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CONCERNING THE STEREOCHEMISTRY OF 9-METHYL-Δ^1-3-OCTALONE

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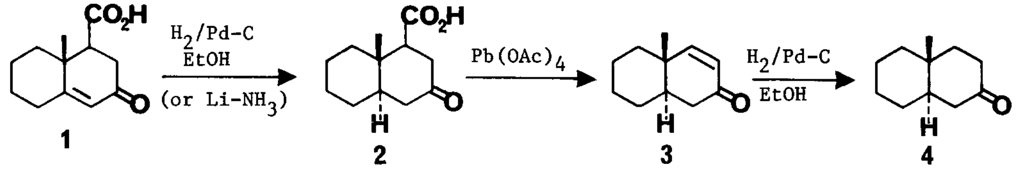
A recent article[1] has described the preparation, characterization and assignment of stereochemistry for the two isomeric 9-methyl-Δ^1-3-octalones. One isomer which was designated as *cis* fused showed a pmr peak due to the angular methyl at 1.08 ppm (in CCl_4) and ir peaks at 1680 and 1605 cm^{-1} (film) and the other isomer presumed to be *trans*, showed a pmr peak due to the angular methyl at 1.23 ppm (in CCl_4) and an ir peak at 1670 cm^{-1} (film). In this note we show that this assignment (designated herein as McMurry *cis* and *trans*) must be reversed.

We recently synthesized by a route which seemed stereochemically definitive[2] the *cis* isomer of 9-methyl-Δ^1-3-octalone (pmr: angular methyl at 1.21 ppm in $CDCl_3$; ir film: 1672 cm^{-1} ; ms: 164, M^+; 69, base; 2,4-DNP ms: 344, M^+, base) only to find that this product corresponded in physical properties to the "McMurry *trans*" material. Still another concern with regard to the McMurry assignment was the report[3] that *trans*-9-methyl-Δ^1-3-octalone prepared by an apparently unequivocal route, showed properties (pmr: angular methyl at 1.04 ppm; ir: 5.95, 6.16 μ) differing from "McMurry *trans*" product.

Since the McMurry assignments seemed not unreasonable, it appeared that the discrepency might be due simply to an interchange of the physical data for the two "McMurry" isomers. Therefore, the work leading to the assigned *cis*-enone ("McMurry *cis*", Scheme I) was repeated. It was found in fact the reported spectral data are correct for this enone (pmr: angular methyl at 1.06 ppm in $CDCl_3$; ir film: 1675, 1605 cm^{-1}). However, hydrogenation of the enone to the corresponding saturated ketone (1 atm H_2/10% Pd-C) afforded not the known *cis*, but rather *trans*-10-methyl-2-decalone **4**[4] identical in all respects with authentic[5] samples of *trans*-10-methyl-2-decalone (pmr: angular methyl at 1.04 ppm in $CDCl_3$; ir: superimposable) and distinctly different from authentic[6] *cis*-10-methyl-2-decalone (pmr: angular methyl at 1.19 ppm in $CDCl_3$). From these results it follows that, somewhat interestingly, the reduction of **1** *both* by catalytic *hydrogenation* and by *lithium-liquid ammonia*[7] affords the same *trans* fused keto-acid **2**.

The stereochemical course of the new annulation process described in the preceding paper is thus completely verified, and the internal consistency of all our previous results is maintained.[8,9]

Scheme I



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1. J. E. McMurry and L. C. Blaszczak, *J. Org. Chem.*, **39**, 2217 (1974).
2. E. J. Corey and D. L. Boger, *Tetrahedron Lett.*, preceding paper.
3. E. Piers, W. DeWaal, and R. W. Britten, *Can. J. Chem.*, **47**, 4299 (1969); E. Piers, W. M. P.-Johnson, and C. Berger, *Ibid.*, **53**, 1291 (1975).
4. M. J. T. Robinson, *Tetrahedron*, **21**, 2478 (1965); accurate pmr chemical shifts in $CDCl_3$ for the angular methyls of *cis* and *trans*-10-methyl-2-decalone are reported which agree with those reported here.
5. We would like to thank Professor R. B. Woodward for generous authentic samples (two) of *trans*-10-methyl-2-decalone **4**.
6. Prepared by the catalytic reduction of 10-methyl-$\Delta^{1(9)}$-2-octalone (H_2, 5% Pd-C, EtOH, H^+); see H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, *J. Amer. Chem. Soc.*, **92**, 2800 (1970); see ref. 4 for pmr spectra in $CDCl_3$.
7. The fact that Birch-reduction of **1** affords the *trans*-keto acid **2** was confirmed by recent experimental work in these laboratories and by one of the authors in ref. 1 (L.C.B.); therefore, the spectral data reported in ref. 1 for the Birch-reduction sequence (see Scheme I) leading to **3** is incorrect and should match those reported for the catalytic hydrogenation route. How the enoic acid **1** was converted to *cis*-9-methyl-Δ^1-3-octalone (i.e. How one obtains the *cis*-fused isomer of the keto-acid **2**) is as yet unclear.
8. *Cis*-9-methyl-Δ^1-3-octalone; pmr ($CDCl_3$, ppm) : 6.53 (1H, dd, $J = 10$ and 1 Hz), 5.84 (1H, d, $J = 10$ Hz), 1.21 (3H, s, angular methyl); ir (film): 1672 cm^{-1}; Ms: 164 (M^+, strong), 69 (base); 2,4-DNP ms: 344 (M^+, base).

   Trans-9-methyl-Δ^1-3-octalone; pmr ($CDCl_3$, ppm): 6.70 (1H, d, $J = 10$ Hz), 5.79 (1H, d, $J = 10$ Hz), 1.06 (3H, s, angular methyl); ir (film): 1675, 1605 cm^{-1}; ms: 164 (M^+); n_D^{26} 1.5006[3]; 2,4-DNP ms: 344 (M^+, base).
9. We are especially grateful to Professor E. J. Corey for his helpful advice, suggestions and valuable discussions throughout this work. This work was assisted financially by a grant from the National Science Foundation.