

- Chaurasia, M. R. and Sharma, S. K., *Heterocycles* 14, 1761 (1980).
- Shishoo, C. J., Devani, M. B., Ullas, G. V., Ananthan, S. S., and Bhadti, V. S., *J. Heterocycl. Chem.* 18, 43 (1981).
- Stankovský, Š. and Sokyrová M., *Collect. Czech. Chem. Commun.* 49, 1795 (1983).
- Stankovský, Š. and Boulmogh, A., *Chem. Papers* 43, 433 (1989).
- Špirková, K. and Stankovský, Š., *Collect. Czech. Chem. Commun.* 56, 1719 (1991).
- Abraham, W. and Barnikov, G., *Tetrahedron* 29, 691 (1973).
- Stanovnik, B., Mozer, A., and Tišler, M., *Rad. Yugosl. Akad. Znam. Umjet. Kem.* 1986, 42561.
- Miller, G. W. and Rose, F. L., *J. Chem. Soc.* 1965, 3357, 3369.
- Pots, K. T., Burton, H. R., and Roy, S. K., *J. Org. Chem.* 31, 265 (1966).
- Pots, K. T. and Schneller, S. W., *J. Heterocycl. Chem.* 5, 485 (1968).
- Pots, K. T. and Brugel, E. G., *J. Org. Chem.* 35, 3448 (1970).

Translated by K. Špirková

## Dihydropyrans from the Heterodienic Reaction of 5-Arylidenerhodanine Derivatives with Isoprene

M. A. ABDEL-RAHMAN

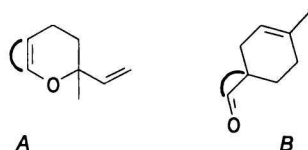
Department of Chemistry, Faculty of Science, Sohag, Egypt

Received 31 August 1992

The reaction of  $\alpha,\beta$ -unsaturated carbonyl system in 5-arylidenerhodanines with isoprene furnishes, in a stereoselective heterodienic reaction, the dihydropyran adducts rather than spirocyclohexene adducts. The reaction is accelerated by using aluminium chloride catalyst.

Hetero Diels—Alder reaction with inverse electron demand, pericyclic ( $4\pi + 2\pi$ ) cycloaddition, is one of the most important methods for construction of the polyfunctionalized cyclic compounds. Therefore, various heterodienes [1—3] and heterodienophiles [4, 5] are developed for this purpose.

The ( $4\pi + 2\pi$ ) cycloaddition reaction between a diene and  $\alpha,\beta$ -unsaturated carbonyl compound leads either to heterodienic adduct A (dihydropyran) from the heterodiene pathway or to dienic adduct B (cyclohexenes) from the Diels—Alder pathway [6—10] (Scheme 1).



Scheme 1

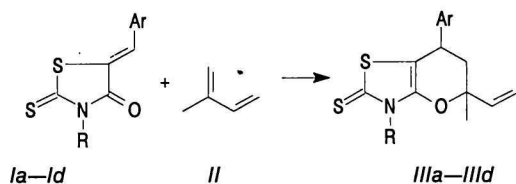
In the heterocyclic field it was found that the Diels—Alder pathway is always preferred to the heterodiene pathway. On the other hand, the heterodiene pathway is more favourable in terms of FMO's theory [4, 5, 11].

Hereafter the results of the reaction of isoprene (II) with 5-arylidenerhodanine derivatives Ia—Id as

an  $\alpha,\beta$ -unsaturated carbonyl system attached to heterocyclic ring are reported.

The thermal cycloaddition reactions between 5-arylidenerhodanines Ia—Id, as heterodienes and II lead to the corresponding aryl 2,3-dihydropyrano[2,3-*b*]rhodanine derivatives IIIa—III d by means of heterodiene pathway [11]. The reaction is carried out in benzene under nitrogen and in the presence of few crystals of hydroquinone. The reaction under these conditions provides a poor yield of the cycloadducts IIIa—III d in long time (several days). To avoid these problems a variety of modified methods are tested. Lewis acid [12—15] and certain lanthanides complexes [16] extremely help in promoting the reaction of labile dienes at low temperature. Remarkable acceleration of enone—diene interaction by aluminium chloride was first reported by Yates and Eaton [17].

It is known that Lewis acid affects not only the rate but also the regioisomerism and stereoisomerism of the Diels—Alder reaction. In addition, Ismail and Hoffmann [18] found that crotonoyl cyanide and 4-methyl-1,3-pentadiene, which did not react under thermal conditions, gave the heterodienic adduct under  $AlCl_3$  catalysis.

R = *m*-tolyl

Ar  
 a *p*-NO<sub>2</sub>Ph  
 b *p*-CH<sub>3</sub>OPh  
 c *p*-ClPh  
 d piperonyl

Scheme 2

Hetero Diels—Alder reaction of compounds *Ia—Id* with *II* provides in the presence of a catalytic amount of AlCl<sub>3</sub> in methylene chloride at 40 °C (Scheme 2) a good yield in a short time (see Experimental). The choice between dienic or heterodienic adducts is easily attained according to the IR and <sup>1</sup>H NMR spectroscopic data. Data of the adducts *IIIa—IIIId* suggest that the single regioisomer is selectively produced. The IR spectra show a strong band in the region of  $\tilde{\nu} = 1670\text{—}1690\text{ cm}^{-1}$  (cf. Table 1) due to the dihydropyran double bond. This suggests that 1,4-cycloaddition reaction takes place. The fact that the carbonyl bands are missing indicates the absence of the regioisomer spirocyclohexene derivatives.

The main features of the <sup>1</sup>H NMR spectra are reported in Table 1. All other protons of the base and of the aromatic rings show an appropriate chemical shift. Moreover, the new methylene —CH<sub>2</sub>— and methine —CH— protons appear at  $\delta = 1.38\text{—}1.60$  and  $6.20\text{—}6.40$ , respectively.

It is known that the coordination of acrolein with an acid results in a significant decrease in its LUMO ( $\alpha$ -carbon) coefficient. Thus if this is taken as a model for compound *I* the lowering of the LUMO (carbon) coefficient in position 4 should favour the heterodiene pathway [19], as it is in the present reaction.

In conclusion, aluminium chloride catalysis in ( $4\pi + 2\pi$ ) cycloaddition is a useful tool to accelerate the reaction through the coordination with hetero atoms, at least the oxygen [20] atom of the  $\alpha,\beta$ -unsaturated carbonyl system (see *I*). The heterodienic adduct is preferred to the dienic adduct; this result is in agreement with predictions of FMO's theory [11, 19].

## EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a Perkin—Elmer 137 spectrophotometer. The <sup>1</sup>H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer.

5-Arylidenerhodanines were prepared according to the method described elsewhere [21].

### Thermal Reaction of *I* with Isoprene (General Procedure)

A mixture of *I* (2.0 mmol) (few crystals of hydroquinone) in benzene (20 cm<sup>3</sup>) was heated under the conditions reported in Table 2. After the evaporation of the solvent, the residue was ground in diethyl ether and the precipitate was filtered off. The product was recrystallized from CHCl<sub>3</sub>—petroleum ether and the corresponding adduct was obtained in a poor yield. IR and <sup>1</sup>H NMR spectra of these adducts are reported in Table 1. Satisfactory elemental analyses were obtained.

### AlCl<sub>3</sub>-Catalyzed Reaction of *I* with Isoprene

To a suspension of AlCl<sub>3</sub> (0.133 g; 1.0 mmol) in anhydrous methylene chloride (10 cm<sup>3</sup>) compound *I* (0.7 g; 2.0 mmol) was added. After 0.5 h stirring at 25 °C, isoprene was added dropwise and the reaction was left under the conditions reported in Table 2. The mixture was poured into the saturated solution of NaHCO<sub>3</sub>, extracted with chloroform, dried over

Table 1. Spectral Data of the Adducts ( $\nu(\text{C}=\text{C})$  of dihydropyran)

Compound	IR, $\tilde{\nu}$ (in KBr)/cm <sup>-1</sup>	<sup>1</sup> H NMR, $\delta$ (in C <sub>6</sub> H <sub>6</sub> )*					
		2-Me	3-CH <sub>2</sub>	H-4	=CH <sub>2</sub>	=CH	H <sub>arom</sub>
<i>IIIa</i>	1690	1.25 (s, 3H)	1.6 (d, 2H)	3.8 (dd, 1H)	5.5 (b, 2H)	6.2 (t, 1H)	7.0—8.2 (m, 8H)
<i>IIIb</i> **	1670	1.20 (s, 3H)	1.35 (d, 2H)	4.95 (dd, 1H)	5.3 (b, 2H)	6.2 (t, 1H)	6.5—7.7 (m, 8H)
<i>IIIc</i>	1675	1.25 (s, 3H)	1.5 (d, 2H)	5.4 (dd, 1H)	5.4 (b, 2H)	6.6 (t, 1H)	7.2—8.0 (m, 8H)
<i>IIIId</i> ***	1680	1.30 (s, 3H)	1.4 (d, 2H)	5.2 (dd, 1H)	5.25 (b, 2H)	6.3 (t, 1H)	6.8—7.8 (m, 7H)

\*Tolyl methyl protons in all adducts appeared as a singlet at  $\delta = 2.25\text{—}2.4$ . \*\*Methoxy protons appeared as a singlet at  $\delta = 3.8$ .

\*\*\* Piperonyl protons O—CH<sub>2</sub>—O appeared as a singlet at  $\delta = 6.1$ .

Table 2. Characterization of the Adducts and the Reaction Conditions of Their Preparation

Compound	Formula $M_r$	M.p. °C	Thermal reaction		Catalytic reaction	
			Reaction time <sup>a</sup>	Yield	Reaction time	Yield
			days	%	h	%
<i>IIIa</i>	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> 424.53	150	10	20	24	76
<i>IIIb</i>	C <sub>23</sub> H <sub>23</sub> N <sub>1</sub> O <sub>2</sub> S <sub>2</sub> 409.56	135	20	16	44	60
<i>IIIc</i>	C <sub>22</sub> H <sub>20</sub> N <sub>1</sub> O <sub>1</sub> S <sub>2</sub> Cl 413.98	125	13	20	30	70
<i>III d.</i>	C <sub>23</sub> H <sub>21</sub> N <sub>1</sub> O <sub>3</sub> S <sub>2</sub> 423.55	130	15	18	40	63

a) The reactions were followed by <sup>1</sup>H NMR spectra (showed a new singlet signal for 2-methyl protons) or IR spectra (the carbonyl bands were missing). The <sup>1</sup>H NMR spectra of the crude reaction mixture showed no other possible diastereoisomers and showed only one stereoisomer.

MgSO<sub>4</sub> and the solvent was evaporated under vacuum. The products were recrystallized from CHCl<sub>3</sub>—petroleum ether. The corresponding adducts were obtained in good yields.

## REFERENCES

1. Boger, D. L., *Chem. Rev.* 1986, 781.
2. Boger, D. L., *Tetrahedron* 39, 2876 (1983).
3. Boger, D. L. and Weinreb, S. M., *Hetero Diels—Alder Methodology in Organic Synthesis*, Chapter 2. Academic Press, San Diego, 1987.
4. Weinreb, S. M. and Stails, R. R., *Tetrahedron* 36, 3087 (1982).
5. Desimoni, G. and Tacconi, G., *Chem. Rev.* 75, 651 (1975) and references cited therein.
6. Drugnolotti, M. et al., *Tetrahedron* 44, 5239 (1988).
7. Coda, A. C., Desimoni, G., Invernizzi, A. G., Righetti, P. P., and Tacconi, G., *Tetrahedron Lett.* 26, 3137 (1985).
8. Richards, C. G. and Thurston, D. E., *Tetrahedron* 39, 1817 (1983).
9. Titouani, S. L., Saufiaui, M., Toupet, L., and Carrie, R., *Tetrahedron* 40, 3869 (1990).
10. Reyes, A. et al., *J. Org. Chem.* 55, 1024 (1990).
11. Brougidou, J. and Christal, H. C. R., *C. R. Acad. Sci., C* 1963, 3323.
12. Benvegna, T., Mastelli, J., Gree, R., and Toupet, L., *Tetrahedron Lett.* 31, 3145 (1990).
13. Denmark, S. E., Moon, Y. C., and Senanyake, C. B. W., *J. Am. Chem. Soc.* 112, 311 (1990) and references cited therein.
14. Bendnerski, M. and Danishefsky, S., *J. Am. Chem. Soc.* 103, 3716 (1981) and cited references; *Tetrahedron Lett.* 25, 721 (1984).
15. Oppolrer, W. and Chapuis, C., *Tetrahedron Lett.* 24, 4665 (1983).
16. Laszlo, P. and Lucchetti, J., *Tetrahedron Lett.* 25, 2147 (1984).
17. Yates, P. and Eaton, P., *J. Am. Chem. Soc.* 82, 4436 (1960).
18. Ismail, Z. M. and Hoffmann, H. M. R., *Angew. Chem., Int. Ed.* 21, 859 (1982).
19. Angli, E. C., Fringuelli, F., Pizzo, F., Porter, B., Taticchi, A., and Wenkert, E., *J. Org. Chem.* 51, 2642 (1986).
20. Fringuelli, F., Pizzo, F., Taticchi, A., and Wenkert, E., *J. Org. Chem.* 48, 2802 (1983).
21. Terri, J. and Azzaro, M., *Bull. Soc. Chim. Fr.* 1978, 238.