146～148°) (*Anal.* Calcd. for $C_{15}H_{13}O_8N_5$: C, 46.04; H, 3.35; N, 17.90. Found : C, 46.23; H, 3.67; N, 17.69).

Condensation of (III) and diethyl ethoxymethylenemalonate by boiling resulted in the formation of 1,3-diethoxycarbonyl-9-methoxymethyl-4-oxoquinolizine (VIIa), m.p. 75～76°. *Anal.* Calcd. for $C_{17}H_{19}O_6N$: C, 61.12; H, 5.7; N, 4.22. Found : C, 61.22; H, 6.52; N, 4.02. U.V. λ_{max}^{MeOH} mμ (log ε) : 263 (4.16), 350 (3.93), 408 (4.24). I.R. $\nu_{max}^{CHCl_3}$ cm^{-1} : 1724 (ester C=O), 1700 (CON<), 1100, 1110 (ether).

On the other hand, condensation of (VI) and diethyl ethoxymethylenemalonate by boiling afforded 1-cyano-3-ethoxycarbonyl-9-methoxymethyl-4-oxoquinolizine (VIIb), m.p. 156～158° *Anal.* Calcd. for $C_{15}H_{14}O_4N_2$: C, 61.31; H, 5.15; N, 10.21. Found : C, 61.07; H, 5.28; N, 9.90. U.V. λ_{max}^{MeOH} mμ (log ε) : 258.5 (4.17), 266.5 (4.21), 346 (3.96). 406 (4.28). I.R. $\nu_{max}^{CHCl_3}$ cm^{-1} : 2227 (CN), 1745 (ester C=O), 1712 (CON<), 1105 (ether).

On boiling (VIIb) with 10% HCl, 1-cyano-9-methoxymethyl-4-oxoquinolizine (VIIIb), m.p. 150～151°, was obtained. *Anal.* Calcd. for $C_{12}H_{10}O_2N_2$: C, 67.28; H, 4.71; N, 13.08. Found : C, 67.09; H, 5.05; N, 12.73. U.V. λ_{max}^{MeOH} mμ (log ε) : 259 (4.13), 272.5 (4.08), 380 (4.20). I.R. $\nu_{max}^{CHCl_3}$ cm^{-1} : 2195 (CN), 1675 (-CON), 1088 (ether).

On boiling (VIIIb) with 20% HCl, a δ-lactone derivative (IX), m.p. 252～254°, was formed. *Anal.* Calcd. for $C_{11}H_{17}O_3N$: C, 65.67; H, 3.51; N, 6.96. Found : C, 65.96; H. 3.70; N, 6.91. U.V. λ_{max}^{MeOH} mμ (log ε) : 254 (3.84), 260.5 (3.87), 288.5 (3.89), 355 (4.18). I.R. ν_{max}^{KBr} cm^{-1} : 1724 (lactone), 1684 (CON<).

(VIIa) forms (IX) under a milder condition than that for (VIIb), with HCl. As an intermediate compound, 1-ethoxycarbonyl-9-methoxymethyl-4-oxoquinolizine (VIIIa), m.p. 83～84.5°, was obtained. *Anal.* Calcd. for $C_{14}H_{15}O_4N$: N, 5.36. Found : N, 5.24. U.V. λ_{max}^{EtOH} mμ (log ε) : 260 (4.14), 381 (4.16). I.R. ν_{max}^{KBr} cm^{-1} : 1712 (ester C=O), 1680 (CON<).

The writer expresses his deep gratitude to Prof. K. Tsuda of the University of Tokyo for his kind and helpful guidance and to Mr. M. Matsui, Director of this Laboratory, for encouragement.

Takamine Research Laboratory
Sankyo Co., Ltd.
Shinagawa-ku, Tokyo

Yoshinobu Sato (佐藤義信)

January 25, 1958.

UDC 547.913.5

Studies on Azulenes : S-Guaiazulene-aldehydes

Although several communications on azulenes having ring-substituted aldehyde group have recently been encountered,[1~5] no detailed report has been made on the synthetic procedure for direct introduction of aldehyde group into azulene rings and properties of the products obtained.

In the course of our studies on azulenes, it was found that an aldehyde group could be substituted directly into S-guaiazulene (I) in a good yield by Friedel-Crafts type substitution reaction and the results will be recorded.

A solution of (I) in *o*-dichlorobenzene was added dropwise into a mixed solution

---

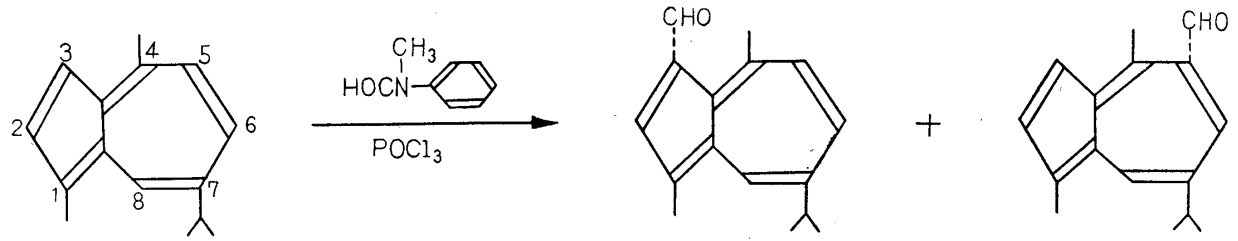
1) E. Heilbronner, R.W. Schmid : Helv. Chim. Acta, **37**, 2018(1954).
2) W.H. Stafford, D.H. Reid : Chem. & Ind. (London), **1954**, 277.
3) W.L. Galloway, D.H. Reid, W.H. Stafford : *Ibid.*, **1954**, 724.
4) H. Arnold, K. Pahls : Ber., **87**, 257(1954).
5) W. Treibs : *Ibid.*, **90**, 761(1957).

of N-methylformanilide and phosphoryl chloride in the same solvent under cooling and stirring and, after additional stirring for a few hours, the reaction mixture was decomposed with aqueous solution containing sodium hydroxide and acetate. The product was purified by column chromatography through activated alumina, using petr. ether and ether as eluting solvents to dark brown needles (II), m.p. 82~83°, in 28.73% yield. U.V. λ_{max}^{EtOH} mμ (log ε); 237 (4.33), 280 (4.15), 402 (4.23); $\lambda_{max}^{ligroine}$ mμ (ε); 548 (745.0), 570 (801.1), 604 (652.1), 680 (180.1). *Anal.* Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found : C, 84.75; H, 7.96.

(II) gave a positive Tollens' test and showed two maximum absorption bands (1640 cm^{-1}, 2718 cm^{-1})* in the infrared region, characteristic for aldehyde group. The following derivatives of (II) were easily prepared : T.N.B.-complex : Brown needles, m.p. 91~92°. *Anal.* Calcd. for $C_{22}H_{21}O_7N_3$: C, 60.13; H, 4.82. Found : C, 60.12; H, 4.70. T.N.T.-complex : Brown needles, m.p. 60~61°(decomp.). *Anal.* Calcd. for $C_{23}H_{23}O_7N_3$: C, 60.92; H, 5.11. Found : C, 61.05; H, 5.13. Semicarbazone : Green needles, m.p. 189~191°. *Anal.* Calcd. for $C_{17}H_{21}ON_3$: C, 72.05; H, 7.47. Found : C, 72.08; H, 7.67. Oxime : Dark green needles, m.p. 128~129°. *Anal.* Calcd. for $C_{16}H_{19}ON$: C, 79.63; H, 7.94. Found : C, 79.55; H, 7.66.

Besides (II), a small amount of red needles (III), m.p. 124.5~125.5°, were obtained. U.V. λ_{max}^{EtOH} mμ (log ε) : 233 (4.57), 277 (4.07), 319 (4.76), 385 (4.15); $\lambda_{max}^{ligroine}$ mμ (ε) : 519 (851), 556 (753), 606 (254.0). *Anal.* Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found : C, 84.90; H, 7.87. This was isolated on chromatographical purification of the product of above substitution reaction. Its infrared spectrum revealed two maxima for aldehyde (1642 and 2725 cm^{-1}).* The derivatives of (III) : T.N.B.-complex : Red needles, m.p. 86~87°. *Anal.* Calcd. for $C_{22}H_{21}O_7N_3$: C, 60.13; H, 4.82. Found : C, 59.92; H, 4.61. Oxime : Violet plates, m.p. 155~156°. *Anal.* Calcd. for $C_{16}H_{19}ON$: C, 79.63; H, 7.94. Found : C, 79.89; H, 7.94.

From the bathochromic shift of absorption maxima of these azulene-aldehydes compared with that of starting S-guaiazulene (I) in visible region, and from known order in reactivities of methine groups in (I), the most possible positions for aldehyde groups substituted in (II) and (III) are at 3 and 5.



(I) (II) (III)

······ Tentatively proposed substituted position

Pharmaceutical Institute, Medical Faculty, University of Tokyo. Hongo, Tokyo

Tyunosin Ukita (浮田忠之進)

Government Forest Experiment Station, Shimomeguro, Meguro-ku, Tokyo

Makoto Miyazaki (宮崎 信)
Mieko Hashi (土師美恵子)

January 31, 1958

* A similar bathochromic shift to these maxima, compared with that reported by Arnold and Pahls[4] for 4,8-dimethylazulene-6-aldehyde (1705 cm^{-1}), was also observed for $\nu_{C=O}$ of 3-acetyl-S-guaiazulene (1660 cm^{-1}).[5] This should be attributed to the substitution of aldehyde groups of both (II) and (III) in odd-numbered positions of (I).

6) T. Ukita, H. Watanabe, M. Miyazaki : Unpublished data.