

[5] Badrieh, Y.; Blum, J., Amer, I.; Vollhardt, K. P. C. *J. Mol. Catal.* **1991**, *66*, 295.

[6] Turro, N. J.; Evenzahv, A.; Nicolaou, K. C., *Tetehedron Lett.* **1994**, *35*, 8089, and references cited therein.

[7] This reaction was carried out in a sealed pressure tube to avoid evaporation of the diene. At 156 °C, the total yield of **4** and **7** was after 5 h 86% and the ratio **4**:**7** was 7:3.

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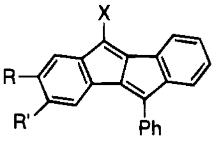
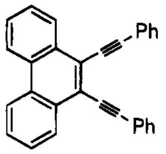
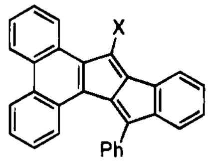
that the formation of each of the halogenated phenylindeno[2,1-*a*]indenes **7**, **8**, **11**, **12**, **15**, and **16** is associated with the elimination of a molecule of HCl. This suggests that **1** and its analogs give initially dihalides **5** which subsequently undergo thermal dehydrohalogenation.[4]



6: R = R' = X = H
7: R = R' = H, X = Cl
8: R = R' = H, X = Br
9: R = CH_3, R' = X = H
10: R = X = H, R' = CH_3
11: R = CH_3, R' = H, X = Cl
12: R = H, R' = CH_3, X = Cl
13: R = Cl, R' = X = H
14: R = X = H, R' = Cl
15: R = X = Cl, R' = H
16: R = H, R' = X = Cl



17

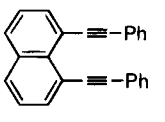


18: X = H
19: X = Cl

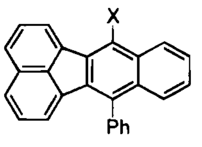
The general nature of the tellurium catalyzed halogen transfer process has been demonstrated by application of five further diynes as starting materials. 4-Methyl-1,2-bis(phenylethynyl)benzene (**2**) gave upon heating with Te in boiling PCE for 5 h, a 1:1 mixture of **11** and **12** in 79% yield. The two isomeric chlorine compounds proved difficult to separate, but pure **11** could be obtained by fractional crystallization from EtOH (see Experimental Section). The methylated analogs of **4** were obtained only in minute quantities as evidenced by the ^{1}H NMR (singlets at 2.49 and 2.53 ppm) and mass spectrum of the reaction mixture (*m*/*z* 366, 364, 362). Likewise, 4-chloro-1,2-bis(phenylethynyl)benzene (**3**) reacted in PCE for 4 h to give 83% of a 1:1 mixture of **15** and **16**, contaminated with hardly any dichloride of type **4**. In analogy to the unsubstituted 5-phenylindeno[2,1-*a*]indene (**6**) also the corresponding methyl- and chloro-substituted analogs **9**, **10**, **13**, and **14** (prepared in analogy to **1** from **2** and from **3**, respectively, and the $PtCl_4$-Aliquat 336 catalyst[5]) proved refractory to boiling PCE and Te. Neither analogs of **4** nor compounds **11**, **12**, **15**, or **16** were formed in these experiments.

9,10-Bis(phenylethynyl)phenanthrene (**17**)[8] in boiling PCE (20 h) yielded in addition to 59.4% of the expected chloro-compound **19**, 6.6% of 9-phenylbenzo[4,5]pentaleno[10,9-*l*]phenanthrene (**18**) which could be easily separated by chromatography on silica gel. The position of the chlorine atom in **19** was determined from the ^{13}C NMR spectrum. The chlorine-free compound **18** was identified by comparison with an authentic sample.[8]

1,8-Bis(phenylethynyl)naphthalene (**20**),[9] in which the two alkyne groups are separated by three carbon atoms, was shown to give in boiling PCE within 3 h 7-chloro-12-phenylbenzo[*k*]fluoranthene (**22**)[5] (26%) admixed with the chlorine-free compounds 7-phenylbenzo[*k*]fluoranthene (**21**)[10,11] (43%) and 12-phenylindeno[2,1-*a*]phenalene (**23**)[10,11] (10%). Since **21** has been reported to be formed simply by heating of **20**[10,11] there is no wonder why **21** is the major product in boiling PCE. The amount of **21** could, however, be reduced by heating the mixture of the tellurium catalyst in boiling PCE for 1 h prior to the addition of **20**. Under these conditions the product mixture consisted after 2 h of 56% of **22**, 20% of **23**, and only 7.5% of **21**.

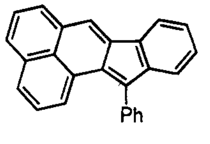


20

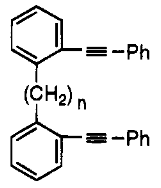


21: X = H
22: X = Cl

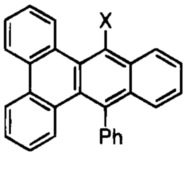
Treatment of diyne **24**[12] with Te in boiling PCE for 24 h afforded a mixture of 52% of 9-chloro-14-phenyldibenz[*a*,*c*]anthracene (**28**) contaminated with 35% of the chlorine-free compound **27**.[13] The structure of **28** was confirmed by 2D NMR (DQF-COSY) measurements.[14]



23

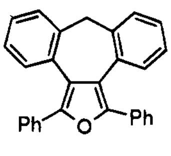


24: n = 0
25: n = 1
26: n = 2



27: X = H
28: X = Cl

Diynes in which the acetylenic groups are further removed one from each other, seem not to undergo tellurium catalyzed transfer halogenation. Under exclusion of oxygen 1,1'-methylenebis[2-(phenylethynyl)-benzene] (**25**)[8] gave, in boiling PCE in the presence of Te, a product that decomposed to a complex mixture of compounds. In the presence of air, the furan derivative **29** was isolated in 67% yield. The structure of **29** was established both by NOESY measurements[15] and by X-ray diffraction analysis of a single crystal.[3]



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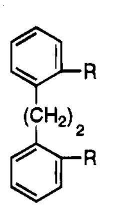
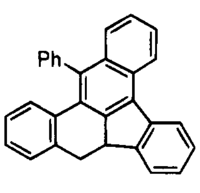


30: R = R' = I
31: R = I, R' = PhC≡C



32

The alkyne moieties in 1,1'-(1,2-ethanediyl)bis[2-(phenylethynyl)benzene] (**26**) are separated by six carbon atoms. This compound, which was prepared by the Heck enthynylation reaction from the diiodo-compound **30**[16] (and was fully characterized by X-ray diffraction analysis),[3] was transformed in boiling PCE in the presence of an equimolar quantity of Te to a mixture of 41% of 8b,9-dihydro-14-phenyldibenz[*a*,*j*]aceanthrylene (**32**) and 15% of the aromatized compound **33**. The structure of **32** was established by NOESY measurements as well as by X-ray diffraction analysis. The formation from **26** involves not only tellurium-associated intramolecular cyclization reac-

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[8] Baidossi, W.; Schumann, H.; Blum, J. Unpublished results.

[9] Tribble, M. T.; Traynham, J. G. *J. Am. Chem. Soc.* **1969**, *91*, 379.

[10] (a) Bossenbroek, B.; Shechter, H. *J. Am. Chem. Soc.* **1967**, *89*, 711. (b) Bossenbroek, B.; Sanders, D. C.; Curry, H. M.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 371.

[11] Staab, A.; Ipaktschi, J. *Chem. Ber.* **1971**, *104*, 1170.

[12] Kandil, S. A.; Dessy, R. *J. Am. Chem. Soc.* **1966**, *68*, 3027.

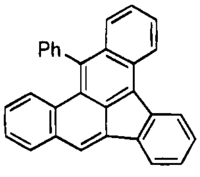
[13] White, E. H.; Sieber, A. F. *Tetrehedron Lett.* **1967**, *28*, 2713 and references cited therein.

[14] Dorome, A. E.; Williamson, M. P. *J. Magn. Reson.* **1990**, *88*, 177.

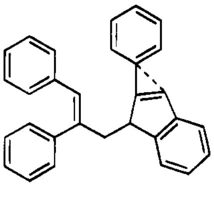
[15] Bodenhausen, G.; Kogler, H.; Ernst, R. R.; *J. Magn. Reson.* **1984**, *58*, 370.

[16] Leffler, J. E.; Wilson, A. F. *J. Org. Chem.* **1960**, *25*, 424.

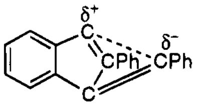
tions, but also a phenyl group walk (possibly in an intermediate step such as **34**) from an original β- to an α-acetylenic carbon atom. The conversion of **26** into **32** is associated with the elimination of hydrogen as H_2Te. When **32** was heated at 156 °C in the presence of Te a further molecule of H_2Te was evolved. Consequently, **33** was formed. This explains the contamination of **32** by **33** in the transformation of **26**.



33



34



35

Although no tellurium catalyzed halogen transfer has been investigated in the past, several cases of chlorination of double and triple bonds by $TeCl_4$ have been reported.[17] In order to be sure that our halogenation processes are basically different from that by $TeCl_4$, we heated the various phenylated diynes with $TeCl_4$ (as well as with Te_3Cl_2) in boiling PCE and in boiling mesitylene. In none of these experiments could we detect any of the chlorinated polycyclics formed under our standard conditions (Te in PCE).

In light of these experiments and those described above, we assume that the transformations of **1** to **4** and **7** follow two independent pathways. We postulate that the formation of **4**, which is neither affected by free radical initiators nor by free radical scavengers, but is enhanced by water, results from a dipolar addition of dihalogen or alkyltellurium halide to intermediate **35**.[18] The transformation of **1** to **7**, which is affected by 1,4-cyclohexadiene can result from homolytic addition of an alkyltellurium halide to a precursor of **6**[19] followed by elimination of an alkyltellurium molecule under pyrolytic conditions.[20,21] The involvement of organotellurium halides in the transfer halogenation processes explains the difference between the results obtained when Te, PCE, and **20** were heated together, and those obtained when Te and PCE were preheated prior to the addition of the diyne.

Experimental Section

1,2-Bis(phenylethynyl)benzene (**1**),[9] 9,10-bis(phenylethynyl)phenanthrene (**17**),[8] 9-phenylbenzo[4,5]pentaleno[10,9-*l*]phenanthrene (**18**),[8] 1,8-bis(phenylethynyl)naphthalene (**20**),[5] 2,2′-bis(phenylethynyl)[1,1′-biphenyl] (**24**),[12] and 1,1′-methylenebis[2-(phenylethynyl)benzene] (**25**)[8] were prepared as previously described.

3-Methyl-1,2-bis(phenylethynyl)benzene (2). A mixture of 10.3 g (30 mmol) of 3,4-diiodotoluene, 6.6 g (65 mmol) of phenylacetylene, 420 mg (0.6 mmol) of $(Ph_3P)_2PdCl_2$, 60 mg (0.15 mmol) of Cu_2I_2, and 20 mL of triethylamine was stirred under an Ar atmosphere at 60 °C for 6 h. The mixture was treated with excess 10% HCl solution, the amine hydrochloride was filtered off, and the resulting oil was diluted with ether, washed with water, dried and chromatographed on silica gel (using a mixture of 98% hexane and 2% ether as eluent) to give 7.62 g (87%) of pale yellow crystals; mp 95–96 °C (from hexane); 400-MHz ^1H NMR ($CDCl_3$) δ 2.37 (s, 3), 7.13 (dd, 1, $J_{3,5}$ = 1.8 Hz, $J_{5,6}$ = 7.5 Hz), 7.32–7.36 (m, 6), 7.40 (d, 1, $J_{3,5}$ = 1.8 Hz) 7.47 (d, 1, $J_{5,6}$ = 7.5 Hz), 7.57 (m, 4); 100-MHz ^{13}C NMR ($CDCl_3$) δ 21.22, 88.45, 88.47, 92.85, 93.19, 122.86, 123.36, 123.47, 125.59, 128.19, 128.30, 128.31, 129.02, 131.55, 131.61, 131.62, 132.29, 132.29, 138.15; MS (70 eV, 100 °C) *m*/*z* 292 ($M^{\cdot+}$, 100).[22] Anal. Calcd for $C_{23}H_{16}$: C, 94.52; H, 5.48. Found: C, 94.23; H, 5.58.

3-Chloro-1,2-bis(phenylethynyl)benzene (3) was obtained in 79% yield by a similar method from 3,4-diiodochlorobenzene; mp 103–104 °C (from hexane) 400-MHz ^1H NMR ($CDCl_3$) δ 7.30 (dd, 1, $J_{3,5}$ = 1.8 Hz, $J_{5,6}$ = 7.7 Hz), 7.39–7.41 (m, 6), 7.52 (d, 1, $J_{5,6}$ = 7.7 Hz), 7.60 (d, 1, $J_{3,5}$ = 1.8 Hz), 7.63–7.66 (m, 4); 100-MHz ^{13}C NMR ($CDCl_3$) δ 87.08, 87.36, 94.41, 94.70; 122.73, 122.93, 124.24, 127.26, 128.22, 128.31, 128.33, 128.52, 128.68, 131.41, 131.55, 131.64, 132.69, 133.70; MS (70 eV, 100 °C) *m*/*z* 314, 312 ($M^{\cdot+}$, 100).[22] Anal. Calcd for $C_{22}H_{13}Cl$: C, 84.48; H, 4.16. Found: C, 84.64; H, 4.32.

General Procedure for the Transfer Chlorination of Diynes. Typically, a stirred mixture of 1 mmol of the diyne, 0.02–1 mmol of tellurium powder, and 2 mL of either $(CHCl_2)_2$ or C_2HCl_5 was refluxed to allow the reaction to reach full conversion. (The progress of the process was monitored by TLC and/or NMR). The cooled mixture was diluted with CH_2Cl_2, and the Te was filtered off with the aid of Celite. The solvent was removed under reduced pressure, and the residue chromatographed on silica gel using mixtures of hexane and ether as eluent.

(*Z*)-3-(2-Chloro-2-phenylethynyl)-2-phenyl-1-chloroindene (4). Equimolar amounts of **1** and Te in $(CHCl_2)_2$ gave after 25 h 51% of yellow **4**: mp 168–169 °C; 400-MHz ^1H NMR ($CDCl_3$) δ 6.96 (m, 8), 7.11 (m, 2), 7.45 (m, 3), 8.58 (d, 1, $J_{3,4}$ = 7 Hz); MS (70 eV, 90 °C) *m*/*z* 352, 350, 348 ($M^{\cdot+}$, 42).[22] Anal. Calcd for $C_{22}H_{14}Cl_2$: C, 75.66; H, 4.04; Cl, 20.30. Found: C, 75.60; H, 4.17; Cl, 20.07.

A suitable crystal for X-ray diffraction analysis was obtained by slow crystallization from a 1:9 mixture of ether and hexane. Details of the crystal data, the experimental conditions, and a summary of the solution and refinement are given in Table 1.[3]

Reaction of 1 and Te in C_2HCl_5. When the previous experiment with 1 mmol of **1** was conducted in boiling C_2HCl_5 (156 °C) for 24 h followed by chromatography on silica gel (with mixtures of hexane and ether as eluent) the main product (213 mg, 61%) was the known 5-chloro-10-phenylindeno[2,1-*a*]indene (**7**) (identical in every respect with an authentic sample prepared according to Müller et al.[4] from 5-phenylindeno[2,1-*a*]indene (**5**) and $SOCl_2$). The minor product (37.5 mg 12%) was compound **4**.

5-Bromo-10-phenylindeno[2,1-*a*]indene (8). When 1 mmol of **1** in 4 mL of $(CHBr_2)_2$ was treated for 2 h with Te at 170 °C the only characterized solid product was 21.5 mg (6%) of **8** that proved identical with an authentic sample prepared by bromination of **5**.[4] The distilled solvent obtained after the reaction was separated by GC (Apiezon L) into the starting tetrabromoethane and 1,2-dibromoethene.

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[17] See e.g., (a) Back, T. G. in: *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S. Ed.; Wiley: Chichester, UK, 1987; Vol. 2, pp 94–213. (b) Irgolig, K.J. In *Methods of Organic Chemistry (Houben-Weyl)*, 4th ed.; Klamann, D. Ed.; Thieme Verlag: Stuttgart, Germany, 1990; Vol. E12b, and references cited therein. (c) Sudha, N.; Singh, H. B. *Coordin. Chem. Rev.* **1994**, *135/136*, 469.

[18] Cf., e.g., the addition of $RTeCl_3$ to C–C double bonds reported by Bäckvall, J. E.; Bergmann, J.; Engman, L. *J. Org. Chem.*, **1983**, *48*, 3918.

[19] Cf., Müller, E.; Munk, K.; Ziemek, P.; Sauerbier, M. *Justus Liebigs Ann. Chem.* **1968**, *247*, 153.

[20] See e.g. (a) Arpe, H. J.; Kuckertz, H. *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 73. (b) Ogawa, M.; Ishioka, R. *Bull. Chem. Soc.* **1970**, *43*, 496.

[21] One reviewer commended that the evidence at hand do not exclude the possibility that vinyl radicals are the reactive intermediates from which **4** originates by halogen abstraction, and **7** or its analogs, by an intramolecular homolytic aromatic substitution.

[22] Detailed mass spectral data are presented as supporting information.

[23] All non-hydrogen atoms were found by using the results of SHELXS86 direct-method analysis: Sheldrick, G. M. In, *SHELXS86. Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C.; Goddard, R. Eds.; Oxford University Press: London, 1986; pp 175–189. All crystallographic computing was done on a VAX9000 computer at the Hebrew University of Jerusalem, using the TEXSAN Structure Analysis Software.

Table 1. Summary of Crystal Data and Details of Strucutre Determination for 4, 26, 29, and 32

	4	**26**	**29**	**32**
empirical formula	$C_{22}H_{14}Cl_2$	$C_{30}H_{22}$	$C_{29}H_{20}O$	$C_{30}H_{20}$
fw	349.26	382.51	384.48	380.49
space group	$P\bar{1}$	$Pca2_1$	$C2/c$	$P2_1/n$
a, Å[a]	9.178 (3)	24.878(3)	43.581 (5)	14.846 (5)
b, Å	12.214 (4)	5.380 (1)	5.591 (1)	11.434 (2)
c, Å	8.847 (2)	16.018 (2)	17.972 (2)	12.057 (4)
α, deg	105.12 (2)			
β, deg	112.62 (2)	107.74(1)		105.50 (3)
γ, deg	68.05 (1)			
V, Å^3	841.1 (8)	2144.1 (5)	4171.0 (8)	1972 (1)
Z	2	4	8	4
ϱ_{calcd}, g cm^{-3}	1.38	1.19	1.22	1.28
μ, cm^{-1}	(Mo K_α) 3.84	(Cu K_α) 4.74	(Cu K_α) 5.27	(Cu K_α) 5.15
diffraction	PW 1100/20	CAD-4	CAD-4	CAD-4
radiation, Å	0.71069	1.54178	1.54178	1.54178
scanning technique	$\omega-2\theta$	$\omega-2\theta$	$\theta-2\theta$	$\theta-2\theta$
2θ, min, max, deg	3−50	3−120	3−120	3−120
scan width, deg	$1.00 + 0.35 \tan\theta$	$0.80 + 0.15 \tan\theta$	$0.80 + 0.15 \tan\theta$	$0.80 + 0.15 \tan\theta$
no. of unique reflections	2946	2372	3045	3104
no. of reflections with $I \geq 2\sigma(I)$	2457	1952	2247	2316
solution method	direct (SHELX86)[23]	direct (SHELX86)[23]	direct (SHELX86)[23]	direct (SHELX86)[23]
R[b]	0.037	0.063	0.034	0.043
R_w[c]	0.051	0.081	0.057	0.058

[a] Cell dimensions were determined by least squares fit of the setting angles for 24 reflections with 2θ in the range of 11−15° for **4**, 24−33° for **26**, 24−30° for **29**, and 22−29° for **32**. [b] $R = \Sigma|F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

2-Methyl- and 3-Methyl-5-phenylindeno[2,1-*a*]indene (9 and 10, respectively). A solution of 25 mg (0.075 mmol) of PtCl$_4$, in 2 mL of deionized water, and a solution of 61 mg (0.15 mmol) of Aliquat 336 and 292 mg (1 mmol) of **2** was refluxed (internal temperature 104 °C) and vigorously stirred for 6 h. After cooling, phase separation, and workup of the organic layer, the residual material was purified by column chromatography (95% hexane and 5% ether as eluent) to give 260 mg (89%) of a 1:1 mixture of **9** and **10** as dark red crystals from which **9** could be obtained in pure state by fractional crystallization from EtOH as pale yellow crystals: mp 158−159 °C. The structure of **9** was deduced from NOESY measurements (coupling through space of H1 and H10); 400-MHz ^{1}H NMR (CDCl$_3$) δ 2.19 (s, 3), 6.44 (s, 1), 6.57 (d, 1, $J_{1,3}$ = 1 Hz, $J_{3,4}$ = 7.7 Hz), 6.75 (d, 1, $J_{1,3}$ = 1 Hz), 6.88−7.00 (m, 3), 7.03 (d, 1, $J_{3,4}$ = 7.7 Hz), 7.11 (dd, 1, J_o = 5.2 Hz, J_m = 1 Hz), 7.40−7.44 (m, 3), 7.64 (dd, 2, $J_{2',3'}$ = 7 Hz, $J_{2',4'}$ = 1.5 Hz); 100-MHz ^{13}C NMR (CDCl$_3$) δ 21.38, 121.73, 121.92, 122.17, 124.47, 125.35, 127.27, 127.33, 127.80, 128.35, 128.59, 128.72, 131.94, 133.84, 135.23, 138.15, 140.24, 143.82, 148.57, 149.77, 150.49; MS (70 eV, 100 °C) m/z 292 (M$^{\cdot+}$, 100). Anal. Calcd for $C_{22}H_{16}$: C, 94.52; H, 5.48. Found: C, 94.22; H, 5.69.

The ^{1}H NMR spectrum of **10** was obtained by subtraction of the spectrum of **9** from the spectrum of the mixture of **9** and **10**: δ 2.13 (s, 3), 6.46 (s, 1), 6.67 (d, 1, $J_{1,2}$ = 7.8 Hz), 6.80−7.44 (m, 9), 7.63 (dd, 2, $J_{2',3'}$ = 7 Hz; $J_{2',4'}$ = 1.5 Hz).

10-Chloro-2-methyl- and 10-Chloro-3-methyl-5-phenylindeno[2,1-*a*]indene (11 and 12, respectively). The reaction of **2** and Te in PCE afforded after 4 h a 1:1 mixture of **11** and **12** in 79% yield. Fractional crystallization from EtOH gave pure **11** as orange crystals: mp 135−136 °C; 400-MHz ^{1}H NMR (CDCl$_3$) δ 2.55 (s, 3), 6.68 (dd, 1, $J_{1,3}$ = 0.9 Hz; $J_{3,4}$ = 7.6 Hz), 6.85 (d, 1, $J_{1,3}$ = 0.9 Hz), 6.95−6.99 (m, 3), 7.03 (d, 1, $J_{3,4}$ = 7.6 Hz), 7.38 (dd, 1, J_o = 6.8 Hz, J_m = 1.8 Hz), 7.41−7.54 (m, 3), 7.62 (dd, 2, $J_{2',3'}$ = 8.1 Hz, $J_{2',4'}$ = 1.2 Hz); 100-MHz ^{13}C NMR (CDCl$_3$) δ 21.43, 121.47, 121.92, 122.47, 122.86, 127.56, 127.94, 128.13, 128.40, 128.52, 128.67, 128.88, 130.96, 133.60, 133.68, 138.32, 139.89, 141.17, 142.03, 146.98, 148.98. Anal. of the mixture of **11** and **12**. Calcd for $C_{25}H_{15}Cl$: C, 84.53; H, 4.59; Cl, 10.87. Found: C, 84.83; H, 4.76; Cl, 10.68.

The ^{1}H NMR spectrum of **12** was obtained by subtraction of the spectrum of **11** from the spectrum of the mixture of both isomers: δ 2.17 (s,3), 6.78 (d, 1, J = 7.6 Hz), 6.90 (d, 1, J = 7.6 Hz), 6.89 (d, 1, $J_{2,4}$ = 0.9 Hz), 6.92 (dd, 1, J_o = 7.6 Hz, J_m = 1 Hz), 6.95−7.00 (m,2), 7.03 (d, 1, J = 7.6 Hz), 7.41−7.54 (m,3) 7.62 (dd, 2, $J_{2',3'}$ = 8 Hz, $J_{2',4'}$ = 1.2 Hz).

2-Chloro- and 3- Chloro-5-phenylindeno[2,1-*a*]indene (13 and 14, respectively). Under the conditions described for the preparation of **9** and **10**, diyne **3** was rearranged to a 1:1 mixture of dark red **13** and **14** in 92% yield. Compound **13** was obtained isomerically pure after chromatography on silica gel using a mixture of 97% hexane and 3% ether as eluent: mp 149−150 °C. The structure of **13** was deduced from NOESY measurements (coupling through space of H1 and H10); 400-MHz ^{1}H NMR (CDCl$_3$) δ 6.42 (s, 1), 6.74 (dd, 1, $J_{1,3}$ = 2 Hz; $J_{3,4}$ = 8.1 Hz), 6.89 (d, 1, $J_{1,3}$ = 2 Hz), 6.91−7.02 (m, 3), 7.03 (d, 1, $J_{3,4}$ = 8.1 Hz), 7.14 (dd, 1, J_o = 5.2 Hz, J_m = 2 Hz), 7.44−7.56 (m, 3), 7.63 (dd, 2, $J_{2',3'}$ = 8.1 Hz, $J_{2',4'}$ = 1.1 Hz); 100-MHz ^{13}C NMR δ 122.31,122.36, 122.64, 123.48, 123.99, 126.40, 127.79, 128.28, 128.30, 128.74, 129.13, 132.90, 133.38, 133.66, 135.00, 142.19, 142.57, 149.55, 149.68, 151.77; MS (70 eV, 100 °C) m/z 314, 312 (M$^{\cdot+}$, 100). Anal. Calcd for $C_{22}H_{13}Cl$: C, 84.48; H, 4.16; Cl, 11.36. Found: C, 84.69; H, 4.21; Cl, 11.37.

The ^{1}H NMR spectrum of **14** was obtained by subtraction of the spectrum of **13** from the spectrum of the mixture of **13** and **14**: δ 6.44 (s, 1), 6.83 (dd, 2, J_o = 7.8 Hz, J_m = 1.4 Hz), 6.91−7.02 (m, 3), 7.06 (d, 1, $J_{2,4}$ = 1.4 Hz), 7.15 (dd, 1, J_o = 6 Hz, J_m = 2 Hz), 7.44−7.55 (m, 3), 7.65 (dd, 2, $J_{2',3'}$ = 8 Hz, $J_{2',4'}$ = 1 Hz).

2,10-Dichloro- and 3,10-Dichloro-5-phenylindeno[2,1-*a*]indene (15 and 16, respectively). The reaction of **3** and Te in PCE for 5 h gave a 1:1 mixture of **15** and **16** in 83% yield. Fractional crystallization from EtOH afforded 95% isomerically pure **15** as red crystals: mp of this mixture 145−146 °C; 400-MHz ^{1}H NMR of **15** (CDCl$_3$) δ 6.84 (dd, 1, $J_{1,3}$ = 1.7 Hz; $J_{3,4}$ = 7.7 Hz), 6.95 (d, 1, $J_{1,3}$ = 1.7 Hz), 6.98−7.01 (m, 3), 7.04 (d, 1, $J_{3,4}$ = 7.7 Hz), 7.37 (dd, 1, J_o = 7.2 Hz, J_m = 1.9 Hz), 7.44−7.56 (m, 3), 7.61 (dd, 2, $J_{2',3'}$ = 7 Hz, $J_{2',4'}$ = 1.5 Hz); 400-MHz ^{1}H NMR of **16** (CDCl$_3$) δ 6.97 (overlapping d and dd, 2, $J_{1,2}$ = 7.8 Hz; $J_{2,4}$ = 1.3 Hz), 7.02 (m, 3H), 7.08 (d, 1, $J_{2,4}$ = 1.3 Hz), 7.34 (dd, 1, J_o = 7.2 Hz, J_m = 1.9 Hz), 7.44−7.62 (m, 5); 100-MHz ^{13}C NMR (**15** and **16**) δ 121.25, 121.41, 1121.89, 122.17, 122.92, 123.06, 123.08, 123.22, 127.57, 127.63, 128.05, 128.17, 128.32, 128.35, 128.37, 128.48, 18.57, 128.80, 128.90, 129.27, 129.34, 129.38, 131.88, 133.00, 133.11, 133.46, 133.58, 133.90, 134.26, 135.116, 139.76, 139.95, 141.73, 142.02, 132.36, 143.10, 145.06, 148.34, 148.41, 148.71; MS (**15** and **16**, 70 eV, 100 °C) m/z 350, 348, 346 (M$^{\cdot+}$, 100).[22] Anal. (**15** and **16**). Calcd for $C_{22}H_{12}Cl_2$: C, 76.08; H, 3.46; Cl, 20.46. Found: C, 76.36; H, 3.51; Cl, 20.76.

14-Chloro-9-phenylbenzo[4,5]pentaleno[10,9-*l*]phenanthrene (19). Reaction of **17** and Te gave after 20 h 66% of a 1:9 mixture of **18** and **19** that could easily be separated by chromatography on silica gel using a mixture of 97% hexane and 3% ether as eluent. Compound **19** crystallized as pale yellow needles; mp 232−233 °C (from hexane); 400-MHz ^{1}H NMR (CDCl$_3$) δ 6.34 (d, 1, $J = 7.2$ Hz), 6.82 (dt, 1, $J_d = 1$ Hz; $J_t = 7.5$ Hz), 6.87−6.94 (m, 2), 7.07 (dd, 1, $J_o = 7.7$ Hz, $J_m = 1$ Hz), 7.28 (d, 1, $J = 7.4$ Hz), 7.35 (dt, 1, $J_d = 7.7$ Hz; $J_t = 1$ Hz), 7.46−7.56 (m, 7), 8.46 (d, 1, $J = 8.4$ Hz), 8.60 (m,1), 9.05 (m,1); 100-MHz ^{13}C NMR (CDCl$_3$) δ 122.07, 122.96, 123.21, 123.47, 123.66, 126.17, 126.21, 126.28, 126.73, 126.80, 127.00, 127.99, 128.28, 128.75, 128.78, 128.92, 129.02, 129.18, 130.57, 131.29, 131.37, 134.41, 134.68, 138.68, 142.87, 143.81, 146.37, 150.44; MS (70 eV, 75 °C) *m/z* 414, 412 ($M^{\cdot+}$, 100).[22] Anal. Calcd for $C_{30}H_{17}Cl$: C, 87.27; H, 4.11. Found: C, 86.98; H, 4.28.

Reaction of 20 and PCE in the Presence of Te. (a) When the reaction was conducted for 3 h under the conditions described above as the general procedure, a mixture of 43% of 7-phenylbenzo[*k*]fluoranthene (**21**),[10] 26% of 7-chloro-12-phenylbenzo[*k*]fluoranthene (**22**),[5] and 10% of 12-phenylindeno[2,1-*a*]phenalene (**23**)[11] was obtained. (b) A mixture of 127 mg (1 mmol) of Te and 2 mL of PCE was refluxed for 1 h. To the boiling mixture was added at once 328 mg (1 mmol) of **20**. After 2 h the reaction mixture was worked up and chromatographed on silica gel (using mixtures of hexane and ether as eluent) to give 24.6 mg (7.5%) of **21**, 203.6 mg (56%) of **22** and 65.6 mg (20%) of **23**. The three products were found to be identical with authentic samples prepared previously.[5]

Reaction of 24 and PCE in the Presence of Te. Under the standard conditions (24 h) a mixture of 35% of 9-phenyldibenz[*a,c*]anthracene (**27**) and 52% of 9-chloro-14-phenyldibenz[*a,c*]anthracene (**28**) was obtained. The two products were separated by chromatography on silica gel (using a 98:2 mixture of hexane and ether as eluent). The first and second fraction were **28** and **27**, respectively. Compound **27**: pale yellow crystals; mp 229 (lit.[13] 227 °C); 400-MHz ^{1}H NMR (CDCl$_3$) δ 6.99 (dt, 1, $J_d = 1.4$ Hz, $J_t = 8.1$ Hz), 7.26−7.46 (m, 4), 7.53−7.68 (m, 7), 7.74 (d, 1, $J = 8.5$ Hz), 8.12 (d, 1, $J = 8.1$ Hz), 8.45 (dd, 1, $J_o = 8.1$ Hz, $J_m = 1.2$ Hz), 8.5 (dd, 1, $J_o = 8.1$ Hz, $J_m = 1.6$ Hz), 8.75 (dd, 1, $J_{1,2} = 8.1$ Hz, $J_{1,3} = 1.7$ Hz, H1), 9.14 (s, 1, H14); 100-MHz ^{13}C NMR (CDCl$_3$) δ 121.98, 123.17, 123.20, 123.70, 123.95, 125.41, 125.85, 126.01, 126.78, 126.81, 127.26, 127.39, 127.56, 127.66, 128.21, 129.25, 130.45, 130.46, 130.47, 130.68, 131.27, 131.70, 131.85, 132.31, 137.30, 142.28. Compound **28**: pale yellow crystals, mp 199−200 °C; 400-MHz ^{1}H NMR (CDCl$_3$) δ 6.97 (dt, 1, $J_{6,7,8} = 7.6$ Hz, $J_{5,7} = 1.3$ Hz, H7), 7.35 (dt, 1, $J_{5,6,7} = 7.6$ Hz, $J_{6,8} = 1.3$ Hz, H6) 7.41 (dd, 1, $J_{6,8} = 1.3$ Hz, $J_{7,8} = 7.6$ Hz, H8), 7.47−7.55 (m, 7, H2, H7, H11, H2′, H4′, H5′, H6′), 7.60 (dt, 1, $J_{1,3} = 1$ Hz, $J_{2,3,4} = 7.1$ Hz, H3) 7.68 (dt, 1, $J_{10,12} = 1.2$ Hz, $J_{11,12,13} = 8.6$ Hz, H12), 7.85 (dd, 1, $J_{10,11} = 8.6$ Hz, $J_{10,12} = 1.2$ Hz, H1), 8.28 (d, 1, $J_{5,6} = 7.6$ Hz, H5), 8.34 (d, 1, $J_{3,4} = 7.1$ Hz, H4), 8.63 (d, 1, $J_{12,13} = 8.6$ Hz, H13), 9.09 (dd, 1, $J_{1,2} = 8.1$ Hz, $J_{1,3} = 1$ Hz, H1); 100-MHz ^{13}C NMR (CDCl$_3$) δ 123.46, 123.49, 125.07, 126.13, 126.42, 127.03, 127.06, 127.10, 127.14, 127.18, 127.86, 128.34, 128.60, 129.13, 129.52, 129.59, 129.62, 130.00, 130.58, 130.74, 131.74, 131.76, 132.31, 132.32, 134.51, 141.00; MS (70 eV, 170 °C) *m/z* 390, 388 ($M^{\cdot+}$, 100).[22] Anal. Calcd for $C_{28}H_{17}Cl$: C, 86.49; H, 4.38. Found: C, 86.18; H, 4.63.

1,3-Diphenyl-8*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*c*]furan (29). Under the conditions described for the preparation of **9** and **10,** diyne **25** afforded the chlorine-free **29**. The compound was purified by chromatography on silica gel, using a 1:9 mixture of ether and hexane as eluent. Yield 67%; colorless crystals; mp 222−223 °C (from EtOH and CH$_2$Cl$_2$); 400-MHz ^{1}H NMR (CDCl$_3$) δ 3.73; 4.20 (two d, 2, $J = 13$ Hz, two H8), 7.06 (dt, 2, $J_{4,5,6} = J_{10,11,12} = 7.6$ Hz, $J_{5,7} = J_{9,11} = 1.2$ Hz, H5, H11), 7.22 (dt, 2, $J_{5,6,7} = J_{9,10,11} = 7.6$ Hz, $J_{4,6} = J_{10,12} = 1.2$ Hz, H6, H10), 7.29 (m, 2, H4′, H4″), 7.33−7.38 (m, 6, H7, H9, H3′, H3″, H5′, H5″), 7.42 (dd, 2 $J_{4,5} = J_{11,12} = 7.6$ Hz, $J_{4,6} = J_{10,12} = 1.2$ Hz, H4, H12), 7.73 (dd, 4, $J_{2',3'} = J_{2',3'} = J_{5',6'} = J_{5'',6''} = 8$ Hz, $J_{2',4'} = J_{2'',4''} = J_{4',6'} = J_{4'',6''} = 1.2$ Hz, H2′, H2″, H6′, H6″); 100-MHz ^{13}C NMR (CDCl$_3$) δ 41.02, 122.56, 126.26, 126.77, 127.78, 127.80, 127.92, 128.41, 129.68, 130.56, 131.21, 140.61, 148.14; MS (70 eV, 150 °C) *m/z* 384 ($M^{\cdot+}$, 100).[22] Anal. Calcd for $C_{29}H_{20}O$: C, 90.60; H, 5.24. Found: C, 90.60; H, 5.24.

A suitable crystal for X-ray diffraction analysis was obtained by slow crystallization from a mixture of EtOH and CH$_2$Cl$_2$. Details of the crystal data, the experimental conditions and a summary of the solution and refinement are given in Table 1.[3]

1,1′-(1,2-Ethylenediyl)bis[2-(phenylethynyl)benzene] (26). A mixture of 5 g (11.5 mmol) of 1,1′-(1,2-ethylenediyl)-bis(2-iodobenzene) (**30**),[16] 2.35 g (213 mmol) of phenylacetylene, 166 mg (0.23 mmol) of PdCl$_2$(PPh$_3$)$_2$, 20 mg (0.05 mmol) of Cu$_2$I$_2$, and 20 mL of dry Et$_3$N was stirred at 60 °C with the exclusion of air. After 6 h the cooled reaction mixture was washed with excess 10% hydrochloric acid, the organic material was extracted with ether. The concentrated ethereal solution was chromatographed on silica gel (using a mixture of 96% hexane and 4% ether as eluent), and the resulting colorless semisolid was crystallized from EtOH to give 440 mg (74%) of **26**. Concentration of the mother liquor afforded 28.5 mg (7%) of the pure monoacetylene **31**. Compound **31**: pale yellow oil; 400-MHz ^{1}H NMR (CDCl$_3$) δ 29.1 (t, 2, $J = 7.7$ Hz), 3.17 (t, 2, $J = 7.7$ Hz), 7.12−7.59 (m, 12), 8.70 (d, 1, $J = 7.9$ Hz); 400-MHz ^{13}C NMR (CDCl$_3$) δ 26.66, 28.57, 88.10, 93.32, 122.18, 123.87, 123.91, 126.50, 126.97, 127.70, 128.09, 128.26, 128.37, 131.11, 131.54, 134.08, 134.83, 137.35, 139.30, 143.40; MS (70 eV, 140 °C) *m/z* 280 [$(M - HI)^{\cdot+}$, 100]. Anal. Calcd for $C_{22}H_{17}I$: C, 64.72; H, 4.20. Found: C, 64.63; H, 4.13.

Compound **26**: mp 91−92 °C; 400-MHz ^{1}H NMR (CDCl$_3$) δ 3.28 (s, 4), 7.16−7.24 (m, 6), 7.34−7.42 (m,6), 7.53−7.56 (m,6); 100-MHz ^{13}C NMR (CDCl$_3$) δ 35.80, 88.18, 92.94, 122.66, 123.50, 125.95, 128.13, 128.32, 128.35, 129.10, 131.52, 132.22, 143.68; MS (70 eV, 150 °C) *m/z* 382 ($M^{\cdot+}$, 30].[22] Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.98; H, 5.48.

The structure of **26** was determined unequivocally by X-ray diffraction analysis.[3]

8b,9-Dihydro-14-phenyldibenz[*a,j*]aceanthrylene (32) and 14-Phenyldibenz[*a,j*]aceanthrylene (33). In the presence of equimolar quantities of Te and **26**, the diyne was transformed after 16 h in boiling PCE to a mixture of 41% of **32** and 15% of **33**: Chromatography on silica gel (using hexane with 1% of ether as eluent) followed by repeated recrystallization from ethanol gave the sparingly soluble **33** as yellow needles of mp 173−174 °C concentration of the mother liquor afforded **32** as colorless rhombic crystals of mp 165−166 °C. Compound **32**: 400-MHz ^{1}H NMR (CDCl$_3$) δ 2.66 (t, 1, $J = 1.4$ Hz), 3.49 (dd, 1, $J_1 = 14$ Hz, $J_2 = 5.5$ Hz), 4.04 (dd, 1, $J_1 = 14$ Hz, $J_2 = 5.5$ Hz), 6.90 (m, 2), 7.00 (d, 1, $J= 7.8$ Hz), 7.17 (dt, 1, $J_o = 7.8$ Hz, $J_m = 1.1$ Hz), 7.38−7.60 (m, 6), 7.63−7.81 (m, 5), 8.44 (dd, 1, $J_o = 7.8$ Hz, $J_m = 1.1$ Hz), 8.78 (dd, 1, $J_o = 8.4$ Hz, $J_m = 1.3$ Hz). A suitable crystal for X-ray diffraction analysis was obtained by slow crystallization from EtOH. Details of the crystal data, the experimental conditions, and a summary of the solution and refinement are given in Table 1.[3]

Compound **33**: 400-MHz ^{1}H NMR (the assignment of the protons was obtained by NOESY measurements) (CDCl$_3$) δ 7.21 (dt, 1, $J_{10,12} = 1.5$ Hz, $J_{11,12,13} = 8.5$ Hz, H12), 7.45−7.53 (m, 5), 7.58 (dt, 1 $J_{5,6,7} = 7.8$ Hz, $J_{6,8} = 1.2$ Hz, H6), 7.63−7.68 (m, 4), 7.75 (dt, 1, $J_{1,3} = 1.2$ Hz, $J_{2,3,4} = 8.6$ Hz, H3), 7.76 (d, 1, $J_{1,2} = 9$ Hz, H1), 7.99 (dd, 1, $J_{10,11} = 7.8$ Hz, $J_{10,12} = 1.5$ Hz, H10), 8.13 (dd, 1, $J_{6,8} = 1.2$ Hz, $J_{7,8} = 7.8$ Hz, H8), 8.28 (s, 1, H9), 8.50 (d, 1, $J_{5,6} = 7.8$ Hz, H5), 8.93 (d, 1, $J_{3,4} = 8.6$ Hz, H4);MS (70 eV, 50 °C) *m/z* 378 ($M^{\cdot+}$, 100).[22] Anal. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 94.95; H, 4.64.

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Supporting Information Available: Complete mass spectral data for compounds **2**−**4**, **15**, **16**, **19**, **26**, **28**, **29**, and **33** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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