tert-Butylcyanoketene-substituted styrene cycloadditions. A kinetic study

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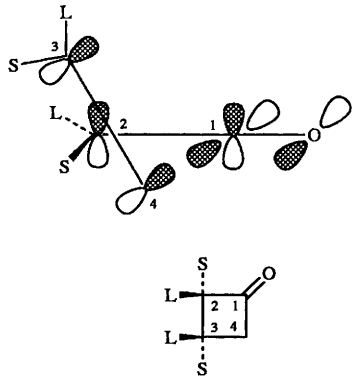
Rate constants for the cycloaddition of *tert*-butylcyanoketene (TBCK) **1** with various substituted styrenes at different temperatures have been determined by ^{1}H NMR spectroscopy. The addition reaction afforded contra-thermodynamic adducts **3** stereoselectively; a way has been found to convert adducts **3** into thermodynamic cyclobutanones **4**. The activation parameters of cycloadditions along with the Hammett reaction constant ρ and the solvent effect on cycloreversion of **3** indicate a concerted asynchronous mechanism involving a transition state with some degree of charge separation. An approximate difference in the energy of activation between the favourable and unfavourable mode of TBCK–*p*-methoxystyrene addition has been determined to be 10.6 kJ mol^{-1}.

The [2 + 2] cycloaddition of ketenes with a variety of ketenophiles is a chemical template of paramount importance for constructing strained four-membered carbo- or hetero-cyclic systems which are otherwise difficult to prepare.[1] While the pathway this pericyclic reaction traverses is still a matter of speculation, a wide body of experimental evidence and theoretical studies involving normal alkenes seem to agree with a concerted non-synchronous mechanism involving a transition state with some degree of charge separation.[2] However, ketene cycloadditions to electron-rich enol ethers or dienes have been shown to be cases of extreme non-synchronism and are suggested to proceed by a zwitterionic (two-step) mechanism.[3] A recent theoretical analysis[2c] by correlation of localized molecular orbitals suggests the reaction mechanism corresponding to the $[\pi^2_s + (\pi^2_s + \pi^2_s)]$ description with the C_1–C_4 distance substantially shorter than C_2–C_3 (Scheme 1). In this



Contra-thermodynamic adduct

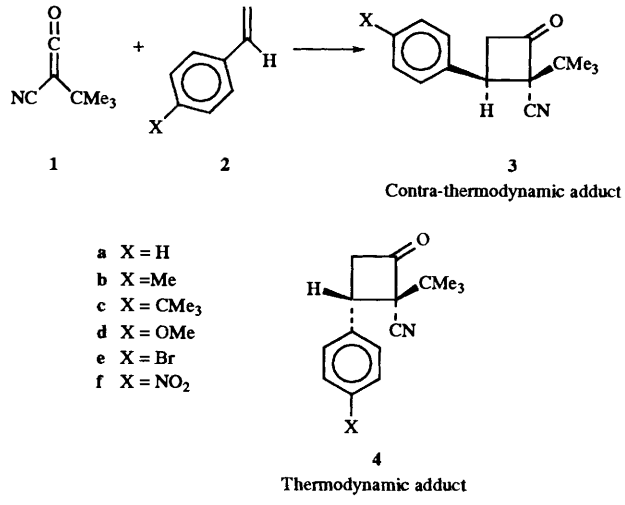
Scheme 1

description the reactants approach one another in a twisted perpendicular fashion and the high regio- and stereo-selectivity are attributed, respectively, to the electronic and steric effects which dictate the *cis* disposition of the bulky substituents in the resulting contra-thermodynamic cyclobutanone.

Among ketenes, the electron-deficient *tert*-butylcyanoketene (TBCK) has received the most attention for investigation of the reaction mechanism.[4] The cycloaddition of TBCK to styrene has been studied in greatest depth.[4a–c,5] The TBCK, being unsymmetrical, has the added advantage of probing the stereochemical pathway this reaction traverses. Herein we report in detail, a systematic kinetic study of TBCK–styrene addition reactions using the ^{1}H NMR technique. We also report for the first time our efforts to convert normal contra-thermodynamic TBCK–styrenes and –normal alkene adducts into the thermodynamic isomers.

Results and discussion

Cycloaddition reactions of the TBCK **1** with a multitude of *para*-substituted styrenes **2** afforded, in each case, a single contra-thermodynamic isomer **3** with a *cis* disposition of the bulky phenyl and the *tert*-butyl substituents (Scheme 2). ^{1}H



Scheme 2

NMR spectra revealed the presence of a triplet (δ 4.38) attributed to the 3-Hs in **3**. While the alkenes **2a–e** underwent smooth reactions at 5–40 °C, the addition of *p*-nitrostyrene **2f** was found to be sluggish, requiring 18 h in refluxing toluene.

Kinetic results obtained for cycloaddition of the TBCK **1** with several styrenes in [$^2H_6$]benzene in the temperature range 5–35 °C are shown in Table 1. The ratio of the concentration of the TBCK and styrenes was determined from time to time by integration of the ^{1}H NMR signals of the *tert*-butyl group of TBCK and the alkenic protons of styrenes and second order rate constants were obtained by linear regression analysis. The low temperature kinetic study virtually ensures that cycloadducts do not revert to the reactants in a cycloreversion process. *p*-Methoxystyrene is found to be the most reactive alkene, undergoing addition reaction 76 times faster than the

Table 1 Rate constants and activation parameters for the addition reactions of TBCK in [$^2H_6$]benzene

Alkene	T/°C	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}	E_a/kJ mol^{-1}	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/J mol^{-1} K^{-1}
Styrene	5.0	0.523	37.6 ± 0.4	35.1 ± 0.4	−181 ± 2
	15.0	0.936			
	25.0	1.59			
	35.0	2.54			
p-Bromostyrene	25.0	0.571	—	—	—
p-Methylstyrene	25.0	9.78	—	—	—
p-Butylstyrene	25.0	5.92	—	—	—
p-Methoxystyrene	15.0	84.7	26.8 ± 0.9	24.3 ± 0.9	−181 ± 3
	25.0	121			
	35.0	175			
	50.0	290[a]			

[a] Extrapolated value.

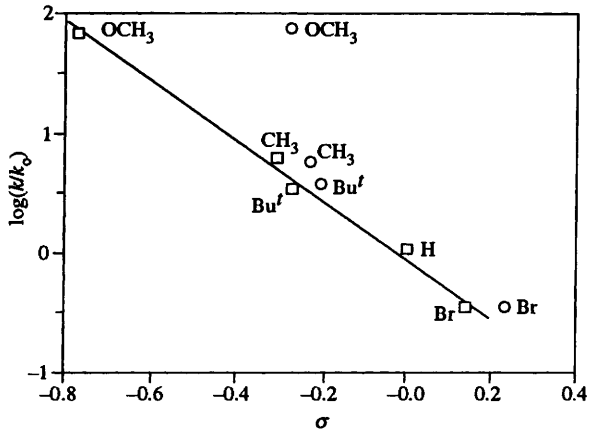
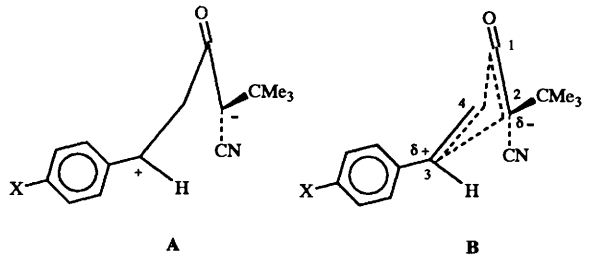


Fig. 1 Hammett plot: (□), σ_p^+; (○), σ_p

parent styrene at 25 °C. Kinetic data on TBCK–*p*-nitrostyrene was not obtained since the addition reaction was found to be too sluggish to measure at 25 °C and at higher temperature (45 °C) ketene polymerization complicates the kinetic study. In a competing reaction of TBCK with one equiv. styrene and 10 equiv. *p*-nitrostyrene at 45 °C, the NMR spectrum revealed the formation of the styrene adduct **3a** alone.

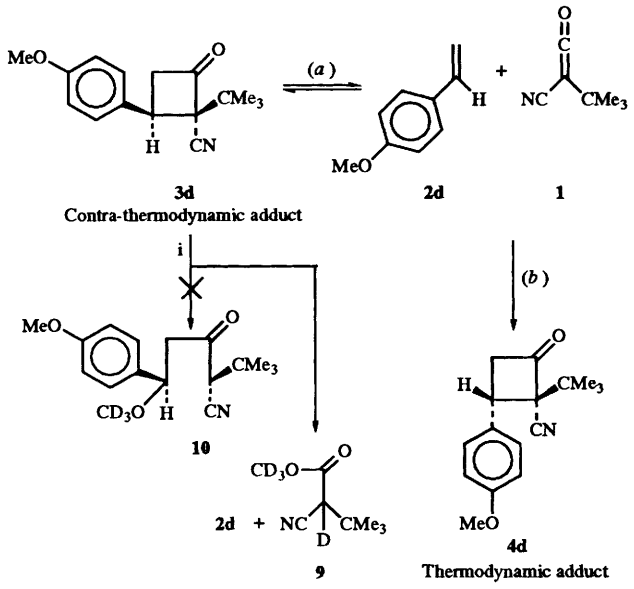
The TBCK was found to be more reactive than diphenylketene. While the rate constant for the TBCK–styrene addition at 35 °C in C_6D_6 was found to be 2.54 × 10^{-3} dm^3 mol^{-1} s^{-1}, the corresponding constant for the diphenylketene–styrene reaction was reported to be 2.30 × 10^{-5} dm^3 mol^{-1} s^{-1} in benzonitrile[6] at 40 °C and 0.700 × 10^{-3} dm^{-3} mol^{-1} s^{-1} in bromobenzene[7] at 120 °C. Our activation parameters are similar to those reported[6,8] for other cases of ketene cycloadditions. While $\Delta H^{\#}$ and $\Delta S^{\#}$ values of the diphenylketene–butyl vinyl ether reaction[6] in benzonitrile in the temperature range 20–40 °C was determined to be 38.9 kJ mol^{-1}, −167.4 J mol^{-1} K^{-1}, respectively, the corresponding values for the dimethylketene–ethyl vinyl ether[8] (bulk) reaction in the temperature range 0–25 °C were reported to be 67 kJ mol^{-1} and −83.7 J mol^{-1} K^{-1}. Low activation energies (37.6 and 26.8 kJ mol^{-1} for the addition of styrene and *p*-methoxystyrene, respectively) and a substantial negative entropy of activation (−181 J mol^{-1} K^{-1}) point toward an early and fairly tight transition state. Fig. 1 is a plot of log [*k*(substituted sytrene)/*k*(styrene)] at 25 °C in C_6D_6 *vs.* the σ_p^+ Hammett substituent constant. An excellent linear free energy relationship is obtained (correlation coefficient, r = 0.998). However, the use of σ_p values does not give a straight line fit. A very high ρ value of −2.48 shows that the transition state for the TBCK–styrene reactions has a substantially higher degree of polar character than the corresponding reactions involving dimethylketene[8] at 100 °C and diphenylketene[7] in bromobenzene at 120 °C with ρ values of −1.4 and −0.73, respectively. It is to be noted that in those studies a straight line fit was obtained in the Hammett plot only when σ_p instead of σ_p^+ values were used. The presence of the cyano group in TBCK presumably makes the process more receptive to the negative charge next to CN in the transition state (Scheme 3).



Scheme 3

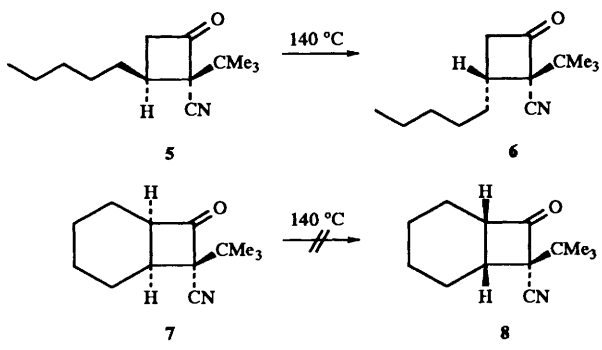
Now, the question arises: is this ρ value large enough to consider these addition reactions to follow a stepwise process involving zwitterionic intermediate **A**? The magnitude of ρ values for typical ionic processes,[9] carried out in solvents of high relative permittivity (alcohols, acids, *etc.*), was found to be in the range of −3.3 to −4.3. The ρ value of −2.48 for the TBCK–styrene reaction in C_6D_6 of low relative permittivity is presumably inflated since most ρ values tend to increase with decreasing relative permittivity of the reaction medium. Most likely, our study agrees with non-synchronous concerted addition with the C_1–C_4 distance substantially shorter than C_2–C_3 and appreciable charge separation in the transition state as depicted in **B** (Scheme 3).

The use of protic solvents in ketene cycloadditions is always avoided since it reacts immediately with ketenes.[10] During our study we observed that the adduct **3d** undergoes cycloreversion at a moderate temperature (45 °C) to the starting alkene **2d** and TBCK (Scheme 4). This offered us an opportunity to study the process in protic or aprotic solvents of different relative permittivities. The principle of microscopic reversibility requires the cycloreversion process to traverse the same reaction coordinates backward as the addition reaction goes forward. The first order rate constant for cycloreversion of **3d** in C_6D_6 ($\varepsilon \approx 2.3$), CD_3OD ($\varepsilon \approx 33$) and $(CD_3)_2SO$ ($\varepsilon \approx 47$) in the presence of trapping agent[10] CD_3OD at 45 °C was found to be 1.01 × 10^{-4}, 1.45 × 10^{-4} and 0.544 × 10^{-4} s^{-1}, respectively (Scheme 4). Such an insensitivity to solvent polarity presumably precludes the formation of the zwitterionic intermediate **A** (X = OMe) (Scheme 3). Even though stereospecificity, effect of solvent on the reaction rate, kinetic isotopic effects and activation parameters are some of the important criteria put forward to face the significant challenge of discriminating between a concerted and a stepwise mechanism,[11] isolation or interception of dipolar



Scheme 4 (*a*) k_r (50 °C) = 0.175 × 10^{-3} s^{-1} (C_6D_6), k_a (50 °C) = 290 × 10^{-3} dm^3 mol^{-1} s^{-1}; (*b*) k_a' (50 °C) (calc.) = 5.57 × 10^{-3} dm^3 mol^{-1} s^{-1}. k_{obs} for **3d** to **4d** conversion = 3.30 × 10^{-6} s^{-1} = (k'_a × k_r)/(k_a + k'_a). (i) CD_3OD, 45 °C.

intermediates does indeed provide definitive proof of a two-step process involving zwitterions.[12] However we were unable to detect any formation of the compound **10** (Scheme 4) which could arise from interception of the intermediate **A** by CD_3OD. One may argue that the zwitterion **A**, resembling an intimate ion-pair, may have an overwhelming preference to go back to the adduct **3d** instead of being intercepted by the trapping agent. In all the addition reactions a single isomer **3** is obtained in each case. A difference in the free energy of activation of greater than 11.4 kJ mol^{-1} in favour of the allowed process would give **3** and **4** in a ratio higher than 99:1. The NMR detection limit would not allow identification of any minor isomer formed in that case. The question arises: how unfavourable are the alternate modes of additions leading to **4** as far as energies of activation are concerned? An answer to this would indeed be of great interest to both theoretical and practical chemists. We realize that the difference in the activation energy for the cycloreversion of **3** and **4** will be much higher than the difference in the two modes of TBCK–styrene addition leading to **3** and **4** since the thermodynamic adduct **4** has a lower ground state energy due to a *trans* disposition of the bulkier groups. Under appropriate conditions it may be possible for the addition mode leading to **3** to be reversible while formation of **4** remains irreversible. With this in mind we performed thermal equilibration of several contra-thermodynamic adducts **3**, **5**, **7** (Schemes 4 and 5). In the absence of trapping agent the adduct **3d** isomerized to the isomer **4d** at 50 °C at a rate (k_{obs}) of 3.30 × 10^{-6} s^{-1}. The rate constant (k_r) for the cycloreversion process in C_6D_6 at 50 °C in the presence of trapping agent CD_3OD was found to be 0.175 × 10^{-3} s^{-1}. The adduct **3d** on cycloreversion reverts to TBCK and *p*-methoxystyrene which then partition between the two modes of addition to give **3d** and **4d** at different rates (Scheme 4). The formation of the adduct **3d** remains reversible at 50 °C, however, the thermodynamic adduct **4d** does not undergo cycloreversion. (A solution of pure **4d** in C_6D_6 remained unchanged at 50 °C for the duration of the above experiment.) The second order rate constant (k_a) for the addition reaction leading to **3d** at 50 °C was extrapolated to a value of 290 × 10^{-3} dm^3 mol^{-1} s^{-1}. Using a steady-state approximation the rate constant (k'_a) for the addition reaction leading to **4d** was determined to be 5.57 × 10^{-3} dm^3 mol^{-1} s^{-1}. Thus **3d** is expected to be formed at a rate 52 times faster than that of **4d** affording **3d** and **4d** in a ratio of 98:2. The ratio of the products **3d** and **4d** from a reaction carried out at 5–35 °C may be much higher and as such we were unable to detect the minor isomer by NMR spectroscopy. The difference in the energy of activation at 50 °C between the two modes of addition was thus approximated to be 10.6 kJ mol^{-1}. The alternate mode of addition leading to **4d** may either involve the approach of styrene with the small group H away from the TBCK or the H rotating past the bulkier *tert*-butyl group on its way to the cyclobutanone (Schemes 1 and 3).



Scheme 5

Isomerization of the styrene adduct **3a** required a higher temperature; at 103 °C it gave a mixture of **3a** and **4a** in a ratio of 12:88, respectively, after 24 h. Ketene–styrene additions have been studied previously in the greatest depth and to our knowledge this is the first time we were able to prepare the thermodynamic adduct **4a**. Likewise, the hept-1-ene adduct **5** was converted into the thermodynamic isomer **6** at 140 °C (Scheme 5). In all the thermodynamic adducts 3-H appears upfield relative to that of the contra-thermodynamic adducts since the 2-CN group is expected to deshield[13] the *cis* disposed 3-H in the contra-thermodynamic adducts. Thermal isomerization of cyclohexene adduct[10] **7** was unsuccessful. Heating at 130 °C for 10 h does not lead to the thermodynamic adduct **8**; NMR spectra revealed only the starting isomer **7**. At 140 °C the adduct **7** decomposed to give cyclohexene and polymeric materials. *p*-Nitrostyrene adduct **3f** also failed to isomerize to **4f** at 110 °C (10 h). Lots of solid material, presumably the ketene polymer was found to be formed along with some starting adduct **3f**. In these two cases the preferable kinetics of ketene polymerization does not allow the reaction to circumvent the seemingly insurmountable activation energy leading to the thermodynamic adducts.

Our kinetic data for the cyclo-addition and -reversion processes, solvent effects, activation parameters, inability to intercept zwitterions and Hammett ρ value all point toward a concerted non-synchronous addition reaction with a polar transition state. In a mechanistic continuum with concerted synchronous bond formation at one end of the scale and a two-step process involving zwitterionic intermediate at the other end, the TBCK–styrene additions lie somewhere in between with the actual position depending on the nature of the *p*-substituents.

Experimental

All mps are uncorrected. Elemental analyses were performed on a Carlo-Erba Elemental analyser 1106. IR spectra were recorded on a Perkin-Elmer instrument Model 237B, and are reported in cm^{-1}. ^1H NMR spectra for the kinetic runs were recorded on a Varian XL 200 NMR spectrometer operating at a proton frequency of 200 MHz and in the pulse Fourier transform mode. A flip angle of 20°, digital resolution of 0.15 Hz,

and four transients were employed in all measurements. The absolute intensity mode was used to measure integrals of relevant peaks, which were well separated without any overlap. The temperature in the probe was controlled by standard Varian equipment and was accurate to ± 0.5 °C. The temperature was controlled by standard chemical shifts of methanol. For analysis of the cycloadducts the ^{1}H NMR spectra were measured in $CDCl_3$ and C_6D_6 with Me_4Si as internal standard. Some of the slow kinetic runs were recorded on a Bruker AC 80 spectrometer, operating at a proton frequency of 80 MHz. Silica gel chromatographic separations were performed with flash silica (Baker Chem. Co). Styrene was washed with 5% NaOH, dried and distilled. *p-tert*-Butyl-, -bromo-, and -methyl-styrene were distilled under vacuum prior to use. Toluene, benzene and [$^2H_6$]benzene was freshly distilled from calcium hydride under nitrogen. TBCK was generated by the procedure of Moore.[10]

Addition reaction of the TBCK with alkenes

The addition reactions were performed under a positive pressure of dry argon. Styrene–TBCK and cyclohexene–TBCK adducts were made as described.[10] In a typical run the TBCK (5.0 mmol) in benzene (50 cm^3) was reacted with alkene (10.0 mmol) at 40 °C for 24 h. However, the reactions of *p*-nitrostyrene and hept-1-ene were carried out in refluxing toluene (18 h) and benzene (12 h), respectively. After removal of the solvent the crude residue was purified by chromatography on silica gel with hexane–ether (5:1) as the eluent. The addition reaction of *p*-methoxystyrene was performed at 0–5 °C (30 min) and in order to avoid chromatographic purification the TBCK and the alkene were used in a ratio of 1.0:0.8. Chromatographic separation leads to decomposition of the adduct **3d**. After removal of the solvent by a gentle stream of nitrogen at 20 °C the residue was taken up in the hexane–diethyl ether and kept in a freezer for crystallization. The isomeric adduct **4d** was not detected in the crude reaction mixture.

(*E*)-2-*tert*-Butyl-2-cyano-3-*p*-tolylcyclobutanone 3b

Colourless needles (74% yield), mp 97–98 °C (hexane–diethyl ether) (Found: C, 79.45; H, 7.8; N, 5.75. $C_{16}H_{19}NO$ requires C, 79.63; H, 7.94; N, 5.81%); ν_{max}(KBr)/cm^{-1} 2954, 2921, 2872, 2227, 1787, 1510, 1465, 1365, 1208, 1118, 1080 and 834; δ_H($CDCl_3$) 0.96 (9 H, s), 2.40 (3 H, s), 3.44 (1 H, dd, *J* 10.0, 18.0 Hz), 3.81 (1 H, dd, *J* 11.0, 18.0 Hz), 4.38 (1 H, t, *J* 10.5 Hz), 7.30 (2 H, d, *J* 8.5 Hz) and 7.41 (2 H, d, *J* 8.5 Hz).

(*E*)-2-*tert*-Butyl-3-*p*-*tert*-butylphenyl-2-cyanocyclobutanone 3c

Colourless crystals (65%), mp 114–115 °C (hexane–diethyl ether) (Found: C, 80.3; H, 8.75; N, 4.9. $C_{19}H_{25}NO$ requires C, 80.52; H, 8.89; N, 4.94%); ν_{max}(KBr)/cm^{-1} 2960, 2906, 2870, 2237, 1788, 1513, 1478, 1415, 1400, 1370, 1272, 1213, 1115, 1100, 1073 and 840; δ_H($CDCl_3$) 0.96 (9 H, s), 1.33 (9 H, s), 3.43 (1 H, dd, *J* 10.3, 18.0 Hz), 3.82 (1 H, dd, *J* 11.3, 18.0 Hz), 4.38 (1 H, t, *J* 10.5 Hz), 7.41 (2 H, d, *J* 9.0 Hz) and 7.49 (2 H, d, *J* 9.0 Hz).

(*E*)-2-*tert*-Butyl-2-cyano-3-*p*-methoxyphenylcyclobutanone 3d

Colourless needles (67%), mp 72–73 °C (diethyl ether–hexane) (Found: C, 74.5; H, 7.4; N, 5.3. $C_{16}H_{19}NO_2$ requires C, 74.68; H, 7.44; N, 5.44%); ν_{max}(KBr)/cm^{-1} 2955, 2230, 1785, 1608, 1509, 1297, 1246, 1072, 1033 and 837; δ_H($CDCl_3$) 0.97 (9 H, s), 3.44 (1 H, dd, *J* 10.0, 18.0 Hz), 3.78 (1 H, dd, *J* 10.0, 18.0 Hz), 3.86 (3 H, s), 4.37 (1 H, t, *J* 10.0 Hz), 6.96 (2 H, d, *J* 9.0 Hz) and 7.37 (2 H, d, *J* 9.0 Hz); δ_H(C_6D_6) 0.81 (9 H, s), 2.61 (1 H, dd, *J* 10.0, 18.0 Hz), 3.05 (1 H, dd, *J* 10.0, 18.0 Hz), 3.28 (3 H, s), 3.86 (1 H, t, *J* 10.0 Hz), 6.67 (2 H, d, *J* 9.0 Hz) and 6.89 (2 H, d, *J* 9.0 Hz).

(*E*)-3-*p*-Bromophenyl-2-*tert*-Butyl-2-cyanocyclobutanone 3e

Colourless needles (70%), mp 101–102 °C (hexane–diethyl ether) (Found: C, 58.7; H, 5.15; N, 4.5. $C_{15}H_{16}BrNO$ requires C, 58.84; H, 5.27; N, 4.58%); ν_{max}(KBr)/cm^{-1} 2956, 2937, 2872, 2230, 1788, 1490, 1407, 1376, 1207, 1070, 1013, 840 and 822; δ_H($CDCl_3$) 0.98 (9 H, s), 3.47 (1 H, dd, *J* 10.5, 18.0 Hz), 3.80 (1 H, dd, *J* 10.5, 18.0 Hz), 4.38 (1 H, t, *J* 10.5 Hz), 7.39 (2 H, d, *J* 8.0 Hz) and 7.62 (2 H, d, *J* 8.0 Hz).

(*E*)-2-*tert*-Butyl-2-cyano-2-*p*-nitrophenylcyclobutanone 3f

Pale yellow crystals (45% yield), mp 141–142 °C (hexane–diethyl ether) (Found: C, 65.95; H, 5.9; N, 10.35. $C_{15}H_{16}N_2O_3$ requires C, 66.16; H, 5.92; N, 10.29%); ν_{max}(KBr)/cm^{-1} 2980, 2963, 2866, 2234, 1791, 1599, 1525, 1345, 1107, 1072, 851, 755 and 698; δ_H($CDCl_3$) 0.97 (9 H, s), 3.47 (1 H, dd, *J* 10.0, 18.0 Hz), 3.78 (1 H, dd, *J* 10.0, 18.0 Hz), 4.48 (1 H, t, *J* 10.0 Hz), 7.60 (2 H, d, *J* 9.0 Hz) and 8.26 (2 H, d, *J* 9.0 Hz).

(*E*)-2-*tert*-Butyl-2-cyano-3-pentylcyclobutanone 5

Colourless liquid (68%) (Found: C, 76.2; H, 10.35; N, 6.4. $C_{14}H_{23}NO$ requires C, 75.97; H, 10.47; N, 6.33%); ν_{max}(neat)/cm^{-1} 2946, 2916, 2866, 2222, 1791, 1468, 1402, 1372, 1214, 1137, 1100 and 1051; δ_H($CDCl_3$) 0.91 (3 H, br t), 1.21 (9 H, s), 1.04–1.46 (6 H, m), 1.74 (1 H, m), 2.02 (1 H, m), 2.94 (2 H, m) and 3.25 (1 H, dd, *J* 12.0, 20.0 Hz); δ_H(C_6D_6) 0.79 (3 H, apparent t, *J* 7.0 Hz), 0.98 (9 H, s), 0.73–1.35 (7 H, m), 1.51 (1 H, m), 2.25 (1 H, dd, *J* 9.0, 16.0 Hz), 2.47 (1 H, m) and 2.64 (1 H, dd, *J* 9.0, 16.0 Hz).

Kinetics of cycloaddition reactions

Kinetic runs were studied by an NMR technique in the following way. An NMR tube containing dried TBCK-precursor 2,5-di-*tert*-butyl-3,6-diazido-1,4-benzoquinone (35.0 mg, 0.116 mmol) and *ca.* 2.0 cm^3 of [$^2H_6$]benzene was heated in an oil bath (80–83 °C) under a positive pressure of dry argon for a period of 45–60 min during which the original deep orange colour of the solution (azide) turned yellow (TBCK). The TBCK solution in the NMR tube was cooled in an ice–salt bath (−15 °C) and an accurately weighed amount of styrene and small amount of Me_4Si was introduced into the NMR tube with a syringe. The TBCK–styrene mixture was properly mixed and a ^{1}H NMR spectrum was recorded immediately. The *tert*-butyl protons of TBCK appeared at δ 0.73 with no other overlapping signals. The concentration of the TBCK was determined by the known concentration of styrene using integration of several proton signals. The ratio of the concentrations of the reactants was determined from time to time. The first spectrum at zero time did not reveal the formation of the adduct. At the end the volume of the reaction mixture was determined. The second order rate constant was measured by linear regression analysis of the data and it was reproducible within 5–7%. One mole of TBCK precursor leads to two moles of TBCK. However, under our experimental conditions the presence of minute amounts of moisture may quench a certain portion of the TBCK. In a typical run the initial concentration of TBCK and styrene were found to be 0.0922 and 0.123 mol dm^{-3}, respectively. The addition reactions were followed up to 40–80% chemical conversion.

Likewise, the second-order rate constant for the TBCK–*p*-bromostyrene reaction in C_6D_6 was determined to be 0.571 × 10^{-3} dm^3 mol^{-1} s^{-1} at 25 °C. A competitive cycloaddition reaction between styrene and *p*-bromostyrene for TBCK was carried out at 25 °C in an NMR tube containing TBCK (generated from 0.116 mol of the precursor), styrene (2.124 mmol), and *p*-bromostyrene (2.123 mmol) in C_6D_6 (total volume 2.30 cm^3). ^{1}H NMR spectra taken after 20 min revealed the presence of the styrene adduct and *p*-bromostyrene adduct in a ratio of 2.67:1, respectively. TBCK was completely

consumed. The second order rate constant for the TBCK–*p*-bromostyrene reaction was found to be 0.596×10^{-3} dm^3 mol^{-1} s^{-1}. The rate constant by the absolute and relative methods was thus found to be identical. In a similar manner competitive reactions between styrene and *p*-methylstyrene, styrene and *p*-*tert*-butylstyrene were carried out.

A competitive addition reaction between *p*-methoxystyrene and styrene was carried out in a dry flask containing *p*-methoxystyrene (0.180 mmol) and styrene (4.173 mmol) in C_6D_6 (2.50 cm^3) at 25 °C. TBCK (0.110 mmol as calculated at the end of the reaction) in C_6D_6 (2.00 cm^3) at 25 °C was injected into the flask, quickly mixed by magnetic stirrer and the ^{1}H NMR spectrum was recorded; after 5 min TBCK was completely consumed. The amount of *p*-methoxystyrene adduct, styrene adduct and unreacted *p*-methoxystyrene was found to be 0.0787, 0.0313 and 0.101 mmol, respectively, as determined by the integration of several proton signals. The rate ratio was calculated by the method of Ingold and Shaw[14] and *p*-methoxystyrene was found to be 76.3 times more reactive than styrene. Likewise the rate ratio was determined at 15 and 35 °C and was found to be 90.5 and 68.8, respectively. The rate ratio was reproducible within 5%. The absolute rate for the addition of *p*-methoxystyrene was calculated from the rate constant of the addition reaction of styrene.

Conversion of contra-thermodynamic adduct 3a into thermodynamic adduct 4a by thermolysis

A mixture of **3a** (1.20 g) and styrene (150 mg) in dry benzene (10 cm^3) was heated in a closed vessel at 103 °C, the ratio of **3a** and **4a** after 6, 20 and 24 h was found to be 60:40, 20:80 and 12:88, respectively. Further heating was discontinued to stop deterioration of the reaction mixture. When the above mixture of non-separable isomers was heated at 92 °C for 4 h in the presence of the trapping agent CH_3OH (200 mg), the contra-thermodynamic adduct **3a** underwent complete cycloreversion and the adduct **4a** remained unchanged. Purification by chromatography using 5:1 hexane–diethyl ether as the eluent gave **4a** as colourless crystals (820 mg), mp 69–70 °C (diethyl ether–hexane) (Found: C, 79.3; H, 7.45; N, 6.2. $C_{15}H_{17}NO$ requires C, 79.26; H, 7.54; N, 6.16%); ν_{max}(neat)/cm^{-1} 2963, 2227, 1784, 1500, 1475, 1454, 1403, 1390, 1373, 1210, 1140, 1081, 1063, 765, 718 and 695; δ_H($CDCl_3$) 1.20 (9 H, s), 3.49 (1 H, dd, *J* 10.5, 19 Hz), 3.61 (1 H, dd, *J* 8.0, 19.0 Hz), 3.84 (1 H, dd, *J* 8.0, 10.5 Hz) and 7.46 (5 H, m); δ_H(C_6D_6) 0.87 (9 H, s), 2.67 (1 H, dd, *J* 10.5, 19.0 Hz), 2.95 (1 H, dd, *J* 8.0, 19.0 Hz), 3.19 (1 H, dd, *J* 8.0, 10.5 Hz) and 7.16 (5 H, m).

Conversion of contra-thermodynamic adduct 3d into thermodynamic adduct 4d by thermolysis

A sealed NMR tube containing the adduct **3d** (50 mg) in dry benzene (0.74 cm^3) was heated at 50 °C. The first order rate constant for the conversion of **3d** into **4d** was determined to be 3.30×10^{-6} s^{-1} (correlation coefficient, $r = 1.000$). The above experiment when carried out in the presence of *p*-methoxystyrene (≈5 mg), the rate constant was found to be similar [3.35×10^{-6} s^{-1} ($r = 0.998$)]. A mixture of **3d**–**4d** in a ratio of 56:44 was heated at 58 °C for 100 h and the ratio of **3d** and **4d** was determined to be ≈0:100. The NMR spectra revealed the absence of any side products. The residue was crystallized from hexane–diethyl ether after standing in the refrigerator to give the thermodynamic adduct **4d** as white crystals; mp 77–78 °C (diethyl ether–hexane) ν_{max}(KBr)/cm^{-1} 2955, 2230, 1783, 1605, 1509, 1455, 1398, 1368, 1285, 1245, 1179, 1064, 1031 and 828; δ_H(C_6D_6) 0.90 (9 H, s), 2.70 (1 H, dd, *J* 10.5, 19.0 Hz), 2.96 (1 H, dd, *J* 8.0, 19.0 Hz), 3.21 (1 H, dd, *J* 8.0, 10.5 Hz), 3.32 (3 H, s), 6.82 (2 H, d, *J* 9.0 Hz) and 7.05 (2 H, d, *J* 9.0 Hz); δ_H($CDCl_3$) 1.18 (9 H, s), 3.52 (2 H, app. d, *J* 11.0 Hz), 3.84 (3 H, s and a 1 H overlapping t), 7.00 (2 H, d, *J* 9.0 Hz) and 7.38 (2 H, d, *J* 9.0 Hz).

Conversion of contra-thermodynamic adduct 5 into thermodynamic adduct 6 by thermolysis

A sealed NMR tube containing the adduct **5** (300 mg), hept-1-ene (100 mg) and dry C_6D_6 (1.8 cm^3) was heated at 140 °C for 100 h. The resultant [$^2H_6$]benzene solution of the adducts **5** and **6**, in a ratio of 25:75, respectively, was heated in the presence of CH_3OH (100 mg) at 120 °C for 36 h in a sealed NMR tube. The reaction mixture was purified by chromatography using hexane–diethyl ether (20:1) as the eluent to give the thermodynamic adduct **6** containing 5% of the minor isomer **5** (colourless liquid 200 mg, 66.7%) (Found: C, 75.8; H, 10.4; N, 6.25. $C_{14}H_{23}NO$ requires C, 75.97; H, 10.47; N, 6.33%); ν_{max}(neat)/cm^{-1} 2960, 2915, 2850, 2230, 1786, 1465, 1368, 1215, 1137 and 1053; δ_H($CDCl_3$) 0.92 (3 H, br t), 1.11 (9 H, s), 1.37 (6 H, m), 1.77 (2 H, m), 2.46 (1 H, m), 2.83 (1 H, dd, *J* 7.0, 19.0 Hz) and 3.22 (1 H, dd, *J* 9.0, 19.0 Hz); δ_H(C_6D_6) 0.86 (9 H, s), 0.89 (3 H, t, *J* 7.0 Hz), 0.94–1.70 (8 H, m), 1.88 (1 H, m), 2.18 (1 H, dd, *J* 7.0, 19.0 Hz) and 2.50 (1 H, dd, *J* 9.0, 19.0 Hz).

Kinetics of cycloreversion of the thermodynamic adduct 3d

In an NMR tube was taken a solution of the adduct **3d** (40.0 mg, 0.155 mmol) in appropriate solvent (1.00 cm^3) containing CD_3OD (10 mg, 0.28 mmol). The NMR tube was then placed in a constant temperature bath at 45 ± 0.5 °C. The first order rate constants for the cycloreversion process in C_6D_6, CD_3OD and $(CD_3)_2SO$ were obtained with excellent correlation coefficients of 0.999, 0.995 and 0.999, respectively, by linear regression analysis and were reproducible within 5%. The concentration of **3d** at various times was determined by integration of the *tert*-butyl signals of **3d**, CD_3OD-trapped ketene **9** and the olefinic protons of **2d** and the reaction was followed up to 50–60% conversions. The above cycloreversion in C_6D_6 was repeated at 50 °C and the rate constant was determined by similar analysis ($r = 0.997$).

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