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Cycloadditions of Constrained Dicyclopropylethylenes and Divinylcyclopropanes with Tetracyanoethylene

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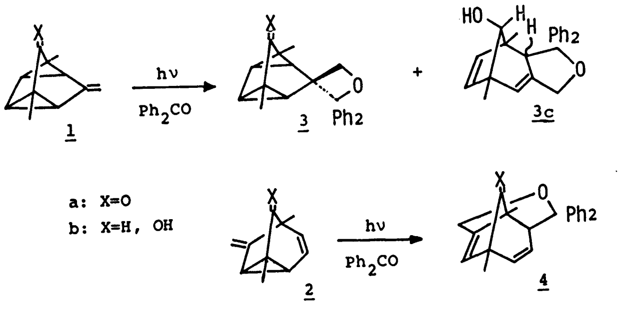
(Received May 14, 1981)

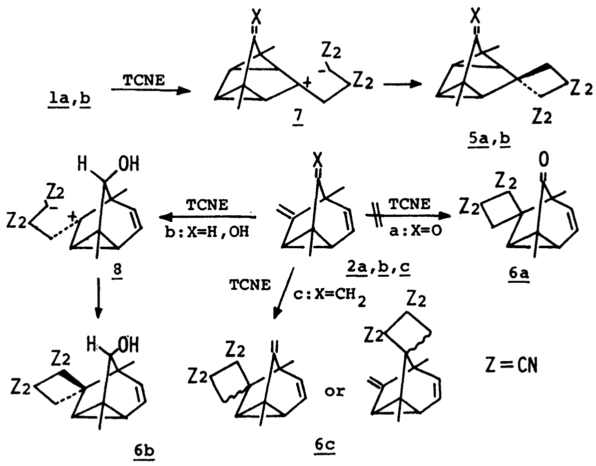
Synopsis. 2,4-Dimethyl-7-methylenetetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-one and its corresponding alcohol were reacted with TCNE to give $\pi2+\pi2$ cycloadducts at the exomethylene group. On the other hand, 1,5-dimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one did not react with TCNE, whereas its corresponding alcohol and 1,5-dimethyl-6,8-dimethylenetricyclo[3.2.1.0^{2,7}]oct-3-ene afforded $\pi2+\pi2$ cycloadducts. The reactivities were correlated with the ^{13}C-NMR data of the exomethylene groups, the electron densities of which are affected by the carbonyl group.

The electronic state and chemical reactivity of cyclopropane have attracted the continuous attention of organic chemists. Previously it has been reported that the photocycloaddition of benzophenone to 2,4-dimethyl-7-methylenetetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-one (**1a**)[1] or its corresponding alcohol **1b**[1] afforded an oxetane, **3a** or **3b** and an adduct, **3c**.[2] The product composition of these reactions was understood by means of the electron-withdrawing property of the carbonyl group. A similar reaction of 1,5-dimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one (**2a**)[3] or its corresponding alcohol **2b**[4] was also investigated to afford **4a** or **4b**, as is summarized in Scheme 1.[5] A $\pi2+\pi2$ cycloaddtion of cyclopropylethylenes with tetracyanoethylene (TCNE) is generally accepted to proceed *via* a zwitterionic intermediate.[6] In this article, the cycloaddition of **1a** and **1b** and of **2a** and **2b**, to TCNE was investigated, and it was clarified that the reactivity of the exomethylene group toward TCNE was affected by the presence of the carbonyl group.



Scheme 1.

The reaction of **1a** and TCNE in acetonitrile at a refluxing temperature for 6 h provided, after recrystallization, an adduct **5a** in a 24% yield. The similar reaction of **1b** in refluxing dichloromethane for 1 h afforded an adduct **5b** in a 37% yield. The reaction of **1b** was faster than that of **1a** and proceeded at a lower temperature. The assignment of these structures, **5a** and **5b** was deduced from the spectral data (see Experimental). The hydroxyl proton in an NMR spectrum of **5b** could not be assigned distinctly. The stereochemistry of oxetane rings of **3a** and **3b** has been confirmed, as is depicted in Scheme 1.[2] This orientation of the benzophenone moiety must be favored by a steric hindrance. On the basis of a comparison with this observation, the stereochemistry of the cyclobutane rings of **5a** and **5b** depicted in Scheme 2 was proposed.



Scheme 2.

On the other hand, the reaction of the tricyclic ketone **2a** and TCNE in refluxing dichloromethane or acetonitrile did not afford any cycloadduct. The similar reaction of **2b** and TCNE in refluxing acetonitrile for 5 h, however, afforded an adduct **6b** in a 31% yield. The NMR spectrum of **6b** exhibited the proton signals of a vinylcyclopropane moiety and a resonable geminal coupling constant (J=14.0 Hz) for the hydrogens of the cyclobutane ring.[7] Therefore, the structure **6b** was deduced to be as is depicted in Scheme 2. Although the evidence for the stereochemistry of the cyclobutane ring of **6b** is not presented, the exo orientation of the TCNE moiety must be favorable because of the steric hindrance.[8]

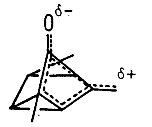
The zwitterionic species, such as **7** and **8**, would be the intermediate in the present cycloaddition reactions.[6] The following intramolecular combination in **7** and **8** from the less sterically hindered site afford the cycloadducts, **5a**, **5b**, and **6b**. The rearrangement of the intermediate **7** or **8** could not be observed. This feature is not like the case of radical reactions.[2,3,9] The corresponding radical species in the photocycloaddition of **1b** or **2a** and **2b** with benzophenone has been observed to rearrange (Scheme 1). The inertness of **2a** toward TCNE is noticeable. The inclusion of an electron-withdrawing substituent, such as CN or CO$_2$Me, in a

Table 1. ^{13}C-NMR chemical shifts of exomethylene group in CDCl$_3$

$\overset{\text{A}}{>\text{C}}=\overset{\text{B}}{\text{CH}_2}$	1a	1b	2a	2b
A	149.6	152.9	148.3	154.2
B	110.9	107.7	112.4	104.5
$\Delta\delta_{\text{AB}}$	38.7	45.2	35.9	49.7
$\Delta\Delta\delta_{\text{AB}}$	6.5		1.38	

cyclopropane ring has been demonstrated to preclude its reaction with TCNE.[10] The rate of the reaction of **1b** with TCNE was faster than that of **1a**. Therefore, the inertness of **2a** toward TCNE under the present conditions may be attributed to the presence of an electron-withdrawing carbonyl group.

The ^{13}C-NMR spectra of **1a**, **1b**, **2a**, and **2b** were recorded, the data for the carbons of the exomethylene groups are summarized in Table 1. Regarding the $\Delta\delta_{AB}$ value in the **1a**—**1b** and **2a**—**2b** pairs, **1b** and **2b** exhibit larger values than the corresponding ketones, **1a** and **2a** respectively. This fact seems to indicate that the polarization of the exomethylene group of **1b** or **2b** is greater than that of **1a** or **2a** respectively.[11] The $\Delta\Delta\delta_{AB}$ value between **1a** and **1b** is 6.5, while the value between **2a** and **2b** indicates the larger value of 13.8. This fact may suggest that the difference in the polarization of the exomethylene group between **2a** and **2b** is very large as compared to that between **1a** and **1b**. The reduction of the polarization may be ascribed to the carbonyl group, which withdraws the electron of the exomethylene group of **1a** or **2a** through the cyclopropane ring, as is depicted in the structural formulae, **9** and **10**. This effect also seems to be reflected by the values of δ_A and δ_B of **1a**, **1b**, **2a**, and **2b**. Therefore, the exomethylene group of **2a** is probably electron-deficient as compared to that of **2b**, so **2a** would be inert to the present reaction. Support for the deactivation by the carbonyl group in **2a** may be given by the following observation. The reaction of TCNE with 1,5-dimethyl-6,8-dimethylenetricyclo[3.2.1.0^{2,7}]oct-3-ene (**2c**), which has a π-electron system similar to that of **2a**, was achieved to afford an adduct **6c** in a 30% yield. The structure of **6c** was deduced from the spectral data to have a cyclobutane ring. There are still two possible structures concerning the reaction site for the **6c** adduct.



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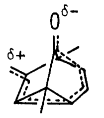

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Experimental

Reaction of 1a with TCNE. A solution of **1a** (160 mg, 1 mmol) and TCNE (192 mg, 1.5 mmol) in 2 cm^3 of acetonitrile was refluxed for 6 h. The reaction mixture was then treated with 100 mg of Norit, and the filtrate was concentrated to give 56 mg (24%) of **5a**: mp 199—200 °C (from benzene): IR (KBr) 2955, 2250, 1710 cm^{-1}; NMR (DMSO-d_6) δ 1.12 (6H, s), 2.24 (2H, d, J=5.0 Hz), 2.72 (2H, d, J=5.0 Hz), 3.37 (2H, s); MS m/e 288 (M$^+$). Found: C, 70.56; H, 3.91; N, 19.80%. Calcd for $C_{17}H_{12}ON_4$: C, 70.82; H, 4.20; N, 19.44%.

Reaction of 1b with TCNE. A solution of **1b** (324 mg, 2 mmol) and TCNE (379 mg, 2.4 mmol) in 2 cm^3 of dichloromethane was refluxed for 1 h. The subsequent evaporation of the solvent afforded a brown solid. This solid was dissolved in 5 cm^3 of acetone, followed by the addition of Norit. The Norit was removed by filtration, and then the acetone was evaporated. The residue was recrystallized from benzene to afford 199 mg (37%) of **5b**: mp 150—151 °C; IR (KBr) 3550, 2250 cm^{-1}; NMR (DMSO-d_6) δ 1.15 (6H, s), 1.70 (2H, d, J=5.0 Hz), 1.98 (2H, d, J=5.0 Hz), 3.30 (2H, s), 3.50 (1H, s); MS m/e 290 (M$^+$). Found: C, 70.16; H, 4.56; N, 19.35%. Calcd for $C_{17}H_{14}ON_4$: C, 70.33; H, 4.86; N, 19.30%.

Reaction of 2a with TCNE. A solution of **2a** (160 mg, 1 mmol) and TCNE (128 mg, 1 mmol) in dichloromethane (3 cm^3) was refluxed for 31 h. After the removal of the solvent *in vacuo*, the residue was chromatographed on florisil, using benzene as the eluent, to give 144 mg (90%) of the starting material **2a**. A similar reaction in refluxing acetonitrile for 10 h afforded no adduct except **2a** in a 77% yield.

Reaction of 2b with TCNE. A solution of **2b** (162 mg, 1 mmol) and TCNE (154 mg, 1.2 mmol) in 5 cm^3 of acetonitrile was refluxed for 5 h. After the removal of the solvent, the residue was chromatographed on florisil. The elution with benzene–dichloromethene (1/1) afforded 94 mg (31%) of **6b**, which was recrystallized from ethanol: mp 186—187 °C; IR (KBr) 3550, 2250 cm^{-1}; NMR (DMSO-d_6) δ 1.26 (3H, s), 1.41 (3H, s), 1.88 (2H, m), 3.13 (1H, d, J=14.0 Hz), 3.29 (1H, d, J=7.0 Hz), 3.31 (1H, d, J=14.0 Hz), 4.56 (1H, d, J=7.0 Hz), 5.17 (1H, d, J=8.0 Hz), 6.38 (1H, m); MS m/e 290 (M$^+$). Found: C, 70.47; H, 4.68; N, 19.00%. Calcd for $C_{17}H_{14}ON_4$: C, 70.33; H, 4.86; N, 19.30%.

Reaction of 2c with TCNE. A solution of **2c**[12] (158 mg, 1 mmol) and TCNE (128 mg, 1 mmol) in acetonitrile (5 cm^3) was refluxed for 7 h. After the removal of the solvent *in vacuo*, the residue was chromatographed on florisil, using benzene as the eluent to give a crystalline solid. This solid was recrystallized from ethanol to give 110 mg (38%) of **6c**: mp 178—179 °C; IR (KBr) 2275, 1650 cm^{-1}; NMR (acetone-d_6) δ 1.16 (3H, s), 1.42 (3H, s), 2.32 (2H, m), 2.66 (1H, d, J=11.0 Hz), 2.75 (1H, d, J=11.0 Hz), 4.78 (1H, s), 4.85 (1H, s), 5.75 (1H, dxd, J=7.0, 2.0 Hz), 6.30 (1H, m); MS m/e 286 (M$^+$). Found: C, 75.15; H, 4.71; N, 19.29%. Calcd for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57%.

^{13}C-NMR Spectra of 1a,b, and 2a,b in $CDCl_3$. **1a**: 212.3, 149.6, 110.9, 44.8, 44.0, 38.9, 17.2 ppm. **1b**: 152.9, 107.7, 80.6, 42.7, 41.6, 37.8, 20.3 ppm. **2a**: 212.6, 148.3, 132.8, 125.5, 112.4, 52.0, 37.8, 36.9, 30.4, 12.2, 11.7 ppm. **2b**: 154.2, 131.6, 131.1, 104.5, 81.7, 51.4, 37.1, 36.6, 33.1, 20.9, 19.4 ppm.

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