NOTES

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The Studies of the Activated Compound. III.[1] A Synthesis of Muscalure: (*Z*)-9-Tricosene

Kyo ABE, Tomio YAMASAKI, Nobuo NAKAMURA, and Takeo SAKAN

Department of Chemistry, Faculty of Science, Osaka City University, Sugimotocho, Sumiyoshi-ku, Osaka 558

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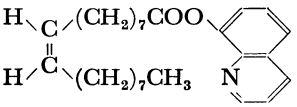
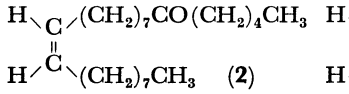
Synopsis. A synthesis of muscalure, (*Z*)-9-tricosene, was carried out as an application of metal-induced acylation.

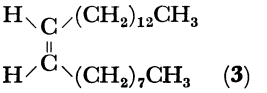
Muscalure, (*Z*)-9-tricosene (**3**), is a sex-attractant pheromone for the female house fly (*Musca domestica L.*). Its synthesis has been accomplished by two groups.[2,3] We ourselves also previously carried out the synthesis of the muscalure as an application of metal-induced acylation.[4,5]



(**1**)



(**2**)



(**3**)

The activated starting material, 8-oleoyloxyquinoline (**1**), was prepared from oleoyl chloride and 8-quinolinol in a good yield by the Schotten-Baumann method. A solution of 8-oleoyloxyquinoline (**1**) in dichloromethane was treated with an ethereal solution of pentylmagnesium bromide at −90 °C to give (*Z*)-14-tricosen-6-one (**2**) as the sole product in a 75% yield. The enone (**2**) was reduced by means of Hung-Minlon's procedure to afford muscalure, (*Z*)-9-tricosene (**3**), in an 84% yield. It was found to be identical to an authentic sample by a study of its IR and NMR.[2] An advantage of this route to muscalure (**3**) is in the preparation of the enone (**2**).

Experimental

Synthesis of 8-Oleoyloxyquinoline (1). To a stirred suspension of 8-quinolinol (2.390 g; 0.02 mol) and powdered sodium hydroxide (0.96 g; 0.02 mol) in tetrahydrofuran (20 ml), we added, drop by drop, a solution of oleoyl chloride (6.020 g; 0.02 mol) in tetrahydrofuran (20 ml) at 0 °C over a period of 15 min under an argon atmosphere. The reaction mixture was then kept at 0 °C for 1 h, allowed to stand at room temperature overnight, poured into ice-cooled water, and extracted with ether (30 ml×3). The extracted organic layer was washed with a 1% aqueous solution of sodium hydroxide (20 ml×2) and saturated brine (10 ml), and dried over sodium sulfate. The removal of the solvent from the organic layer gave a crude product (**1**) (7.20 g; 88% yield), which could be used for the next step without any purification. IR (neat): 1770, 1140, 1120 cm^{-1}. NMR (CCl_4): δ 0.83 (3H. t, J=5 Hz), 1.00—1.60 (broad peak centered at 1.26, 22H), 1.60—2.00 (broad peak centered at 1.94, 4H), 2.26 (2H, t, J=7 Hz), 5.18 (2H, m), 7.00—7.60 (4H, m), 7.90 (1H, dd, J=4, 2 Hz).

Synthesis of (Z)-14-Tricosen-6-one (2). An ethereal solution of pentylmagnesium bromide, generated from magnesium turnings (0.178 g; 7.33 mg atom) and pentyl bromide (1.24 g; 7.33 mmol), and a catalytic amount of iodine in dried ether, was added at −90 °C to a solution of 8-oleoyloxyquinoline (**1**) (2.00 g; 4.9 mmol) in dichloromethane (8 ml) under an argon atmosphere. The reaction mixture was then allowed to warm up to room temperature and left to stand overnight. The yellow precipitate in the reaction mixture was then filtered off and the filtrate was washed with a 1 M aqueous hydrochloric acid solution and with saturated brine, and dried over sodium sulfate. By evaporating the solvent, 1.23 g of the residue was obtained. It was purified by preparative TLC (SiO_2, developed with $CHCl_3$) to give the pure enone (**2**). IR (neat): 3015, 2925, 2850, 1715, 1460, 1380, 725 cm^{-1}. NMR (CCl_4): δ 0.88 (6H, t, J=5 Hz), 0.96—1.60 (28H, broad peak), 1.92 (4H, m), 2.23 (4H, t, J=7 Hz), 5.16 (2H, m). Found: C, 81.71; H, 12.83%. Calcd for $C_{23}H_{44}O$: C, 82.07; H, 13.18%. MS *m/e* 336 (M^+).

Synthesis of (Z)-9-Tricosene (3). A mixture of (*Z*)-14-tricosen-6-one (**2**) (127 mg; 1.14 mmol), 80% hydrazine hydrate (71 mg; 1.14 mmol), and potassium hydroxide (76 mg; 1.14 mmol) in 0.8 ml of diethylene glycol was heated at 140 °C for 1.5 h and then at 190 °C for an addition 4 h. After cooling to room temperature, the reaction mixture was diluted with ice water, neutralized with a 6 M hydrochloric acid solution, and then extracted with pentane (10 ml) several times. The extracted organic layer was washed with saturated brine and dried over sodium sulfate. The removal of the solvent from the organic layer gave a crude product. It was purified by means of column chromatography (SiO_2, eluted with hexane) to give (*Z*)-9-tricosene (**3**) (112 mg; 84% yield). Its IR and NMR spectra were both identical with the spectra of an authentic sample. IR (neat): 3015, 2930, 2855, 1460, 725 cm^{-1}. Found: C, 85.60; H, 13.88%. Calcd for $C_{23}H_{46}$: C, 85.63; H, 14.37%. NMR (CCl_4): δ 0.60—1.60 (40H, m), 1.90 (4H, m), 5.16 (2H, t, J=4 Hz). MS *m/e* 322 (M^+).

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References

1) Part II of this series: K. Abe, T. Sato, N. Nakamura, and T. Sakan, *Chem. Lett.*, **1977**, 817.

2) R. L. Cargill and M. G. Rosenblum, *J. Org. Chem.*, **37**, 3971 (1972).

3) D. A. Carlson, M. S. Mayer, D. L. Silhacek, J. D. James, M. Beroza, and B. A. Bierl, *Science*, **174**, 76 (1971).

4) T. Sakan and Y. Mori, *Chem. Lett.*, **1972**, 793.

5) T. Sakan, Y. Mori, and T. Yamasaki, *Chem. Lett.*, **1973**, 713.