

The aldehyde was obviously  $\alpha,\beta$ -unsaturated judging from the nmr and uv spectra of the hydrolysate,<sup>17</sup> and the value of  $J_{23}$  (15.0 Hz) indicated *trans*-olefinic protons<sup>18</sup> as in **4**. However, it could not be separated from **11** either by chromatography or distillation. The mixture was therefore acetylated at 0° with acetic anhydride and pyridine to enable fractionation by reverse-phase chromatography<sup>19</sup> whereby compound **5** was obtained as an oil:  $\lambda_{\max}$  217 m $\mu$ ;  $[\alpha]_D^{23} + 12.0^\circ$  (*c* 2.32, CHCl<sub>3</sub>). Its 100-MHz nmr spectrum in CCl<sub>4</sub> (TMS)<sup>20</sup> showed: H-1,  $\tau$  0.43 (doublet); H-2, 3.30 (quartet); H-2, 3.81 (quartet of doublets); H-4, 4.30 (triplet of doublets); H-5, 4.82 (multiplet); H-6, 5.75 (quartet); H'-6, 5.81 (quartet). The coupling constants (Hertz) observed<sup>20</sup> were:  $J_{12} = 7.2$ ;  $J_{23} = 15.5$ ;  $J_{24} = 1.5$ ;  $J_{34} = 5.0$ ;  $J_{45} = 5.0$ ;  $J_{56} = 4.0$ ;  $J_{56'} = 5.3$ ;  $J_{66'} = 11.5$ . For the 2,4-dinitrophenylhydrazone of **5**: mp 108–109°;  $\lambda_{\max}$  370 m $\mu$  ( $\epsilon$  22,500). *Anal.* Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>H<sub>10</sub>: C, 47.79; H, 4.42; N, 12.39. Found: C, 47.39; H, 4.06; N, 12.49.

Hydrogenation of an ethanolic solution of **5** at ice-salt temperature using 5% palladized carbon ceased after 1 mol of hydrogen had been consumed. The saturated aldehyde produced (nmr, CCl<sub>4</sub>, TMS,  $\tau$

(16) Although Bergmann represented his "diacetyl pseudoglucal" (**11**) as the open chain form (structure II in ref 11c), it is clear from the text that he believed that the compound existed as, and certainly reacted from, the cyclic form. In this he was indeed correct for under his reaction conditions (15-min reflux) the hydrolysate actually comprised 90–95% of the cyclized structure **11**. (Note that he also represented the "dihydro pseudoglucal" (**12**), 2-deoxyglucose, and glucose itself as open chain structures (VII, VI, and V, respectively.)

(17) Nmr features of **4** recognizable in the mixture (CDCl<sub>3</sub>, TMS): H-1,  $\tau$  0.38 (d); H-2, 3.73 (quartet of doublets); H-3, 3.01 (q);  $J_{12} = 7.5$ ,  $J_{23} = 15.0$ ,  $J_{34} = 5.0$  Hz;  $\mu_{\max}$  (CHCl<sub>3</sub>) 3.58 3.70, 5.88;  $\lambda_{\max}$  (H<sub>2</sub>O) 217 m $\mu$ .

(18) Reference 15, p 87.

(19) B. Wickberg, *Acta Chem. Scand.*, **12**, 615 (1958).

(20) We are grateful to our colleague, Dr. K. Shaw, for this determination using an instrument kindly made available by Professor L. W. Reeves. The coupling constants were read directly from the spectrum.

0.22, -CHO)<sup>18</sup> was characterized as its 2,4-dinitrophenylhydrazone: mp 123–124°;  $\lambda_{\max}$  356 m $\mu$  ( $\epsilon$  18,200). *Anal.* Calcd for C<sub>18</sub>H<sub>22</sub>N<sub>4</sub>O<sub>10</sub>: C, 47.57; H, 4.84; N, 12.34. Found: C, 47.43; H, 4.68, N, 12.20. Upon deacetylation the aldehyde group vanished suggesting that hemiacetal **12** may have formed. This was confirmed by converting olefin **10** into **12** by an alternative route involving (i) hydrogenation, (ii) mild acid hydrolysis, and (iii) deacetylation. This information also indicated that no epimerization had occurred in the formation of **4** from **11**.

The hydroxy aldehyde **13** is undoubtedly the substance initially formed from **11** and subsequently isomerized to **4**. Thus, when the hydrolysis of **1** was done (a) in the presence of 10 mol % of hydroquinone or (b) in the dark, compound **4** was, respectively, completely absent or present in drastically reduced quantities. The inhibition was not in the conversion of compound **11** to **13** since **6** was still completely converted to **8** in the presence of hydroquinone. Evidently small amounts of **13** in equilibrium with **11** undergo photochemical (or less efficiently, thermal) conversion to the more stable *trans* isomer<sup>21</sup> **4**, and it is the latter process that is inhibited by hydroquinone.

Further study of equilibria of the type  $\mathbf{10} \rightleftharpoons \mathbf{13} \rightleftharpoons \mathbf{4}$  is under way and will be reported in due course.

**Acknowledgments.** We acknowledge generous financial support from the National Research Council of Canada and Bristol Laboratories.

(21) P. G. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

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Received March 16, 1970

## Additions and Corrections

**Conformational Analysis. LVII. The Calculation of the Conformational Structures of Hydrocarbons by the Westheimer-Hendrickson-Wiberg Method** [*J. Amer. Chem. Soc.*, **89**, 4345 (1967)]. By NORMAN L. ALLINGER, MARY ANN MILLER, FREDERIC A. VANCATLEDGE, and JERRY A. HIRSCH, Department of Chemistry, Wayne State University, Detroit, Michigan 48202.

The van der Waals equation in Table II should read

$$E_v = -2.25\epsilon(d^*/r)^6 + 8.28(10)^5(\epsilon)\exp(-r/0.0736d^*)$$

The correct form of the equation was used for all of the calculations reported. We are indebted to Dr. Steven D. Stellman for calling this misprint to our attention.

**On the Question of Bridge-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornene and Related Systems** [*J. Amer. Chem. Soc.*, **90**, 3724

(1968)]. By ALAN P. MARCHAND and JOSEPH E. ROSE, Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069.

The captions under Figures 5 and 6 have been reversed. As they appear in the paper, Figure 5 shows the nmr spectrum of isodrin (IX); Figure 6 shows the nmr spectrum of aldrin (VIII).

**Ligand Penetration Rates into Metal Ion Coordination Spheres. Aluminum(III), Gallium(III), and Indium(III) Sulfates** [*J. Amer. Chem. Soc.*, **90**, 6967 (1968)]. By JOHN MICELI and JOHN STUEHR, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

The quantity  $F_4$ , defined as  $1 + [C_H(1 + d \ln \gamma_{SO_4/d} \ln C_{SO_4})(K'_{14} + C'_H) + K'_{14}C'_{SO_4}]/[K'_a(K'_{14} + C'_{MeOH}) + C'_H(K'_a + C'_{SO_4})]$  was omitted in the follow-