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Reaction of Some Compounds Having Both Endo and Exo Olefinic Bonds with 1,2,4-Triazoline-3,5-diones

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Synopsis. Reaction of piperitenone, (+)-limonene, or styrene with 1,2,4-triazoline-3,5-dione (TAD) produces adducts by ene reaction. The reaction of (+)-limonene gives a 2:1 adduct which results from further addition of TAD to an intermediary ene reaction product. The reaction of styrene gives 2:1 adducts *via* further addition of TAD to the Diels-Alder reaction product.

1,2,4-Triazoline-3,5-dione (TAD) and its 4-phenyl (PTAD) and 4-methyl (MTAD) derivatives have widely been used as dienophiles or enophiles.$^{1)}$ An extensive mechanistic study$^{1)}$ revealed that derivatives of TAD were the most reactive dienophiles or enophiles. In the present study, we are interested in reactions of PTAD with two monoterpenoid ring compounds, *i.e.*, 3-methyl-6-isopropylidene-2-cyclohexen-1-one (piperitenone)$^{2)}$ and (+)-limonene, and with styrene.

(+)-Pulegone and mesityl oxide are known to be reactive enophiles with PTAD,$^{3)}$ however no studies have been reported on reactions with PTAD of such compounds as contain both endo and exo olefins, *e.g.*, piperitenone and (+)-limonene.

Results and Discussion

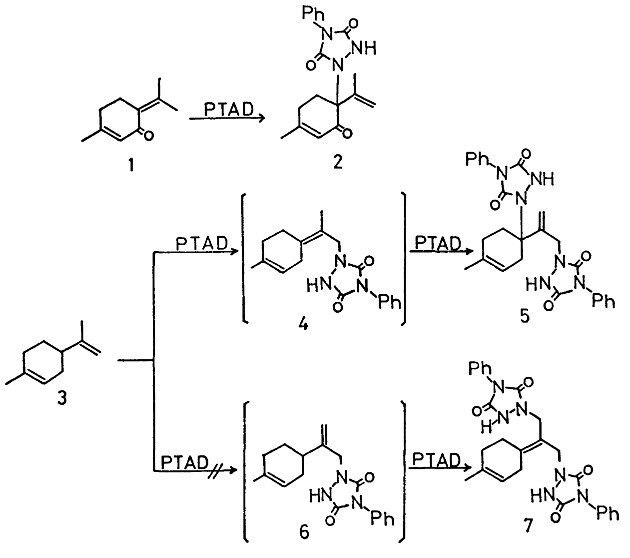
A reaction of equimolar amounts of PTAD and piperitenone (**1**) in ethyl acetate or dichloromethane for 12 h at ambient temperature gave, on work up, compound **2** in 64% yield. Under the same conditions (+)-limonene (**3**) gave adduct **5** in 64% yield.

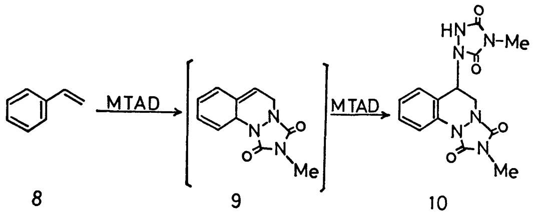
The structures of products **2** and **5** were determined from ^{1}H NMR, mass, and IR spectra by identifying the olefin protons of the isopropenyl groups, the molecular ion peaks, and the absorption of the vinylidene olefin groups, respectively.

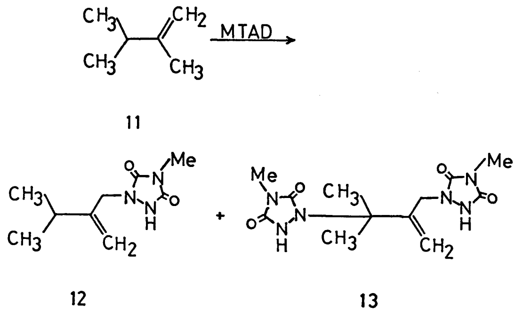
Adduct **2** is exactly of the same type as the compound afforded by the reaction of (+)-pulegone or mesityl oxide, which gives an isopropenyl group on the 6-position *via* a hydrogen abstraction from the methyl group. Product **5** is a 2:1 adduct, which we can easily infer to have been formed *via* an addition of PTAD to the isopropenyl group through ene reaction to give intermediate **4**, which is successively subject to an ene reaction on the 4-position with the second PTAD to generate product **5**. Formation *via* 1:1 adduct **6** of 2:1 adduct **7**, which should have no isopropenyl proton, is denied on the basis of ^{1}H NMR spectra.

Under the same conditions styrene (**8**) gave 2:1 adduct **10** in quantitative yield. The above results indicate that the ene reaction$^{4)}$ of a reactive enophile of TAD derivative with the exo cyclic olefin in compound **4** or **9** takes place by involving a proton transfer, thus leading to a 2:1 adduct in the reaction of **3** or **8** with TAD. Diels-Alder adduct **9** possesses the structure of conjugated endo cyclic diene, however it gave 2:1 adduct **10**, as a result of ene reaction with the second MTAD, rather than the Diels-Alder reaction product.

The above results, have first revealed that the reaction of a compound having both endo and exo olefinic bonds with TAD proceeds predominantly *via* addition to the exo olefin. The reaction of 2,3-dimethyl-1-butene (**11**) with MTAD has clearly demonstrated that MTAD first attacks the isopropenyl group, with a subsequent reaction with another molecule of enophile leading to a 2:1 adduct.







Experimental

Measurements. Melting points were measured on a Yanagimoto Seisakusho micro melting point apparatus. ^{1}H

NMR spectra were recorded on a Hitachi R-24 (60 MHz) spectrometer with TMS as an internal standard, IR spectra on a JASCO A-3 infrared spectrophotometer, and mass spectra on a Hitachi RMU 7MG GC-MS spectrometer.

*Reaction of **1** with PTAD.* *Typical Procedure*: To a solution of 0.5 g (3.33 mmol) of **1** in 10 ml of ethyl acetate or dichloromethane, 0.6 g (3.33 mmol) of PTAD was added all at once. The mixture was stirred magnetically at room temperature with light excluded for protection until the red color of PTAD had faded completely (12 h) and a light yellow solution had appeared. The solution was poured into petroleum ether to precipitate colorless crystalline product **2** (0.7 g, 64% yield): mp 194—196 °C (needles from ethanol ethyl acetate); ^{1}H NMR (CDCl$_3$) δ=1.88 (s, 3H, CH$_3$), 1.95 (s, 3H, CH$_3$), 2.33 (br d, J=4.55 Hz, 2H, CH$_2$), 2.65 (br d, J=4.5 Hz, 2H, CH$_2$), 4.87 $\left(\text{s, 1H, } \begin{array}{ccc} \underline{H} & & CH_3 \\ & C{=}C & \\ H & & \end{array}\right)$, 5.19 $\left(\text{s, 1H, } \begin{array}{ccc} H & & CH_3 \\ & C{=}C & \\ \underline{H} & & \end{array}\right)$, 5.93 (s, 1H, endo olefin), 7.44 (s, 5H, Ph), and 8.72 (br, 1H, NH); IR $\nu_{\max}^{\text{KBr}}$ 3360, 1780, 1700, and 1620 cm^{-1}; MS *m/e* 325 (M$^+$) and 149 (M$^+$−PTADH).

Found: C, 66.26; H, 5.83; N, 13.05%. Calcd for $C_{18}H_{19}N_3O_3$: C, 66.46; H, 5.85; N, 12.92%.

*Reaction of **3** with PTAD.* A reaction of **3** with PTAD in the same procedure as described above gave 2:1 adduct **5** in 64% yield: mp 150—151 °C; ^{1}H NMR (CDCl$_3$) δ= 1.97 (s, 3H, CH$_2$), 1.48 2.40 (br m, 6H, ring CH$_2$), 4.31 (br, 2H, N CH$_3$), 6.35 (br s, 2H, NH), 7.43 (s, 10H, Ph); IR $\nu_{\max}^{\text{KBr}}$ 3460, 1785, 1725, and 1600 cm^{-1}; MS *m/e* 482 (M$^+$), and 130 (M$^+$−2PTADH).

Found: C, 64.78: H, 4.71; N, 17.46%. Calcd for $C_{26}H_{24}N_6O_4$: C, 64.46; H, 4.96; N, 17.36%.

*Reaction of **8** with MTAD.* As soon as MTAD was added all at once to **8** under the same condition as above, white crystals precipitated. After stirring for 15 min, the white precipitate, which is 2:1 adduct **10**, was collected by filtration in quantative yield: mp 270—273 °C; ^{1}H NMR (DMSO-d_6) δ=3.15 (s, 3H, N CH$_3$), 3.23 (s, 3H, N CH$_3$), 3.85 (d, J=12.5 Hz, 2H, CH$_2$), 5.76 (s, 1H, N CH), 7.33 (m, 4H, aryl), and 8.33 (br, 1H, NH); MS *m/e* 330 (M$^+$).

Found: C, 50.95; H, 4.21; N, 25.28%. Calcd for $C_{14}H_{14}N_6O_4$: C, 50.99; H, 4.24; N, 25.46%.

*Reaction of **11** with MTAD.* A reaction of **11** with MTAD gave 1:1 **12** and 2:1 **13** adducts in 73 and 15% yields, respectively. Major product **12**: oil; ^{1}H NMR (CCl$_4$) δ=1.46 (s, 3H, CH$_3$), 1.67 (s, 3H, CH$_3$), 2.17 (m, 1H, CH), 3.01 (s, 3H, N CH$_3$), 4.16 (s, 2H, CH$_2$), 4.96 $\left(\text{s, 2H, } \begin{array}{cc} \diagdown & \\ & C{=}CH_2 \\ \diagup & \end{array}\right)$, and 8.92 (br, 1H, NH). Minor product **13**: Colorless needles; mp 160—161 °C; ^{1}H NMR (DMSO-d_6) δ=1.46 (s, 3H, CH$_3$), 1.96 (s, 3H, CH$_3$), 3.04 (s, 6H, N CH$_3$), 4.30 (s, 2H, N CH$_2$), 4.87 $\left(\text{s, 1H, } \begin{array}{ccc} \diagdown & & \underline{H} \\ & C{=}C & \\ \diagup & & H \end{array}\right)$, 5.08 $\left(\text{s, 1H, } \begin{array}{ccc} \diagdown & & H \\ & C{=}C & \\ \diagup & & \underline{H} \end{array}\right)$, and 8.99 (br, 2H, NH); MS *m/e* 310 (M$^+$).

Found: C, 46.48; H, 5.88; N, 27.04%. Calcd for $C_{12}H_{18}N_6O_4$: C, 46.45; H, 5.81; N, 27.10%.

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