

## Polar Cycloaddition (1) Reactions of Some 2,3-Disubstituted Isoquinolinium Salts

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The addition of four vinyl ethers and of cyclopentadiene to 2,3-dimethylisoquinolinium salts occurs stereoselectively affording only *syn* adducts. The attack of nucleophiles on the vinyl ether adducts (4-9) occurs at position 3. Similar stereoselective cycloadditions may be carried out using berberinium chloride as the electrophile.

In earlier communications, it was shown that 2,3-dimethylisoquinolinium salts (**1**) undergo cycloaddition with vinyl ethers (**2**) and with cyclopentadiene (**4**) and that both reactions are quantitatively regio- and stereoselective. It has been pointed out (3,4) that this type of stereoselectivity is understandable in terms of the coulombic repulsion arising between the developing and receding positive charges involved in the alternative transition states leading to the establishment of the second sigma bond.

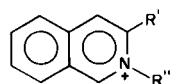
The purpose of the present paper is to provide experimental details about the cycloadditions and some information concerning the chemistry of the cycloadducts. In addition to the very stereoselective addition of methyl, ethyl, and butyl vinyl ethers to the 2,3-dimethylisoquinolinium cation **1**, it was found that divinyl ether underwent 1,4-cycloaddition although more slowly than the alkyl vinyl ethers. Like the adducts reported earlier (**4-6**), the new adduct (**7**, X = I) gave pmr evidence of only a single stereoisomer even when the crude product (96% yield) was examined. The new vinyl ether adduct (**7**) was easily hydrolyzed at room temperature to afford the *syn*-1,4-dihydro-9-hydroxy-2,3-dimethyl-1,4-ethanoisoquinolinium ion (**8**).

An experimentally simple approach to the addition of vinyl ethers to isoquinolinium salts involves mixing 3-methylisoquinoline, the alkyl halide and the vinyl ether in a suitable solvent. With methyl iodide and ethyl vinyl ether, the yield of **5** for the one-pot reaction was 79%. The cycloaddition of ethyl vinyl ether with 2-methyl-3-styrylisoquinolinium iodide (**3**) (**14**) afforded **9** in 58% yield as a single geometrical isomer.

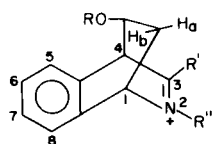
Although adducts **4-9** are the first compounds formed by 1,4-cycloaddition with isoquinolinium salts, they are not the first examples of 1,4-dihydro-1,4-ethanoisoquinolinium salts. Walker and Alkalay (5,6), in the interest of finding improved diuretics (**7**), have prepared a number of such compounds by an elaborate synthesis involving over ten steps (5,6,8-13).

As a group, all 9-alkoxyethano derivatives (**4-9**) proved thermally unstable and operations such as evaporation of solvents or crystallization were usually carried out near room temperature. A sample of the ethyl vinyl ether adduct **5** refluxed for three hours in acetonitrile solution (b.p. 82°) underwent cycloreversion affording a quantitative yield of the 2,3-dimethylisoquinolinium salts (**1**).

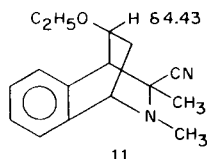
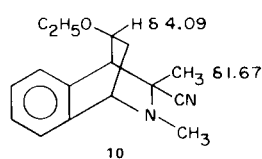
The vinyl ether adducts (**4-9**) are iminium salts and are quite reactive. As has been reported (2), the iminium group of **5** can be hydrogenated affording a 1,2,3,4-tetrahydro derivative. The protons of the methyl group at position 3 of **5** undergo exchange in neutral deuterium oxide even at room temperature. With potassium cyanide solution at room temperature, **5** is attacked at position 3 affording a mixture of geometrically isomeric nitriles (**10** and **11**) in a yield of 93%. Examination by pmr of a crude sample of the product in chloroform showed two isomers with the minor component constituting about 20% of the mixture. Within 30 minutes, the proportion of the minor component had doubled and later, when equilibrium had been attained, the proportion of **10** and **11** was roughly equal.



1. R' = R'' = Me
2. R' = Me, R'' = Et
3. R'' = Me, R' = PhCH=CH



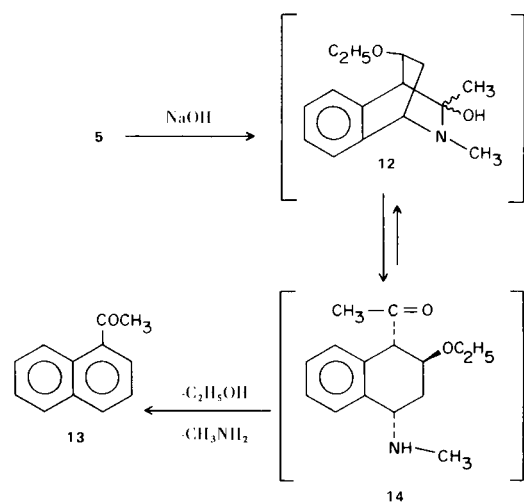
4. R = R' = R'' = Me
5. R = Et, R' = R'' = Me
6. R = Bu, R' = R'' = Me
7. R = CH<sub>2</sub>=CH, R' = R'' = Me
8. R = H, R' = R'' = Me
9. R = Et, R' = PhCH=CH, R'' = Me



Assignment of structures to the isomers was possible on the basis of the chemical shifts of the resonances assigned to the hydrogen at position 9 and the methyl protons at position 3. The aromatic ring should deshield the methyl hydrogens in **10** and shield them in **11**. Since the isomerization is rapid, the initial relative concentrations of the two stereoisomers is not known, but in any case, **10** is the major product under conditions of kinetic control in the addition process.

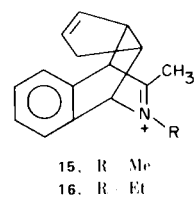
The cyano group could be removed from the nitriles **10** and **11** by the action of silver nitrate, leading back to the adduct **5** (recovered as the perchlorate).

If the ethyl vinyl ether adduct (**5**) was treated with sodium hydroxide, a novel and potentially useful transformation occurred. The product, which contained no nitrogen and was isolated in 83% yield, was identified as methyl-1-naphthyl ketone (**13**). The transformation was rationalized by the assumption that the carbinolamine (**12**) produced by attack of hydroxide ion at position 3



would be in equilibrium with its ring-opened tautomer (**14**). Base-catalyzed elimination of ethoxide ion followed by elimination of methylamine leads to **13**. The methyl vinyl ether adduct (**4**) also affords **13** (85% yield) on treatment with base.

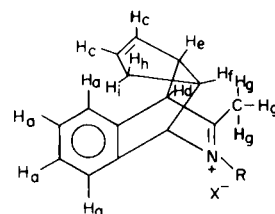
It has been previously announced (4) that cyclopentadiene adds to 2-alkyl-3-methylisoquinolinium salts. The structure of only one of these adducts (**16**) has been demonstrated by single crystal x-ray analysis (4). That the methyl analog (**15**) of **16** must have the same stereochemistry seems evident from the pmr data obtained. Table I records the similarity in chemical shift and



multiplicity of the signals from comparable protons in the two systems. Detailed discussion will be confined to **15**. The doublets at  $\delta$  5.50 ( $J = 3.5$  Hz) and  $\delta$  4.87 ( $J = 3.0$ ) were assigned to the bridgehead hydrogens Hb and Hd

TABLE I

Comparison of Chemical Shifts (a) ( $\delta$ ) of Related Protons in Adducts of Cyclopentadiene with 2-Alkyl-3-methylisoquinolinium Ions



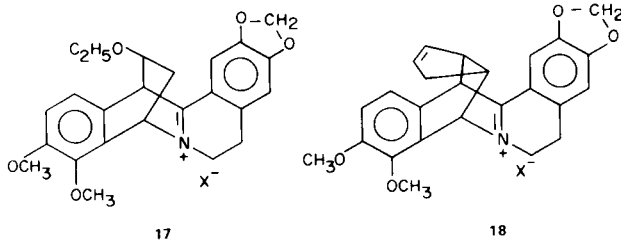
Protons	Et-Me-Isoquinolinium Adduct <b>16</b>		Di-Me-Isoquinolinium Adduct <b>15</b>	
	Chem. Shift	Multiplicity	Chem. Shift	Multiplicity
a	7.42	m	7.44	m
b	5.73	d	5.50	d
c	5.23	s	5.30	s
d	4.95	d	4.87	d
e	3.90-3.10	m	3.62	m
f	3.90-3.10	m	3.38	m
g	2.88	s	2.83	s
h	2.67-1.57	m	2.48	m
i	2.67-1.57	m	1.87	m

(a) Nmr in trifluoroacetic acid solution.

respectively, since Hb should be more strongly deshielded by the adjacent positively charged nitrogen. Spin decoupling experiments were required to locate the chemical shift of the resonances for He and Hf. These appeared as complex overlapping multiplets between  $\delta$  3.90 and  $\delta$  3.10. Irradiation at  $\delta$  3.62 resulted in the collapse to a singlet of the resonance ( $\delta$  4.87) assigned to Hd. Similarly irradiation at  $\delta$  3.38 caused collapse to a singlet of the doublet assigned to Hb. The chemical shift of proton Hf ( $\delta$  3.38) makes it clear that the proton must be over the quaternary nitrogen and showed that the cyclopenteno ring was inclined in the same direction as it is in the higher homolog **16**.

The case of dissociation of these adducts was demonstrated by allowing a solution of the cyclopentadiene adduct of 1,2-dimethylisoquinolinium adduct **15** to stand at room temperature in acetonitrile solution (reaction conditions for the original cycloaddition) using tetracyanoethylene as a scavenger to remove any cyclopentadiene released. After two weeks, nmr analysis showed that 17% of the adduct had dissociated as evidenced by re-formation of the isoquinolinium salt (**5**).

In the first communication (2) on the cycloaddition reactions of 2,3-dimethylisoquinolinium salts, it was shown that berberinium chloride will undergo cycloaddition with ethyl vinyl ether. As would be expected from the like charge repulsion rule (4), the product is only a single geometrical isomer and has been assigned the *syn* structure (**17**). Cyclopentadiene also adds stereoselectively to berberinium chloride affording what is believed to be **18**.



## EXPERIMENTAL.

The elemental analyses were carried out by M-H-W Laboratories, Garden City, Michigan. Melting points were determined in capillary tubes with a Thomas Hoover Melting Point Apparatus and are uncorrected. Uv absorption spectra were determined in methanol with a Beckman Model DB-G spectrophotometer. Infrared spectra were determined on Perkin Elmer Model 137 and Model 237 spectrophotometers on potassium bromide discs. Proton magnetic resonance spectra were obtained at 60 MHz on Varian A-60 and T-60 spectrometers using tetramethylsilane as the internal standard. Spin-spin decoupling experiments were performed on Varian T-60 and Bruker HF-A-10 spectrometers. Cycloaddition Reactions.

All cycloadditions were carried out at room temperature and, with noted exceptions, the solvent used was acetonitrile or methanol and the volume used was the minimum which would hold the salt in solution after the alkene (excess) was added. Except as noted, hydroquinone was added, the approximate concentration being 0.025 g. per milliliter of the alkene. Before working up, the reaction mixtures were checked for disappearance of uv absorption at 340 nm, but the reaction times here reported are not necessarily minimal. Vacuum evaporation (rotary evaporator) was used without raising the temperature above 35° and the product was initially precipitated (except as noted) by the addition of ether. Except as noted, recrystallization was accomplished by dissolving the adduct at room temperature in methanol or acetonitrile and adding ether or ethyl acetate. In every case, the nmr (trifluoroacetic acid) showed the presence of

TABLE II  
Addition of Vinyl Ethers to 3-Alkyl-2-methylisoquinolinium Iodides

Isoquinolinium Iodide R'	Vinyl Ether R	Solvent	Time, Days	Yield %	M.p., °C	Formula	C		H		N	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
Me	Me	MeCN (a)	14 (b)	97	155 (c,d)	C <sub>14</sub> H <sub>18</sub> INO	48.99	49.11	5.29	5.39	4.08	4.04
Me	Et	MeOH	2.7	85	212-215 (e,f)	C <sub>15</sub> H <sub>20</sub> INO	50.43	50.45	5.64	5.64	3.92	3.79
Me	Bu	MeCN	5	60	218-221 (e,g)	C <sub>17</sub> H <sub>24</sub> INO	52.99	52.93	6.28	6.50	3.64	3.41
Me	Vinyl	MeOH	32	96	183 (c,h,i)	C <sub>15</sub> H <sub>18</sub> INO	50.72	50.46	5.11	4.86	3.92	3.72
Styryl	Et	DMF (j)	9	58	110 (c,k)	C <sub>22</sub> H <sub>24</sub> INO	59.33	59.53	5.43	5.59	3.15	3.08

(a) Inhibitor was *p*-methoxyphenol. (b) This reaction was carried out in a glass lined bomb. (c) Decomposed. (d) From acetonitrile as colorless laths. (e) Melted with decom-  
position. (f) Crystallized from acetonitrile-ether as a microcrystalline powder; ir (potassium bromide) 1667 cm<sup>-1</sup> (C=N<sup>+</sup>), pmr (trifluoroacetic acid), δ 7.60 (m, 4, aromatic), 5.67 (q, 1, H-1), 5.24 (d, 1, H-4), 4.60 (m, 1, H-9), 3.93 (m, 2, CH<sub>2</sub>CH<sub>3</sub>), 3.83 (s, 3, 2-Me), 2.95 (o, 1, anti-H-10), 2.83 (s, 3, 3-Me), 1.93 (m, 1, syn-H-10), 1.27 ppm (t, 3, CH<sub>2</sub>-CH<sub>3</sub>). (g) A colorless microcrystalline powder: pmr (trifluoroacetic acid), δ 7.63 (m, 4, aromatic), 5.67 (q, 1, H-1), 5.23 (d, 1, H-4), 4.37 (m, 1, H-9), 3.75 (m, 2, *o*-CH<sub>2</sub>Pr), 3.65 (s, 3, 2-Me), 2.92 (o, 1, anti-H-10), 2.80 (s, 3, 3-Me), 1.95 (m, 1, syn-H-10), 1.72-0.75 ppm (complex, 7, C<sub>3</sub>H<sub>7</sub>). (h) This reaction was quite slow and a total of 100 ml. of divinyl ether was added in two portions to 25 g. of **1**. (i) From methanol as tan prisms; pmr (DMSO-d<sub>6</sub>), δ 7.38 (m, 4, aromatic), 6.33 (q, 1, CH=CH<sub>2</sub>), 5.83 (q, 1, H-1), 5.16 (d, 1, H-4), 4.72 (m, 1, H-9), 4.12 (m, 2, CH=CH<sub>2</sub>), 3.67 (s, 3, 2-Me), 2.80 (o, 1, anti-H-10), 2.72 (s, 3, 3-Me), 1.33 ppm (m, 1, syn-C-10). (j) Dimethylformamide. (k) From acetonitrile-ethyl acetate as light brown plates, pmr (trifluoroacetic acid) δ 8.52 (d, J = 15, 1, vinyl), 8.10-7.43 (complex, 10, aromatic), 7.33 (d, J = 15, 1, vinyl), 5.80 (d, 1, H-4), 5.55 (q, 1, H-1), 4.50 (m, 1, H-9), 4.07 (m, 2, CH<sub>2</sub>CH<sub>3</sub>), 3.88 (s, 3, 2-Me), 3.00 (o, 1, anti-H-10), 1.98 (m, 1, syn-H-10), 1.30 ppm (t, 3, CH<sub>2</sub>CH<sub>3</sub>).

only a single geometrical isomer (racemate). Cycloaddition reactions of 3-substituted isoquinolinium salts with vinyl ether have been summarized in Table II.

*syn*-1,4-Dihydro-9-ethoxy-2,3-dimethyl-1,2-ethanoisoquinolinium iodide (**5**, X = I) from 3-Methylisoquinoline.

A mixture containing 10 g. (70 mmoles) of 3-methylisoquinoline, 5.2 ml. (83 mmoles) of iodomethane and 33 ml. of ethyl vinyl ether plus about 0.5 g. of *p*-methoxyphenol in 500 ml. of acetonitrile was allowed to stand for one week. Worked up in the usual way, it afforded 19.7 g. (79%) of **5**.

*syn*-1,4-Dihydro-9-hydroxy-2,3-dimethyl-1,4-ethanoisoquinolinium iodide (**8**, X = I).

A few drops of dilute hydriodic acid was added to a saturated methanol solution containing a small quantity of the 9-vinyloxy compound (**7**). After the mixture had stood overnight at room temperature, ether was added and the mixture cooled. The resulting precipitate crystallized from acetonitrile-ether as tan needles, m.p. 220° dec.; pmr (trifluoroacetic acid):  $\delta$  7.60 (m, 4, aromatic), 5.73 (q, 1, H-1), 5.20 (d, 1, H-4), 5.17 (s, 1, OH), 4.97 (m, 1, H-9), 3.87 (s, 3, 2-Me), 3.00 (o, 1, anti-H-10), 2.85 (s, 3, 3-Me), 1.85 ppm (m, 1, *syn*-H-10).

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>INO: C, 47.43; H, 4.90; N, 4.26. Found: C, 47.43; H, 4.83; N, 4.01.

9-Ethoxy-1,2,3,4-tetrahydro-2,3-dimethyl-1,4-ethanoisoquinolinium Hydriodide.

To a solution of 3 g. of the ethoxy adduct (**5**) in a mixture of 150 ml. of methanol and 15 ml. of acetic acid, 0.15 g. of platinum oxide catalyst was added and the mixture hydrogenated at atmospheric pressure. After absorption of hydrogen was complete (about 2 hours) the catalyst was removed by filtration and the solution concentrated. Addition of ethyl acetate afforded 2.1 g. (69%) of a light tan solid which on recrystallization from methanol afforded colorless prisms, m.p. 257-258°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>22</sub>INO: C, 50.15; H, 6.17; N, 3.90. Found: C, 50.31; H, 6.28; N, 3.72.

9-Ethoxy-1,2,3,4-tetrahydro-2,3-dimethyl-3-cyano-1,4-ethanoisoquinoline (Mixture of **10** and **11**).

To a solution of 5.0 g. of the ethoxy adduct (**5**, X = I) in 75 ml. of deionized water, a solution of 1 g. of potassium cyanide in 2 ml. of water was added dropwise. After 1 hour, the resulting precipitate was washed with deionized water yielding 3.35 (93%) of a colorless microcrystalline solid, m.p. 114-116°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O: C, 74.97; H, 7.86; N, 10.93. Found: C, 75.17; H, 7.84; N, 11.14.

Reconversion of the 3-Cyano Stereoisomers (**10** and **11**) to the Ethoxy Adduct (**5**, X = ClO<sub>4</sub>).

To a solution of 2 g. (7.8 mmoles) of the nitrile mixture (**10** and **11**) in 150 ml. of methanol, 1.3 g. (7.7 mmoles) of silver nitrate was added. After the solution had been stirred for 2 hours, the precipitated silver cyanide was removed by filtration and the filtrate concentrated. Addition of ether precipitated crude **5** as the nitrate. To the crude nitrate in 10 ml. of methanol, 0.96 g. (7.8 mmoles) of sodium perchlorate was added. The resulting product was collected and washed with methanol; yield 1.55 g. (60% overall) of a colorless microcrystalline solid, dec., 131°. The analytical sample (dec., 132°) was recrystallized from methylene chloride-ethyl acetate, and by means of ir and mixture melting point determinations was shown to be identical with a sample prepared from the iodide (**5**, X = I).

*Anal.* Calcd. for C<sub>15</sub>H<sub>20</sub>ClNO<sub>5</sub>: C, 54.63; H, 6.11; N, 4.25. Found: C, 54.84; H, 5.96; N, 4.04.

Methyl 1-Naphthyl Ketone (**13**).

To a suspension of 10 g. (28 mmoles) of the ethyl vinyl ether adduct (**5**) in 50 ml. of methanol, 11 g. (27.5 mmoles) of carbonate-free 10% sodium hydroxide solution was added dropwise. The solution became purple, but the color was discharged by boiling the mixture for 5 minutes. The product was taken up in ethyl ether and the extract washed with 3.7% hydrochloric acid and then with water and finally dried over potassium carbonate. Removal of the solvent under reduced pressure left 3.94 g. (83%) of a yellow liquid;  $n_D^{25}$  1.6257 (lit. (15)  $n_D^{25}$  1.6280) which was identified by comparison of the pmr spectrum with that of an authentic sample of 1-acetonaphthalene (**13**).

Following the same procedure but starting with the methyl vinyl ether adduct (**4**), an 85% yield of 1-acetonaphthalene was obtained.

*syn*-2,3-Dimethyl-1,4-( $\Delta$ 12-cyclopenteno)-1,4-dihydroisoquinolinium Iodide (**15**).

To a solution of 3.2 g. (11.2 mmoles) of 2,3-dimethylisoquinolinium iodide (**1**) in 250 ml. of acetonitrile, 9 ml. (110 mmoles) of cyclopentadiene was added. After two weeks, the mixture was worked up in the usual way affording 3.4 g. (86%) of adduct. Crystallization from ethanol-ether gave light pink needles, dec., 165-170°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>IN: C, 54.71; H, 5.16; N, 3.99. Found: C, 54.91; H, 5.29; N, 3.93.

2-Ethyl-3-methylisoquinolinium Bromide (**2**).

A solution containing 5 g. of 3-methylisoquinoline and 10 ml. of bromomethane in 20 ml. of acetonitrile was refluxed for 72 hours. On cooling, 8.2 g. (93%) of **2** was obtained as a colorless microcrystalline solid, m.p. 200-201.5°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>BrN: C, 57.16; H, 5.60; N, 5.55. Found: C, 56.92; H, 5.74; N, 5.37.

*syn*-2-Methyl-3-ethyl-1,4-( $\Delta$ 12-cyclopenteno)-1,4-dihydroisoquinolinium Bromide (**16**).

From 7.0 g. of the quaternary bromide (**2**) and 30 ml. of cyclopentadiene in 60 ml. of methanol, 8.0 g. (91%) of product was obtained in a reaction time of three days. Recrystallization from acetonitrile-ethyl acetate afforded colorless hygroscopic crystals, dec., 176°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>20</sub>BrN: C, 64.16; H, 6.33; N, 4.40. Found: C, 63.97; H, 6.23; N, 4.33.

The perchlorate of **16** crystallized from acetonitrile as colorless prisms, dec., 167-169°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>20</sub>ClNO<sub>4</sub>: C, 60.45; H, 5.97; N, 4.15. Found: C, 60.40; H, 5.72; N, 4.20.

Adduct (**17**) of Berberinium Chloride with Ethyl Vinyl Ether.

To a solution of 2 g. of berberinium chloride dihydrate in 50 ml. of methanol, 10 ml. of ethyl vinyl ether was added and after five days the mixture worked up as usual. Since the chloride of the adduct (**17**) was an oil when isolated, a methanolic solution of sodium perchlorate was added to precipitate the product, 2.3 g. (93%) as the perchlorate salt (**17**, X = ClO<sub>4</sub>). The product crystallized from methanol as yellow plates, m.p. > 300°; pmr (trifluoroacetic acid):  $\delta$  7.70-6.98 (m, 4, aromatic), 6.23 (s, 2, OCH<sub>2</sub>O), 5.92 (q, 2, H-8), 5.60 (d, 1, H-13), 4.83-2.78 (complex, 14), 1.98 (m, 1, *syn*-H-15), 1.35 ppm (t, 3, CH<sub>3</sub>CH<sub>2</sub>).

*Anal.* Calcd. for  $C_{24}H_{26}ClNO_9$ : C, 56.75; H, 5.16; N, 2.76.  
Found: C, 56.73; H, 5.09; N, 2.69.

Adduct (**18**) of Berberinium Chloride with Cyclopentadiene.

The cycloaddition of berberinium chloride dihydrate with cyclopentadiene was carried out essentially as in the preparation of **17**, X = ClO<sub>4</sub> except that cyclopentadiene was used in place of ethyl vinyl ether, affording a 94% yield of **18**, X = ClO<sub>4</sub> as a yellow microcrystalline solid, m.p. > 300°; pmr (trifluoroacetic acid):  $\delta$  7.78-6.88 (m, 4, aromatic), 6.22 (s, 2, OCH<sub>2</sub>O), 5.80 (d, 1, H-8), 5.50 (s, 2, vinyl), 5.33 (d, 1, H-13), 4.55-1.70 ppm (complex, 14).

*Anal.* Calcd. for  $C_{25}H_{24}ClNO_8$ : C, 59.83; H, 4.82; N, 2.79.  
Found: C, 59.66; H, 4.86; N, 2.53.

Acknowledgement.

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#### REFERENCES

- (1) R. R. Schmidt, *Angew. Chem. Intern. Ed. Engl.*, **12**, 212 (1973).
- (2) C. K. Bradsher and F. H. Day, *Tetrahedron Letters*, 409 (1971).
- (3) C. K. Bradsher, F. H. Day, A. T. McPhail, and P. S. Wong, *J. Chem. Soc. Chem. Commun.*, 156 (1973).
- (4) C. K. Bradsher, F. H. Day, A. T. McPhail, and P. S. Wong, *Tetrahedron Letters*, 4205 (1971).
- (5) G. N. Walker and D. Alkalay, *J. Org. Chem.*, **32**, 2213 (1967).
- (6) G. N. Walker and D. Alkalay, *ibid.*, **36**, 491 (1971).
- (7) R. Gaunt, E. Gisoldi, J. Kerkiner, N. Howie, and A. A. Renzie, *Endocrinology*, **83**, 927 (1968).
- (8) G. N. Walker, U. S. Patent, 3,379,731; *Chem. Abstr.*, **68**, 96, 497 (1968).
- (9) G. N. Walker, French Patent, 1,458,074; *Chem. Abstr.*, **68**, 59, 449 (1968).
- (10) G. N. Walker and R. B. Margerison, U. S. Patent, 3,324,136; *Chem. Abstr.*, **68**, 21, 854 (1968).
- (11) Ciba Corp., Netherlands Patent Application 6,411,613; *Chem. Abstr.*, **63**, 8327 (1965).
- (12) G. N. Walker, French Patent, 1,449,604; *Chem. Abstr.*, **67**, 21, 847 (1967).
- (13) Ciba Ltd., Netherlands Patent Application 6,504,323; *Chem. Abstr.*, **64**, 8155 (1966).
- (14) L. G. S. Brooker and F. L. White, *J. Am. Chem. Soc.*, **73**, 1094 (1951).
- (15) R. C. Weast, "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1967, 48th Edition, c414.