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ADDITION REACTIONS OF TERT-BUTYLCYANOKETENE TO SILYL ENOL ETHERS AND CONJUGATED DIENES.

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Abstract: A study of the addition reactions of tert-butylcyanoketene with several 1-aryl-1-trimethylsiloxy ethenes and acyclic conjugated dienes has been carried out. These reactions are suggested to proceed by stepwise pathways involving zwitterionic intermediates.

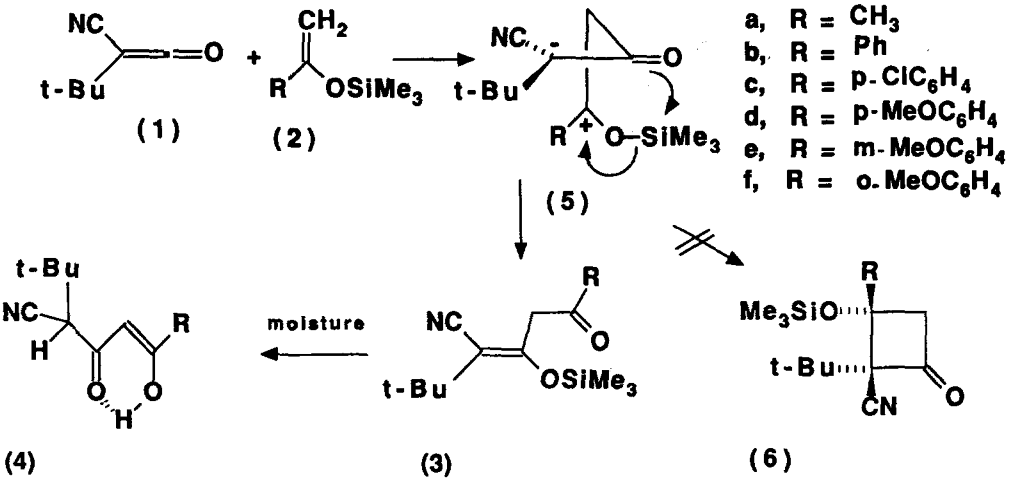
INTRODUCTION

The 2+2 cycloaddition reactions involving ketenes with a variety of ketenophiles provide an important chemical template in the arsenal of synthetic chemists for constructing four membered ring systems.[1] A great deal of work has appeared concerning both inter- and intra-molecular[2] addition reactions. Because of several experimental advantages, t-butylcyanoketene (TBCK) has received the most attention for investigations of the mechanisms of 2+2 cycloaddition reactions.[3] Although the cycloaddition of TBCK onto normal alkenes is best rationalized in terms of a concerted $2\pi_a + 2\pi_s$ reaction mode[3], recent studies involving TBCK and electron rich alkenes point to a stepwise mechanism involving zwitterionic intermediates.[4] However, asynchronous picture of the transition states, in which the bonding between the ketenic carbonyl carbon and the more nucleophilic carbon of the alkene is considerably advanced over the development of the second bond, sometimes provide better understanding of the mechanism of certain intramolecular ketene-alkene cycloadditions.[5]

In this report, we want to examine the addition reaction of tert-butylcyanoketene with several silyl enol ethers and conjugated dienes. Such a study would indeed be of both theoretical and practical importance.

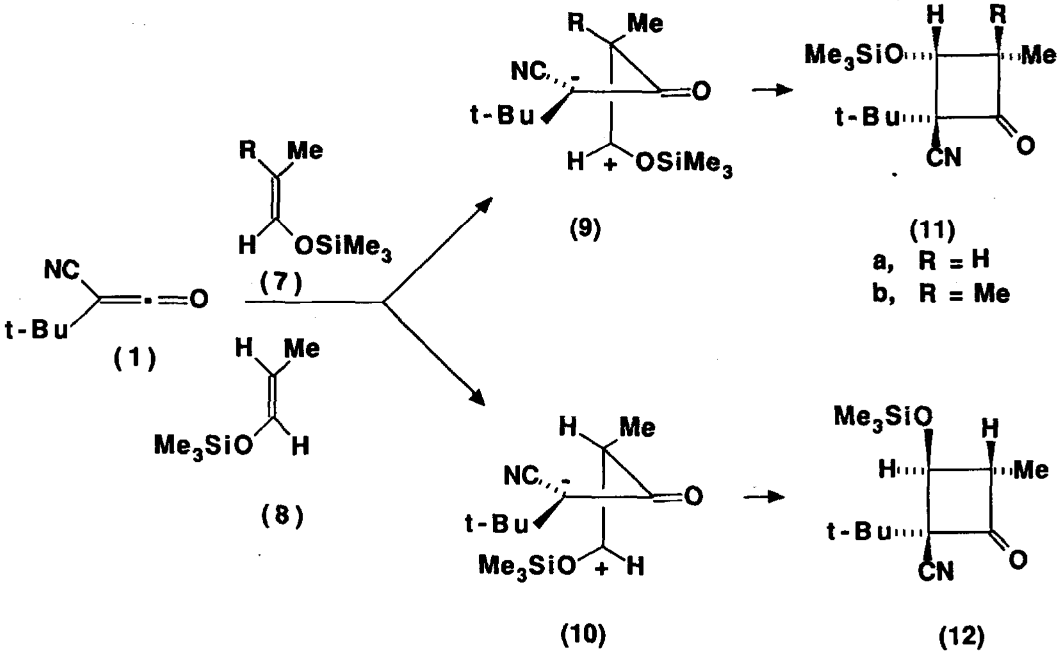
RESULTS AND DISCUSSION

TBCK was generated[6] in refluxing benzene in the presence of trimethylsilyl enol ether (2). The results of the addition reactions of TBCK (1) with various silyl enol ethers (2) and reaction conditions are given in Table 1. Careful analysis of NMR spectra of the reaction mixtures failed to detect any formation of the anticipitated cyclobutanone adduct (6). Instead, an open chain product (3) and in some cases a mixture of products (3) and (4) are obtained. The silyl enol ethers (3) seem to be moisture sensitive and on hydrolysis afforded the products (4) in some cases. A stepwise mechanism involving a zwitterionic intermediate (5) may be involved in the addition reaction. Nucleophilic attack by the enol ether (2) onto the TBCK from its least hindered side affords the most stable zwitterion (5) regioselectiviely (Scheme 1).



Scheme 1

Because of the severe steric encumbrance in a 2,2,3,3-tetrasubstituted cyclic system, the dipolar intermediate (5) rearranges to the observed acyclic product instead of the ring closure to the cyclobutanone (6).



Scheme 2

The E-geometry of the alkenes **(3)** is based on the assumption that the least hindered approach of the enol ether would give the intermediate **(5)** which, as shown in scheme 1, should afford the E-alkene **(3)**. Infrared and NMR spectra reveal the structure of the hydrolysis product as depicted in **(4)** with intra-molecular hydrogen bonding as well as extended conjugation.

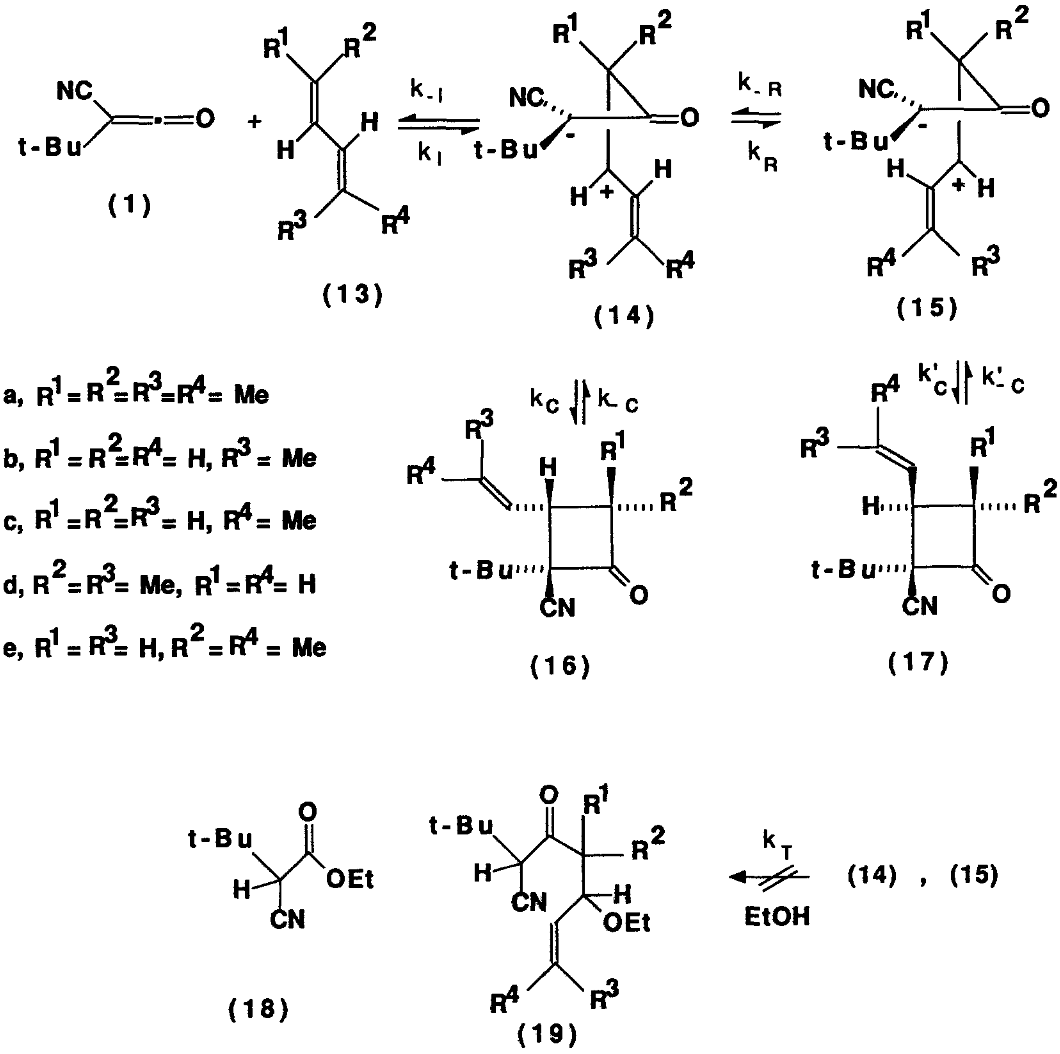
The cycloaddition reactions of TBCK **(1)** with cis- and trans - isomers of 1-(trimethylsiloxy) propene **(7a** and **8)** and 2-methyl-1-(trimethylsiloxy)propene **(7b)** under kinetic reaction conditions were shown to proceed via zwitterionic intermediate of structural types **(9)** and **(10)** to afford **(11)** and **(12)** as the major adducts[4]. Thus, while the silyl enol ether of 1,2-di-and 1,2,2-tri-substituted alkene types **(7,8)** afforded the cyclobutanones, the corresponding addition reaction of silyl enol ether **(2)** afforded only the acyclic products. This observation can be appreciated by reallizing the tremendous steric interaction between the tert-butyl group and two other groups in the vicinal position if a cyclobutanone is formed (Scheme 2).

Table 1. Addition reaction of TBCK **(1)** with silyl enol ethers **(2)** in benzene.

Alkene (2)	Temp (°C)	Reac'n time (h)	Isolated Yield (%)	
			(3)	(4)
a	25	40	-	60
b	25	72	27.4	35.5
c	80	24	32	32
d	80	17	26	26
e	80	31	-	64
f	80	28	-	56

Next we focussed our attention on the addition reaction of TBCK onto acyclic conjugated dienes. The results are given in Table 2. Previous work on TBCK-dienes cycloadditions[7] involved cyclic dienes mainly and a brief report on acyclic dienes[1b]. One such system which has been investigated in some detail, is 1,3-cyclopentadiene. In those studies it has been shown that the unsymmetrical ketenes undergo cycloaddition to the cyclic dienes in such a way that the bulkier substituent exclusively assumes the most crowded endo position to give the contrathermodynamic kinetic product.

In the reaction of TBCK with 2,5-dimethyl-2,4-hexadiene **(13a)**, two cyclic products **(16a)** and **(17a)** were isolated after 24 h in refluxing benzene. Cycloaddition did not occur at 25°C. When a solution of **(16a)** and **(17a)**, (0.43 mmol), in a respective ratio of 1:2, in dry benzene (15 mL) containing ethanol (1 mL) was refluxed for 16 h, the ratio becomes 1:5, respectively. The experiment confirms the stereochemistry of the thermodynamic adduct as depicted in **(17a)**. A concerted mechanism for this cycloaddition is expected to give **(16a)** on the basis of the least hindered approach of the ketene and diene. One may be tempted to assume the cycloreversion of the kinetic adduct **(16a)** to the starting diene and TBCK which under thermodynamic conditions recombine to give the stable adduct **(17a)**. This is, however, not the fact since the regenerated ketene would react with the trapping agent ethanol to afford the trapped ester **(18)** immediately in a fast reaction. The NMR spectrum ruled out the formation of the ester **(18)**. The results seem to confirm a zwitterionic mechanism. Least hindered approach of the diene in the rate determining step would give the zwitterion **(14a)** which in a fast way either ring close to **(16a)**, or rearrange to zwitterion **(15a)** which in turn affords cyclobutanone **(17a)**. It is to be noted that the zwitterions **(14)** and **(15)** are not intercepted by ethanol to give **(19)**. All these evidences support a reaction path in which the rate constants for cyclization (k_C) or bond rotation (k_R) are very much greater than that of the reversal (k_{-I}) to the reactants and interception of the zwitterions (k_T).



Scheme 3.

Favourable least hindered approach was also observed in the addition reactions of several other diens. When TBCK was allowed to react with cis-1,3-pentadiene **(13b)** at 25°C, two cyclobutanones **(16b)** and **(17b)** were obtained in a respective ratio of 5:1. When the above mixture of products in benzene-d_6 was heated at 100°C in a sealed NMR tube, the ratio was changed to 1:1 after 5 h and after 40 h, **(16b)** was completely converted to **(17b)**. The reaction of TBCK with trans-1,3-pentadiene **(13c)** at 25°C gave two cycloadducts **(16c)** (major) and **(17c)** (minor). A mixture of **(16c)** and **(17c)** in a respective ratio of 5:1 when heated in benzene-d_6, at 100°C, was changed to 1:1 after 5h and the isomerization was complete in 40 h.

Table 2. Cycloaddition reaction of TBCK (1) with conjugated dienes **(13)** in benzene.

Diene (13)	Temp (°C)	Reaction time (h)	Composition of adduct **(16)**:**(17)**	Isolated Yield (%)
a	80	24	1:2[a]	75
b	25	5	5:1	86
c	25	5	5:1	82
d	25	5	100:~0	63
e	25	12	100:~0	89
f	25	72	~0:100	66

[a] after 15 h reaction time the ratio was 2:1

Cycloaddition of TBCK with *cis*, *cis*-2,4-hexadiene **(13d)** at 25°C was completed after 5 h and afforded the only cyclobutanone **(16d)** both regio-and stereo-specifically. No thermal rearrangement of **(16d)** took place when it was refluxed in benzene for 24 h. The cycloaddition reaction of TBCK onto the *cis* double bond of *cis*, *trans*-2,4-hexadiene **(13e)** was complete after 12 h at 25°C to give the sole adduct **(16e)**.The corresponding addition of *trans*, *trans*-2,4-hexadiene **(13f)** onto TBCK was complete only after 3 days at 25°C and gave the cyclobutanone **(17f)** ($R^2 = R^4 =$ Me, $R^1 = R^3 =$ H) as the sole adduct. Again, no thermal rearrangement of **(17f)** was observed after refluxing a benzene solution for 24 h. In these addition reaction *cis* double bonds are found to react faster than their *trans* counterparts. The configurations as depicted in **(16)** and **(17)** are based on thermal study and proton NMR analysis. In **(16)** the C-3 H, being *cis* to the C-2 cyanide group, always appears at down field compared to the C-3 H of **(17)** which is shielded by the bulky t-butyl group.[8]

Attempted additions of 1,4-diphenylbutadiene, 2,3-diphenyl-1,3-butadiene and hexachloro-1,3-butadiene onto TBCK showed no sign of reaction even after prolonged refluxing in benzene (72 h). The inertness of these dienes may be attributed to the steric encumbrance encountered in their respective transition states leading to the products.

The above addition reactions fit a stepwise mechanism with a dipolar intermediate. The fact that only acyclic products were obtained in addition reactions of silyl enol ether really draw the line favoring rearrangement over ring closure to cyclobutanones. Cycloaddition reactions of the dienes demonstrated the effects of structure on the diene reactivity toward TBCK.

EXPERIMENTAL

Elemental analysis were performed on a Carlo-Erba elemental analyser 1106. I.r. spectra were recorded on a Nicolet 5 DBX FT IR and are reported in cm^{-1}, ^{1}H NMR spectra were recorded on a Bruker AC-80 using deuterochloroform, unless otherwise stated, as solvent and TMS as internal standard. All m.p.s. were determined with an electrothermal capillary melting point apparatus and were corrected. tert-Butylcyanoketene was generated by the procedure of Moore[6]. Trimethylsilyl enol ethers were prepared according to literature proceedures[9], and were distilled prior to use. The benzene was freshly distilled from calcium hydride under nitrogen. The addition reactions were performed under a positive pressure of dry argon.

Reaction of the TBCK with 2-Trimethylsiloxypropene (2a).- To the solution of TBCK (20.0 mmol) in dry benzene (50 mL) was added the silyl enol ether **(2a)** (25.0 mmol) and the reaction was stirred under argon at 25°C for 40 h. After removal of the solvent the residual liquid was Kugelrohr distilled (60°C, 0.05 mm Hg) to give **(4a)** as a colorless liquid (2.17 g, 60%), (Found: C, 66.03; H, 8.31; N, 7.59. $C_{10}H_{15}NO_2$ requires C, 66.27; H, 8.34; N, 7.73%), $\upsilon_{max.}$ (neat) 2969, 2246, 1729, 1606, 1376, 1212 and 941 cm^{-1} δ_H 1.15 (s, 9H), 2.15 (s, 3H), 3.15 (s, 1H), 5.75 (s, 1H).

Reaction of the TBCK with 1-phenyl-1-trimethylsiloxyethene(2b).- A solution of TBCK (6.6 mmol) and silyl enol ether **(2b)** (9.9 mmol) in benzene was stirred at 25°C for 72 h. After removal of the solvent under vacuum the residual solid was washed with petroleum ether to give a mixture of **(3b)** and **(4b)** in an approximate 1:1 ratio (63%). The mixture of products on crystallization from ether afforded **(4b)**. Concentration and crystallization of the mother liquor gave **(3b)**.

Compound **(3b)**: colourless crystals, m.p. 52-54°C (Found: C, 68.50; H, 7.88; N, 4.65. $C_{18}H_{25}NO_2Si$ requires C, 68.52; H, 7.99; N, 4.44%); $\upsilon_{max.}$ (KBr) 2968, 2200, 1685, 1613, 1332, 852, and 739 cm^{-1}; δ_H 0.20 (s, 9H), 1.30 (s, 9H), 4.20 (s, 2H), and 7.50-8.00 (m, 5H).

Compound **(4b)**: Colorless crystals, m.p. 66-68°C. (Found: C, 74.04; H, 6.93; N, 5.97. $C_{15}H_{17}NO_2$ requires C, 74.05; H, 7.05; N, 5.76 %); $\upsilon_{max.}$ (KBr), 2970, 2242, 1597, 1575, 1491, 1160, 774, and 700 cm^{-1}; $^{\delta}$H 1.20 (9 H, s), 3.30 (1 H, s), 6.40 (1 H, s), 7.45-7.60 (3 H, m) and 7.90 (2 H, dd, J 2.0, 8.0 Hz).

Reaction of TBCK with 1-p-Chlorophenyl-1-trimethylsiloxyethene(2c).— A solution of TBCK (6.6 mmol) and silyl ether **(2c)** (9.9 mmol) was refluxed for 24 h. After removal of the solvent the residual solid was washed with petroleum ether to give a mixture of products **(3c)** and **(4c)** in an approximate ratio of 1:1 (64%). Fractional crystallization from diethyl ether afforded the compound **(4c)** and crystallization from mother liquor gave **(3c)** as colourless crystals.

Compound **(3c)**: m.p. 50-53°C (Found: C, 61.71; H, 6.57; N, 4.20. $C_{18}H_{24}NO_2SiCl$ requires C, 61.78; H, 6.91; N, 4.00 %), $\upsilon_{max.}$ (KBr) 2968, 2200, 1688, 1605, 1316, 1110 and 848 cm^{-1}; δ_H 0.25 (9 H, s), 1.25 (9 H, s), 4.15 (2 H, s), 7.45 (2 H, d, J 9.0 Hz), and 7.90 (2 H, d, J 9.0 Hz).

Compound **(4c)**: m.p. 74-76°C (Found: C, 64.91; H, 5.64; N, 4.85. $C_{15}H_{16}NO_2Cl$ requires C, 64.86; H, 5.81; N, 5.04 %); $\upsilon_{max.}$ (KBr), 2963, 2239, 1595, 1562, 1488, 1441, 1251, 1091, and 802 cm^{-1}; $^{\delta}$H 1.20 (9 H, s), 3.27 (1 H, s), 6.37 (1 H, s), 7.45 (2 H, d, J 9.0 Hz), and 7.85 (2 H, d, J 9.0 Hz).

Reaction of 1-p-Methoxyphenyl-1-trimethylsiloxyethene (2d).— A solution of the TBCK (9.9 mmol) and the silyl enol ether **(2d)** (9.9 mmol) in benzene (50 mL) was stirred at 25°C for 12 h and then refluxed for 17 h. After removal of the solvent the residual liquid was Kugelrohr distilled. Two acyclic products **(3d)** (0.89 g, 26%) and **(4d)** (0.70 g, 26%) were obtained in succession as colourless liquids (65°C, 0.05 mm Hg).

Compound **(3d)**: $\upsilon_{max.}$ (neat), 2970, 2201, 1705, 1598, 1250, 1040, and 850 cm^{-1}; δ_H 0.75 (9 H, s), 1.27 (9 H, s), 3.87 (3 H, s), 4.15 (2 H, s), 6.95 (2 H, d, J 10.0 Hz), and 7.90 (2 H, d, J 10.0 Hz).

Compound **(4d)**: $\upsilon_{max.}$ (neat) 2970, 2245, 1600, 1253, and 850 cm^{-1}; δ_H 1.20 (9 H, s), 3.25 (1 H, s), 3.87 (3 H, s), 6.35 (1 H, s), 6.95 (2 H, d, J 10.0 Hz), and 7.90 (2 H, d, J 10.0 Hz).

Reaction of the TBCK with 1-m-Methoxyphenyl-1-trimethylsiloxyethene (2e). — A solution of the TBCK (6.6 mmol) and the silyl enol ether **(2e)** (13.2 mmol) in benzene (50 mL) was refluxed for 31 h. After removal of the solvent the residual liquid was Kugelrohr distilled (65°C, 0.05 mm Hg) to give **(4e)** (1.15 g, 64%) as a colourless liquid. (Found: C, 70.03; H; 6.93; N; 4.88. $C_{16}H_{19}NO_3$ requires C, 70.31; H, 7.01; N, 5.13%) $\upsilon_{max.}$ (neat) 2968, 2246, 1600, 1581, 1500, 1220, 1048 and 794 cm^{-1}; $^{\delta}$H 1.20 (9 H, s), 3.20 (1 H, s), 3.80 (3 H, s), 6.28 (1 H, s), 6.90-7.26 (4 H, m).

Reaction of the TBCK with 1-O-methoxyphenyl-1-Trimethylsiloxyethene (2f). — A solution of the TBCK (6.6 mmol) and the silyl ether (**2f**) (13.2 mmol) in benzene (50 mL) was refluxed for 28 h. After removal of the solvent the residual liquid was Kugelrohr distilled (65°C, 0.05 mm Hg) to give the acyclic dione (**4f**) as a colourless liquid (1.01 g, 56%). $\upsilon_{max.}$ (neat) 2968, 2254, 1606, 1565, 1491, 1253, 909 and 736 cm^{-1}; $^{\delta}$H 1.20 (9 H, s), 3.20 (1 H, s), 3.84 (3 H, s), 6.68 (1 H, s), and 6.94-7.80 (4 H, m).

Cycloaddition of the TBCK to 2,5-Dimethyl-2,4-hexadiene (13a). — A solution of the TBCK (6.6 mmol) and the diene (**13a**) (13.2 mmol) in benzene was refluxed for 24 h. After removal of the solvent and excess diene the residual liquid was Kugelrohr distilled (65°C, 0.05 mm Hg) to give a mixture of cyclobutanones (**16a**) and (**17a**) in a respective ratio of 1:2, as a colourless liquid (1.15 g, 75%). (Found: C, 76.90; H, 9.75; N, 5.91. $C_{15}H_{23}NO$ requires C, 77.20; H, 9.93; N, 6.00 %). IR and NMR spectra of the adducts (**16a**) and (**17a**) were deduced from the spectra of their mixtures.

Compound (**16a**): $\upsilon_{max.}$ (neat) 2968, 2877, 2238, 1786, 1466, 1368, and 1220 cm^{-1}; δ_H 1.13 (9 H, s), 1.20 (3 H, s), 1.45 (3 H, s), 1.75 (3 H, d, J 1.5 Hz), 1.82 (3 H, d, J 1.5 Hz) 3.60 (1 H, d, J 10.3 Hz), 5.43 (1 H, m).

Compound (**17a**): $\upsilon_{max.}$ (neat) 2970, 2254, 1786, 1753, 909 cm^{-1}; δ_H 1.10 (9 H, s), 1.17 (3 H, s), 1.27 (3 H, s), 1.72 (3H, d, J 1.5 Hz), 1.85 (3H, d, J 1.5 Hz), 3.10 (1 H, d, J 9.8 Hz), and 5.55 (1 H, m).

Cycloaddition of the TBCK to cis-1,3-Pentadiene (13b). — A solution of the TBCK (20.0 mmol) and the diene (**13b**) (22.0 mmol) in benzene (50 mL) was stirred at 25°C for 5 h. ^{1}H NMR spectrum of the reaction mixture indicated the formation of the adducts (**16b**) and (**17b**) in a ratio of 5:1, respectively. After stirring at 20°C for a total of 24 h, the solvent and the excess alkene was removed under vacuum. The residual liquid after Kugelrohr distillation (65°C, 0.05 mm Hg) afforded a mixture of (**16b**) and (**17b**) (3.28 g, 86%) as a faint yellow liquid. As described under Results and Discussion the adduct (**16b**) was converted into (**17b**) by heating.

Compound (**16b**): $\upsilon_{max.}$ (neat) 2967, 2229, 1795, 1466, 1401, 1368, 1212, 1105, and 1056 cm^{-1}; δ_H (C_6D_6) 1.00 (9 H, s), 1.38 (3 H, d, J 6.0 Hz), 2.55 (2 H, m), 3.48 (1 H, m), 5.20 (2 H, m).

Compound (**17b**): $\upsilon_{max.}$ (neat) 2970, 2254, 1795, 1475, and 1204 cm^{-1}; δ_H (C_6D_6) 0.80 (9 H, s), 1.48 (3 H, d, J 6.0 Hz), 2.55 (1 H, dd, J 8.5, 17.0 Hz), 2.65 (1 H, dd, J 7.0, 17.0 Hz), 2.97 (1 H, m), and 5.50 (2 H, m).

Cycloaddition of TBCK to trans-1,3-Pentadiene (13c). — A solution of the TBCK (20.0 mmol) and the diene (**13c**) (22.0 mmol) in benzene (50 mL) was stirred at 25°C for 5 h. After removal of the solvent and excess alkene the residual liquid was Kugelrohr distilled (65°C, 0.05 mm Hg) to give a mixture of cycloadducts (**16c**) and (**17c**) in a respective ratio of 5:1, as faint yellow liquid, (3.13 g, 82%). As discussed in the results and discussion the above mixture was thermally isomerized to (**17c**) completely.

Compound (**16c**): $\upsilon_{max.}$ (neat) 2967, 2196, 1794, 1606, 1228, and 1040 cm^{-1}; $^{\delta}$H 1.20 (9 H, s), 1.78 (3 H, d, J 5.5 Hz), 3.28 (2 H, m), 3.54 (1 H, m), and 5.74 (2 H, m).

Compound (**17C**): $\upsilon_{max.}$ (neat) 2970, 2245, 1794, 1606, 1204, and 1007 cm^{-1}; $^{\delta}$H 1.20 (9 H, s), 1.93 (3 H, d, J 6.0 Hz), 3.20 (2 H, m), 3.42 (1 H, m), and 5.90 (2 H, m).

Reaction of the TBCK with cis, cis-2,4-Hexadiene(13d). - From the reaction of the TBCK (20 mmol) and the diene (**13d**) (1.8 g, 22 mmol) in benzene at 25°C was isolated after 5 h a yellow oil which on Kugelrohr distillation (40°C, 0.007 mm Hg) afforded (**16d**) (2.58 g, 63%) as a colourless oil, (Found: C, 75.82; H, 9.34. $C_{13}H_{19}NO$ requires C, 76.06; H, 9.33 %); $\upsilon_{max.}$ (neat) 2980, 2227, 1796, 1372, 922, 763 cm^{-1}; $^{\delta}$H (C_6D_6) (250 Hz) 0.67 (3 H, d, J 7.35 Hz), 1.02 (9 H, s), 1.36 (3 H, dd, J 1.74, 6.85 Hz), 3.38 (1 H, dq, J 7.35, 11.50 Hz), 3.64 (1 H, dd, J 11.10, 11.50 Hz), 5.14 (1 H, ddq, J 1.74, 10.95, 11.10 Hz), 5.37 (1 H, ddq, J 0.87, 6.85, 10.95 Hz).

Reaction of the TBCK with cis, trans-Hexadiene (13e). — From the reaction of the TBCK (30 mmol) and the diene (**13e**) (2.17 g, 27 mmol) in benzene at 25°C, was isolated after 12 h, 5.2 g of a yellow crude oil which was purified by Kugelrohr distillation (40°C, 0.005 mm Hg) to give (**16e**) as a colourless oil (4.9 g, 89%). (Found: C, 76.19; H, 9.60. $C_{13}H_{19}NO$ requires C, 76.06; H, 9.33 %); υ_{max}. (neat) 2990, 2222, 1790, 1370 and 980 cm^{-1}; δ_H (250 MHz) 1.09 (3 H, d, J 7.45), 1.15 (9 H, s), 1.77 (3 H, dd, J 1.56, 6.59 Hz), 3.67 (1 H, dd, J 10.90, 11.50 Hz), 3.98 (1 H, dq, J 7.45, 11.50 Hz), 5.49 (1 H, ddq, J 1.56, 10.90, 14.90 Hz), 5.80 (1 H, dq, J 6.59, 14.90 Hz),

Reaction of the TBCK with trans, trans-2,4-Hexadiene (13f). - From the reaction of the TBCK (25.5 mmol) and the diene (**13f**) (2.05 g, 25.5 mmol) in benzene at 25°C, was isolated after 3 days, 4.2 g of a yellow oil, which, on kugelrohr distillation (45°C, 0.005 mm Hg), afforded (**17f**) as a colourless oil (3.45 g, 66%). (Found: C, 75.94; H, 9.22. $C_{13}H_{19}NO$ requires C, 76.06; H, 9.33%); υ_{max}. (neat) 2980, 2225, 1795, 1374, 965 cm^{-1}; $\delta_H(C_6D_6)$ (250 MHz) 0.77 (3 H, d, J 7.12 Hz), 0.92 (9 H, s), 1.53 (3 H, dd, J 1.50, 6.0 Hz), 2.36 (1 H, dd, J 8.0, 9.20 Hz), 2.88 (1 H, dq, J 7.12, 9.20 Hz), 5.34 (1 H, dq, J 6.35, 15.10 Hz), 5.66 (1 H, ddq, J 1.60, 8.0, 15.10 Hz).

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