Polar Effects in the Reactions of a Series of Substituted Diazodiphenylmethanes with Tetracyanoethylene in Benzene

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The kinetics of the reactions of *meta*- and *para*-substituted diazodiphenylmethanes (DDM) with tetracyanoethylene (TCNE) in benzene are reported. The corresponding 1,1-diaryl-2,2,3,3-tetracyanocyclopropanes were produced almost quantitatively and the second-order rate constants k increased with the electron-donating ability of the substituents: the presence of p-OCH_3 and p'-CH_3 groups resulted in the reaction being *ca.* 6.5 × 10^3 times faster than for the m-Cl substituent. At 30 °C, $\log k = -2.67\sigma^+ - 1.23$ (r −0.989). E.s.r. measurements showed the presence of the radical anion of TCNE, though the counter radical cation derived from the diazo-compounds could not be detected. The mechanism of these reactions is discussed on the basis of initial electron transfer from the diazo-compound to TCNE.

THERE is much interest in the decomposition of aliphatic diazocompounds as several different intermediates may be generated depending on the method of decomposition. For example, carbenes[1] can be formed in thermolysis or photolysis, carbenoids[2] may be produced by employing a metal or metal halide as reagent, and diazonium ions[3] (or carbonium ions derived from them) are obtained with protic acids. However, few examples are known at present of the formation of radical cations from diazo-compounds. The existence of such radical ions was demonstrated by electrochemical oxidation of diazodiphenylmethane(DDM) in acetonitrile.[4] On the other hand, chemical decomposition involving radical-ion formation was attempted by several workers using tetraphenylethylene,[5] electron acceptors,[6] and copper(II) perchlorate[7] as catalyst. We reported previously[6] that some diazoalkanes undergo decomposition under the influence of electron acceptors possibly through the derived radical cations. We have also reported[8] the formation of radical pairs in the systems 9-diazofluorene-(9-DF), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and 2,3-dicyano-*p*-benzoquinone (DCNQ), supported by observations of electronic absorption and e.s.r. spectra at 77 K.

In this paper, we describe studies on the reactions of *meta*- and *para*-substituted DDM with tetracyanoethylene (TCNE) as an electron acceptor and investigate polar effects on the decomposition rates in terms of electron abstraction from the diazo-compounds by TCNE.

RESULTS

E.s.r. Measurements of the Reaction of DDM with TCNE.—When powdered TCNE was dissolved in a benzene solution of DDM and the system degassed, the mixture immediately showed an e.s.r. signal of 11 lines with a spacing of 1.56 G at 20 °C which appears to be identical with the spectrum observed by Phillips and Rowell[9] for $TCNE^{\cdot-}$ (Figure). Changing the solvent from benzene to THF or acetonitrile brought about a change in the signal; only seven lines were discernible in THF, while in acetonitrile a single line was observed (Figure). This reduction and disappearance of the fine structure in polar solvents is attributable to fast electron exchange between $TCNE^{\cdot-}$ and neutral TCNE.[10] In spite of the appearance of the radical anion of TCNE in benzene, the counter radical cation possibly derived from DDM could not be detected under these conditions.

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Polar Effects in Reactions of a Series of meta- *and* para-*Substituted DDM with TCNE in Benzene.*—The reactions of DDM and its *meta*- and *para*-substituted derivatives with an equimolar quantity of TCNE in benzene at room temperature gave nearly quantitatively the corresponding 1,1-diaryl-2,2,3,3-tetracyanocyclopropanes (Table 1).

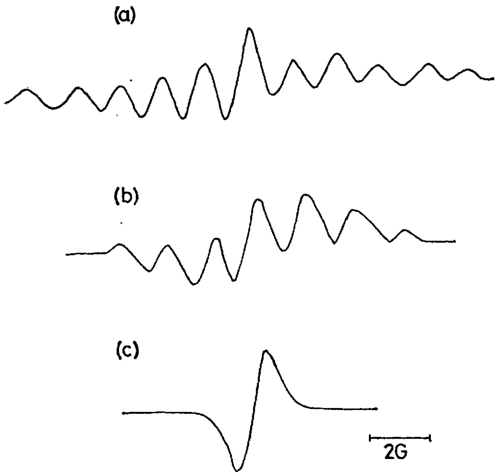
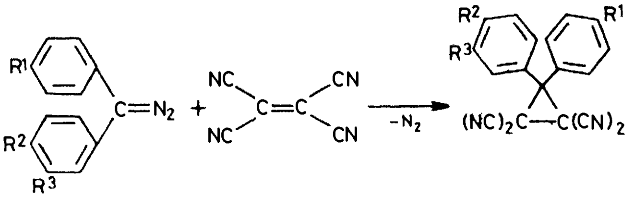


FIGURE E.s.r. spectra of the reaction of DDM with TCNE in (a) benzene, (b) THF, and (c) acetonitrile at 20 °C

It was noticed that the disappearance of the colour of the diazo-compounds and the evolution of nitrogen gas were much accelerated by introducing electron-donating substituents in the *meta*- or *para*-positions of the aromatic rings of the diazo-compounds. In order to estimate this tendency in more detail, the reactions were followed spectrophotometrically, and were found to obey clean second-order kinetics. The values of the rate constants in benzene at various temperatures are given in Table 2 together with the activation parameters.

From the second-order rate constants k, it can be noted that p-OCH$_3$ and p'-CH$_3$ substituents cause a 400-fold increase of the rate compared with the unsubstituted case, while *m*-Cl markedly retarded the reaction. This implies that the rate-determining step of the reactions is influenced by the electronic character of the diazo-carbon.



(1) (2)

	R¹	R²	R³		R¹	R²	R³
a;	OCH$_3$	CH$_3$	H	h;	H	H	H
b;	OCH$_3$	H	H	i;	F	H	H
c;	CH$_3$	CH$_3$	H	j;	I	H	H
d;	OPh	H	H	k;	Cl	H	H
e;	CH$_3$	H	H	l;	Br	H	H
f;	Ph	H	H	m;	Cl	Cl	H
g;	H	H	CH$_3$	n;	H	H	Cl

TABLE 1

Yields and physical data for 1,1-diaryl-2,2,3,3-tetracyanocyclopropanes (2a—n) *

Compound	R¹ (*para*)	R² (*para*)	R³ (*meta*)	Yield (%)	M.p. (°C)	Formula	Found (%) [a] C	H	N
(2a)	OCH$_3$	CH$_3$	H	96	212—213	C$_{21}$H$_{14}$N$_4$O	74.3 (74.6)	4.2 (4.2)	16.5 (16.6)
(2b)	OCH$_3$	H	H	89	206—207.5	C$_{20}$H$_{12}$N$_4$O	74.2 (74.1)	3.9 (3.7)	17.3 (17.3)
(2c)	CH$_3$	CH$_3$	H	97	263—265	C$_{21}$H$_{14}$N$_4$	77.9 (78.2)	4.5 (4.4)	17.2 (17.4)
(2d)	OPh	H	H	96	231.5—233.5	C$_{25}$H$_{14}$N$_4$O	77.9 (77.7)	3.6 (3.7)	14.4 (14.5)
(2e)	CH$_3$	H	H	98	243—245	C$_{20}$H$_{12}$N$_4$	78.2 (77.9)	4.0 (3.9)	18.1 (18.2)
(2f)	Ph	H	H	93	249.5—251.5	C$_{25}$H$_{14}$N$_4$	81.4 (81.1)	3.7 (3.8)	14.8 (15.1)
(2g)	H	H	CH$_3$	91	247—248	C$_{20}$H$_{12}$N$_4$	77.7 (77.9)	3.9 (3.9)	18.1 (18.2)
(2h)	H	H	H	97	276—278 [b]	C$_{19}$H$_{10}$N$_4$	77.5 (77.5)	3.5 (3.4)	19.1 (19.0)
(2i)	F	H	H	91	233—234.5	C$_{19}$H$_9$FN$_4$	72.6 (73.1)	3.0 (2.9)	17.8 (17.9)
(2j)	I	H	H	95	244—245	C$_{19}$H$_9$IN$_4$	54.3 (54.3)	2.2 (2.1)	13.5 (13.3)
(2k)	Cl	H	H	94	236—238	C$_{19}$H$_9$ClN$_4$	69.7 (69.4)	2.8 (2.8)	17.1 (17.0)
(2l)	Br	H	H	92	249—250	C$_{19}$H$_9$BrN$_4$	61.4 (61.1)	2.4 (2.4)	15.1 (15.0)
(2m)	Cl	Cl	H	93	278—280	C$_{19}$H$_8$Cl$_2$N$_4$	62.6 (62.8)	2.4 (2.2)	15.4 (15.4)
(2n)	H	H	Cl	94	240.5—242.5	C$_{19}$H$_9$ClN$_4$	69.9 (69.4)	2.7 (2.8)	16.9 (17.0)

[a] Required values in parentheses. [b] Lit.,[13] 276—278 °C.

* I.r., n.m.r., and mass spectral data are given in Supplementary Publication No. SUP 22352 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

DISCUSSION

Reactions of diazoalkanes with TCNE have already been carried out using diazomethane,[11] ethyl diazo-

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[11] J. Bastus and J. Castells, *Proc. Chem. Soc.*, 1962, 216.

acetate,[12] and DDM,[13] and gave respectively 3,3,4,4-tetracyano-1-pyrazoline, 4-ethoxycarbonyl-5-tricyanovinyl-1,2,3-triazole, and 1,1-diphenyl-2,2,3,3-tetracyanocyclopropane. Because of the absence of a systematic study, however, the mechanisms of these reactions have not been well elaborated. Here, we shall limit our discussion to the mechanism of the reaction of diazodiarylmethanes with TCNE.

The presence of the radical anion of TCNE in the present systems seems to result from initial electron transfer from the diazo-compounds to the electron acceptor, though the corresponding counter radical cation could not be detected under our experimental conditions. This view is supported by the fact that DDM underwent decomposition under the influence of chloranil, which has a smaller electron affinity than TCNE,[14] and produced dimethoxydiphenylmethane in the presence of methanol, this product arising from the radical cation of DDM as previously reported.[6] Further, DCNQ, which is also known to be a weaker electron acceptor [14] than TCNE, decomposed the relatively stable diazo-compound 9-DF at room temperature, and an e.s.r. signal probably due to the radical cation of 9-DF along with the radical anion of DCNQ was observed.[8] From these results, it seems reasonable that TCNE, which is a stronger electron acceptor than the compounds described above, more easily causes electron abstraction from the diazo-carbon, the position of the maximum electron density, than does chloranil or DCNQ.

TABLE 2

Second-order rate constants k (l mol^{-1} s^{-1}) and activation parameters for the reactions of the substituted DDMs (1a—n) with TCNE in benzene

	10^2k			$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}
	30 °C	40 °C	50 °C		
(1a)	3 830 ± 30				
(1b)	605 ± 12				
(1c)	330 ± 4				
(1d)	83.8 ± 1.3	140 ± 4	200 ± 5	34.1 ± 0.5	−134 ± 2
(1e)	63.0 ± 1	111 ± 4	156 ± 3	34.1 ± 0.4	−136 ± 3
(1f)	19.7 ± 0.3	36.2 ± 0.4	57.2 ± 0.3	41.6 ± 0.5	−121 ± 3
(1g)	17.5 ± 0	32.7 ± 0.6	49.5 ± 1.5	39.7 ± 0.5	−128 ± 2
(1h)	9.72 ± 0.08	17.0 ± 0.3	26.8 ± 0.5	39.2 ± 0.8	−135 ± 3
(1i)	6.43 ± 0.04	11.5 ± 0.25	18.2 ± 0.2	40.0 ± 0.8	−135 ± 3
(1j)	2.85 ± 0.03	4.63 ± 0.05	7.72 ± 0.03	37.4 ± 0.3	−150 ± 2
(1k)	2.40 ± 0.02	4.55 ± 0.01	6.70 ± 0.2	44.2 ± 0.7	−130 ± 3
(1l)	2.23 ± 0.07	4.17 ± 0.05	6.78 ± 0.03	45.2 ± 0.6	−127 ± 4
(1m)	0.697 ± 0.004	1.30 ± 0.03	2.15 ± 0.03	43.5 ± 0.4	−142 ± 5
(1n)	0.583 ± 0.014	0.927 ± 0.005	1.33 ± 0.04	31.2 ± 0.5	−184 ± 6

Before electron transfer from the diazo-compounds to TCNE, charge-transfer complexes might exist as transient species. However, any new absorption other than those of both components could not be detected in the electronic absorption spectra in benzene. By contrast, in measurements in Nujol mulls of high concentrations, 9-DF showed a new broad band with a peak at 620 nm due to a charge-transfer complex, but DDM evolved nitrogen gas when mixed with TCNE in this medium. These facts suggest that the charge-transfer complexes are stable only in non-ionizing solvents such as Nujol, otherwise the complexes, even if formed, quickly change to the electron-transfer species; *i.e.*, radical ions.

Jugelt and Pragst [15] studied the electrochemical oxidation of DDM and its derivatives in which process the radical cations of the diazo-compounds are the products, and found a linear dependence between the polarographic half-wave potentials of the compounds investigated and the substituent constants σ^+. They also obtained a linear correlation between the half-wave potentials and the logarithmic rate constants of the decomposition of the diazo-compounds with benzoic acid. This linear relation supported the view that both the potential-determining step of the electrochemical oxidation and the rate-determining proton transfer occur at the diazo-carbon atom.

It is interesting to examine the present systems from this viewpoint, because the initial electron abstraction from the diazo-compounds by TCNE is presumed to be rate determining. It was found that the correlation is better when log k is plotted against σ^+ than against σ. In the normal Hammett treatment, large apparent deviations were observed for (1a and b) which have strong electron-donating substituents. For disubstituted DDM the σ^+ values used are the sums of the σ^+ values for the two substituents. A least squares treatment of these results (for 30 °C) yielded equation (1). A moderately

$$\log k = -2.67\ \sigma^+ - 1.23\ (r\ -0.989,\ n14,\ s\ 0.07) \qquad (1)$$

good fit was also obtained with similar values as for 30 °C when this treatment was applied to results at 40 and 50 °C [equations (2) and (3), respectively]. The existence

$$\log k = -2.78\ \sigma^+ - 0.98\ (r\ -0.967,\ n\ 11,\ s\ 0.15) \qquad (2)$$

$$\log k = -2.74\ \sigma^+ - 0.79\ (r\ -0.966,\ n\ 11,\ s\ 0.16) \qquad (3)$$

of a better correlation with the substituent constants σ^+ and the very large negative ρ value indicate that polar resonance structures such as (I)—(III) might contribute

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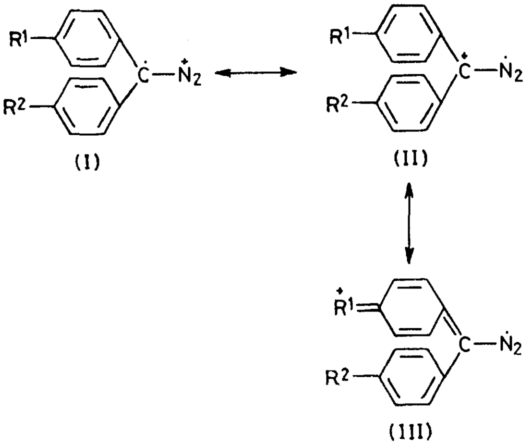
to stabilization of the transition state. Furthermore, the sensitivity of the rates to solvent polarity * supports the intervention of a transition state with an appreciable charge development (Table 3). In fact, an electron-transfer mechanism has been proposed to explain the high dependence upon the polarity of the solvent in the 1,2-cycloaddition reactions of TCNE with a number of donor alkenes such as *p*-methoxystyrene,[17] where acceleration greater than expected from the solvent polarity in dichloromethane and 1,2-dichloroethane was found. This was also the case in our system.



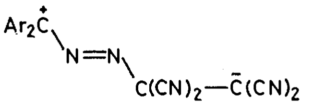
(I) (II) (III)

Table 3

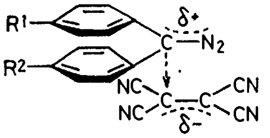
Rate constants *k* (l mol^{-1} s^{-1}) of the reaction of DDM with TCNE in several solvents at 30 °C

Solvent	10^2k
Dichloromethane	195 ± 5
1,2-Dichloroethane	162 ± 1
Acetonitrile	26.8 ± 0.3
Diethyl ether	19.3 ± 0.3
Benzene	9.72 ± 0.08
Ethyl acetate	5.00 ± 0.03
Dioxan	2.50 ± 0.11
Tetrahydrofuran	2.23 ± 0.02

For diazomethane it has been postulated that the 1,3-dipolar cycloaddition with TCNE gives a pyrazoline[11] which is easily transformed into 1,1,2,2-tetracyanocyclopropane. On the other hand, for diaryldiazomethanes the solvent effects, the magnitude of ρ, and the correlation with σ^+ almost certainly rule out a concerted 1,3-dipolar cycloaddition for which correlations[18a-d] are with σ and yield small ρ values, *e.g.* in the addition of substituted phenyl azides to maleic anhydride (ρ −0.8) and *N*-phenylmaleimide (ρ −1.1).[18d] By contrast, a two-step mechanism through the zwitterion intermediate (IV), resulting from nucleophilic attack of the terminal nitrogen of the diazoalkane on TCNE, fits our results. However, to our knowledge, such nucleophilic behaviour of the terminal nitrogen is rarely found, although electrophilic attack is known for the reaction with phosphine.[19] Furthermore, if this were true, the reaction would not require such a high degree of order in the transition state as expected from the large negative entropies of activation ($\Delta S^\ddagger$). These values are appropriate to a concerted process.[18b,20]

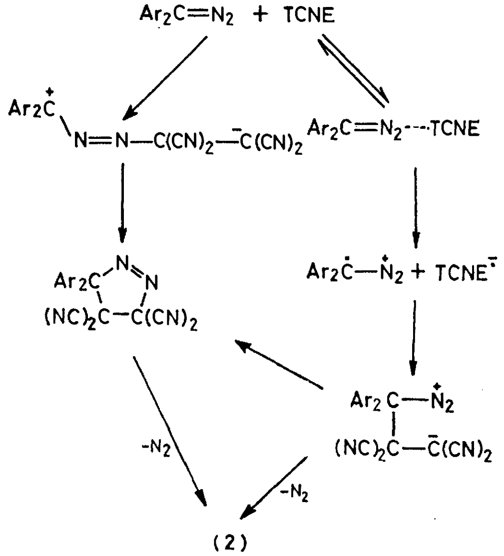


(IV)



(V)

The electron-transfer mechanism sufficiently explains the problem in view of the highly ordered transition state (V) where the molecules are probably oriented in two separate planes to maximize the overlap between DDM and TCNE as in Diels–Alder reactions.[21] The failure to detect DDM$^{+\cdot}$ in the e.s.r. measurements does not support the electron-transfer mechanism; however the possibility that the radical is too unstable to be detected compared with TCNE$^{-\cdot}$ should be considered. Bethell *et al.*[7] observed no signal assignable to DDM$^{+\cdot}$ in the decomposition of DDM with $Cu(ClO_4)_2$ above 0 °C. In addition, DDM$^{+\cdot}$ is known to react with further DDM in a chain process yielding tetraphenylethylene in the absence of additive.[4,7] The corresponding olefins were not isolated in our case and this seems to be the result of the essential suppression of the chain process by preferential collapse with TCNE$^{-\cdot}$. Taking into account these considerations, the reaction probably proceeds by an



(2)

Scheme

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* A simple relationship was not anticipated: retardation in THF and dioxan may be due to the formation of charge transfer complexes with TCNE.[16] Details of these results will be discussed elsewhere.

[16] D. F. Ilten and M. Calvin, *J. Chem. Phys.*, 1965, **42**, 3760.

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[18] (*a*) P. K. Kadaba and T. F. Colturi, *J. Heterocyclic Chem.*, 1969, **6**, 829; (*b*) M. K. Meilahn, B. Cox, and M. E. Munk, *J. Org. Chem.*, 1975, **40**, 819; (*c*) R. Sustmann, *Tetrahedron Letters*, 1974, 963; (*d*) R. Huisgen, G. Szeimies, and L. Möbius, *Chem. Ber.*, 1967, **100**, 2494.

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initial rate-determining electron transfer from the diazoalkanes to TCNE, followed by collapse of the radical ion pair to give the zwitterion or the pyrazoline from which nitrogen is lost yielding the related cyclopropane, though the participation of the two-step mechanism through (IV) can not be fully ruled out (Scheme).

EXPERIMENTAL

N.m.r. spectra were obtained with a Varian EM-360 instrument. I.r. spectra were recorded with a Hitachi 215 grating i.r. spectrophotometer. E.s.r. spectra were observed with a JEOL JES-NE2X instrument. Preliminary e.s.r. measurements of the system TCNE–benzophenone azine in benzene showed no signal indicating that TCNE does not abstract an electron from the azine, the most probable impurity in DDM.

Materials.—Benzene was dried over sodium and fractionated. TCNE was prepared by the method of Carboni [22] and purified by sublimation at least three times, m.p. 200 °C. Diaryldiazomethanes were synthesized from the corresponding hydrazones by oxidation with yellow mercury(II) oxide by a procedure analogous to that described by Smith and Howard.[23] The crystalline diazo-compounds were recrystallized from ether or light petroleum, and the oils were ascertained not to contain hydrazones by n.m.r. measurements. The diazo-compounds prepared and some of their physical properties are listed in Table 4.

TABLE 4

Physical properties of substituted DDMs (1a—n) $(XC_6H_4)(YC_6H_4)CN_2$

	X	Y	M.p. (°C)	Lit. m.p. (°C)	Ref.	$\lambda_{max.}(C_6H_6)$/nm	ε
(1a)	4-OCH_3	4-CH_3	75—76			544	91
(1b)	4-OCH_3	H	55—56	56	24	527	98
(1c)	4-CH_3	4-CH_3	102—103	100—101	25	538	89
(1d)	4-OPh	H	53—54			531	102
(1e)	4-CH_3	H	55—56	53—55	26	532	102
(1f)	4-Ph	H	118—119	118—120	24	529	140
(1g)	3-CH_3	H	Oil			528	98
(1h)	H	H	29—30	29	25	527	102
(1i)	4-F	H	34—36	34—35	27	529	86
(1j)	4-I	H	Oil			525	78
(1k)	4-Cl	H	31—33	26—27	28	526	104
(1l)	4-Br	H	35—36	39—41	27	524	81
(1m)	4-Cl	4-Cl	105—106	70	25	524	120
(1n)	3-Cl	H	Oil			520	84

Kinetic Measurements.—Solutions for kinetic experiments were prepared separately just before use in a volumetric flask with a stopper. TCNE solution (*ca.* 10^{-2}M) was introduced into a stoppered quartz optical cell (10 mm) and kept at the given temperature (±0.05 °C) in a thermostatically controlled cell-holder of a Hitachi 323 spectrophotometer. The reaction was initiated by rapid addition of the requisite volume of the diazo-compound solution (*ca.* 10^{-2}M), preheated in the bath to the same temperature as the cell-holder. In the case of (1a), because of the very rapid decomposition, it was necessary to follow the reaction with a Union SM-401 spectrophotometer by using a highly dilute solution (*ca.* 10^{-3}M) preheated at 30.0 °C. No appreciable change of temperature of the mixture was observed during the short reaction period (40 s). The change in optical density of the mixture at the wavelength of the absorption maximum of the diazo-compound was followed continuously over at least two half-lives for (1a—l) and one half-life for (1m and n). The second-order rate constants (k) were determined graphically from plots of $[1/(a-b)]\ln[b(a-x)/a/(b-x)]$ against time, where a, b, and x are the concentrations of TCNE, the diazo-compound, and the product, respectively. In all cases excellent straight lines were obtained and rate constants (usually 2—4 determinations) were reproducible to within ±5%.

Product Analyses.—In benzene solution (10 ml), diazo-compound (200 mg) and an equimolar quantity of TCNE were mixed at room temperature and the solution was shaken to dissolve TCNE completely. Evolution of nitrogen gas was vigorous for (1a—i) with accompanying precipitation of the cyclopropane products, moderate for (1j—l), and slow for (1m and n). The mixtures were still allowed to stand for 1 h for (1a—i), 6 h for (1j—l), and overnight for (1m and n). For (1j—n) crystalline products were formed on concentration of the solution. Samples for analysis were prepared by recrystallization from benzene, and structures were confirmed by i.r., n.m.r., and mass spectra and elemental analyses.

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