Studies on Pheromones of Female Eri-Silk Moth, I. Preparation of C_6–C_{11} 2-Alkenyl Triphenylphosphonium Bromides

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Some C_{16}–C_{17} conjugated alkadienals assumed to have pheromonal activity toward male Eri-silk moth, *Philosamia cynthia ricini*, based on our earlier studies.[1,2] We proposed to prepare these substances and in this paper describe syntheses of the titled compounds, which are intermediate in the syntheses. The syntheses were carried out in the conventional way (scheme)[4] : Propargyloxy tetrahydropyran (**1**) was condensed with alkyl bromides (**2**) using the classical Na in liq. ammonia method to give alkynyloxy tetrahydropyran (**3**), which were then hydrolyzed to the corresponding free alcohols (**4**). These were converted either to the (*Z*)-alkenols (**5**(*Z*)) by hydrogenation over Lindlar catalyst[5] or to the (*E*)-alkenols (**5**(*E*)) by treating with lithium tetrahydroaluminate according to the Rossi's procedure.[6] Each product was converted to the corresponding bromides (**6**(*Z*) or **6**(*E*)) on treatment with 47% HBr aq, and these were then converted to the corresponding triphenylphosphonium bromides (**7**).

The intermediate compounds, **3**, **4**, **5** and **6**, were characterized by IR- and NMR- spectral analyses. As far as observed from spectral data, allylic rearrangement product could not be detected in **6**, and, however, the stereoselectivity of β, γ-double bond seems to be not distinctly retained in the bromination as revealed from IR-spectra. The final products **7** were at any rate obtained as analysis-pure substances. Their NMR-analyses were also satisfactorily coincident to the structures, although the geometrical purity can not be critically detected. These products were, however, used for the further syntheses, because it was not absolutely necessary to use the geometrically absolutely pure substances for our present purpose.[3]

EXPERIMENTAL PROCEDURES

Mps and bps were not corrected. PMR spectra were taken on a Hitachi R-24

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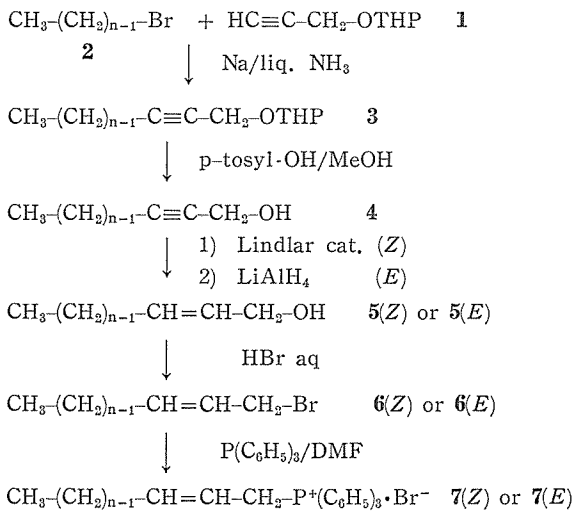
Fig 1. General Scheme for Syntheses of Alkenyl Triphenylphosphonium Bromide



2 ~ 7	n
a	3
b	4
c	5
d	6
e	7
f	8

(60MHz) NMR-spectrometer, TMS as standard in $CDCl_3$. For taking IR-spectra a Hitachi EPI spectrometer was used, liquids as film and solids matter as KBr-discs.

1) *2-(2'-alkynyloxy)-tetrahydropyran* (**3a-f**) : To liq. NH_3 at $-40°$ were added according to the Lit.[4] 2-propargyloxy tetrahydropyran ($bp_{12}66°$), a crystal of ferric nitrate and metallic sodium (1.5eq) under stirring. Upon discharge of the blue colour, the corresponding alkyl bromide **2a-f** was added to this solution and stirred for 4h. The reaction mixture was then treated as described in the Lit.[4] and the reaction product fractionally distilled. Yield : 51-61%; Bp (°C/mmHg): **a** 126/8, **b** 118/10, **c** 113/1.5, **d** 127/0.4, **e** 148/1.0 and **f** 152/1.8; IR(cm^{-1}): C≡C 2200-2230(w), NMR(δ) 4.05-4.18 (t, J=2Hz, =C-C$\underline{H_2}$-O) 4.67-4.76 (b-s, H-C-C).
-O⟋⟍O-

2) *Hydrolysis of pyranyl ether to alkynol* (**4a-f**) : The corresponding pyranyl ether **3a-f** (40m mole) was dissolved in MeOH (85ml) containing p-toluene sulfonic acid (2.5m mole). The solution was allowed to stand overnight under stirring. The reaction mixture was then treated in the usual manner and the neutral fraction fractionally distilled. Yield: 76-96%; Bp (°C/mmHg): **a** 84/18, **b** 80/16, **c** 100/15, **d** 85/0.3, **e** 114/4 and **f** 101/0.2; IR (cm^{-1}):OH 3350, C≡C 2200-2220 (w);NMR(δ): 4.1-4.2 (t, J=2Hz, =CH-C$\underline{H_2}$-O); TLC (Rf):0.5-0.6.

3) *Hydrogenation of alkynol to (Z)-2-alkenol* (**5a-f**(Z)): It was carried out in MeOH usually by using Lindlar catalyst[5] poisoned with a small amount of quinoline.

Yield; 69–84%;Bp (°C/mmHg): **a** 58/12, **b** 75–6/14, **c** 87/18, **d** 101–2/12, **e** 85–6/0.3 and **f** 102/0.7; IR(cm^{-1}): OH 3320–3330 C=C 1650–1660 (w); NMR(δ):3.8–4.1 (d, J= 5Hz or m, =CH–C$\underline{H_2}$–O), 5.0–5.9 (m, CH=CH); TLC (Rf):0.51–0.59.

4) *Hydrogenation of alkynol to (E)-2-alkenol* (**5b-f**(*E*)): According and analogous to the Lit.[6] the corresponding alkynol **4b-f** was reduced to (*E*)-alkenol (**5b-f**(*E*)) with excess of $LiAlH_4$ in the mixture of tetrahydrofuran and diglyme. **5a**(*E*) was commercially available. Yield:29–63%;Bp (°C/mmHg):**b** 82/18, **c** 94–5/15, **d** 76.5/0.4, **e** 89/0.7 and **f** 102/0.8; IR(cm_{-1}): OH 3300–3340, C=C 1670–1680 and 960–980(s); NMR(δ): 3.6–4.1 (b-d or m, =CH–C$\underline{H_2}$–O) 5.4–5.7 (m, CH=CH);TLC (Rf): 0.45–0.59.

5) *Bromination of alkenol to alkenyl bromide* (**6a-f**(*Z*) and **6a-f**(*E*)): The corresponding alkenol (**5a-f**(*Z*) and **5a-f**(*E*) (10m mole) was treated with a mixture (44 ml) of 47% HBr aq and 95% H_2SO_4 (10:1) for 3 days at room temperature under stirring. The reaction mixture was treated in the usual way and the neutral fraction fractionally distilled. Yield:56–88% ; Bp(°C/mmHg): **a**(*Z*) 42/12, **b**(*Z*) 68/16, **c**(*Z*) 81–2/17, **d**(*Z*) 104/18, **e**(*Z*) 90/2.0, **f**(*Z*) 93–4/0.6, **a**(*E*) 40/13, **b**(*E*) 75/20, **c**(*E*) 82/14, **d**(*E*) 95/14, **e**(*E*) 84–5/1.2 and **f**(*E*) 92–3/0.6; IR(cm_{-1}): C=C 1640–1660 (w) 960 (m or w in **b-f**(*Z*), s in **a-f**(*E*)) 720–750 (s or m in **b-f**(*Z*), w or very w in **a-e**(*E*) and m in **f**(*E*)). NMR (δ):3.7–4.0 (m, =CH–C$\underline{H_2}$–Br) 5.1–6.1 (m, CH=CH, more simply splitted pattern in **b-f**(*E*).

6) *2-Alkenyl triphenylphosphonium bromide* (**7a-f**(*Z*) and **7a-f**(*E*)) : The corresponding alkenyl bromide (**6a-f**(*Z*) and **6a-f**(*E*) (20m mole) and triphenyl phosphine (1.1 eq) were dissolved in benzene (30ml) and allowed to stand for 2–3 days at room temperature (A) or refluxed for 2 days (B) or better dissolved in dimethyl formamide (30 ml) and refluxed for 3h at 140°C (C). The precipitated crystals were separated and refluxed in abs. ether for 5h to give white crystals. Yield:40–89%;Mp (°C) and reaction conditions:**a**(*Z*) 120 (A) (Lit.[4] 127–130), **b**(*Z*) 129–131(A), **c**(*Z*) 139–9(A), **d**(*Z*) 121–139 (A), **e**(*Z*) sirup(B), **f**(*Z*) 98–102 (adhesive solid matter) (C), **a**(*E*) 143(A), **b**(*E*) 141–6 (A) (Lit.[9] 156), **c**(*E*) 177–180 (A), **d**(*E*) 174–5(A), (Lit.[8] 170), **e**(*E*) 116–120(B) and **f**(*E*) 99–104 (adhesive solid matter) (C); NMR (δ):4.3–4.9 (m or dd, J=7 and 15 Hz) 4.9–6.3 (m, CH=CH) 7.1–8.5 (m, $(C_6H_5)_3$). All compounds were elemental-analytically pure except **a**(*Z*).

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摘　　要

エリ蚕雌フエロモンに関する研究　I
C_6～C_{11}の2－アルケニルトリフェニルホスホニウム塩の調製

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我々は以前の研究において，エリ蚕の雌の性フェロモンは C_{16}～C_{17} の共役二重結合をもったアルカジエニル化合物であろうと推定したが，本報ではその合成中間物質である標題の化合物の合成について報告する。合成は従来の方法で行った。すなわち，プロパルギルアルコールのテトラヒドロピラニルエーテルを出発物質とし，これに液安中ナトリウムを用いて各種炭素数のアルキルブロマイドを作用させて，2―アルキニル化合物とする。これを一度遊離のアルコールに戻したのち，リンドラー触媒を用いた接触還元でZ体，またRossiの過剰の水素化アルミニウムリチウムを用いる還元法でE体の2―アルケノールに導いた。各々はブロマイドにしたのち，トリフェニルホスフィンと作用させて，標題の化合物に導き，元素分析一致の生成物を得た。各段階における精製，収量，スペクトルデータによる確認について記載した。