Tetrahedron Letters No. 31, pp 2679 - 2682, 1975. Pergamon Press. Printed in Great Britain.

A FACILE BIS-NORCARADIENE REARRANGEMENT

E. Vedejs and W. R. Wilber
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

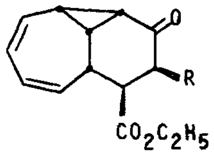
(**Received in USA 20 May 1975; received in UK for publication 17 June 1975**)

As part of a synthetic approach to $(CH)_{12}$ hydrocarbons, we had prepared cyclopropyl ketones 1 and 2 (by $CuSO_4$-induced decomposition of 3) and the enolate-derived α-bromoketones 4 and 5.[1] An attempt to dehydrobrominate 4 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave two unexpected products instead of the desired α,β-unsaturated ketone 6. One of these products is an isomer of 6 ($C_{14}H_{14}O_3$) which retains the cyclopropyl ketone (broad carbonyl absorption at 1725-1680 cm^{-1}) and has six cyclopropyl protons and two vinyl protons in the nmr spectrum.[2] This evidence suggests structure 7, derived from 6 by a reasonable internal Diels-Alder reaction.

The other product has the formula $C_{14}H_{12}O_3$, corresponding to loss of two hydrogens from 6. The compound is yellow and contains at least one aromatic ring according to spectral data; nmr (CCl_4, δ): 7.3-7.6 (4H,m), 7.35 (1H,d,J=13Hz), 6.77 (1H,d,J=2Hz), 6.60 (1H,dd,J=13,2Hz), 4.36 (2H,q,J=7Hz), 1.40 (3H,t,J=7Hz); UV (cyclohexane) λ_{max}: 345 nm (800), 329 nm (sh. 1430), 269 nm (15,200), 231 nm (16,400); ir (neat): 1725, 1625, 1610, 1590, 1550 cm^{-1}.

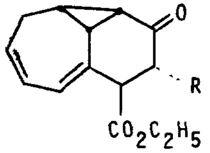
Treatment of 4 with an equivalent of 1,4-diazabicyclo[2.2.2]octane under nitrogen results in formation of 7 (75% isolated) and only traces of other products. A similar experiment using DBU as the base (nitrogen atmosphere, RT, $CHCl_3$ solution) followed by dilute acid workup and chromatography over silica gel gives a ca. 1:1 mixture of 7 and a new isomeric keto ester 8; nmr (CCl_4, δ): 7.3 (4H,s), 7.0 (1H,d,J=12.4Hz), 6.08 (1H,dd,J=12.4,1.2Hz), 4.16 (2H,q,J=7Hz), 3.92 (1H,dd,J=6.8,2.4Hz), 3.20 (1H,ddd,J=17.2,6.8,1.2Hz), 2.90 (1H,dd,J=17.2,2.4

Hz), 1.25 (3H,t,J=7 Hz); UV (ethanol) λ_{max}: 294 nm (9030), 232 nm (9310); ir (neat) 1725, 1653 cm^{-1}; exact mass, 230.092. Attempted chromatography of the crude product over silica gel without prior removal of DBU by aqueous acid extraction results in rapid conversion of 8 into the yellow product isolated initially from 4. The spectral data suggest that 8 is a benzocycloheptadienone and the oxidation product must therefore be the benzotropone 9. From comparisons with spectral data of analogous compounds[3] it is clear that the ultraviolet and infrared absorptions of 9 are uniquely consistent with the benzotropone structure.



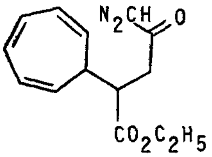
1, R = H

4, R = Br

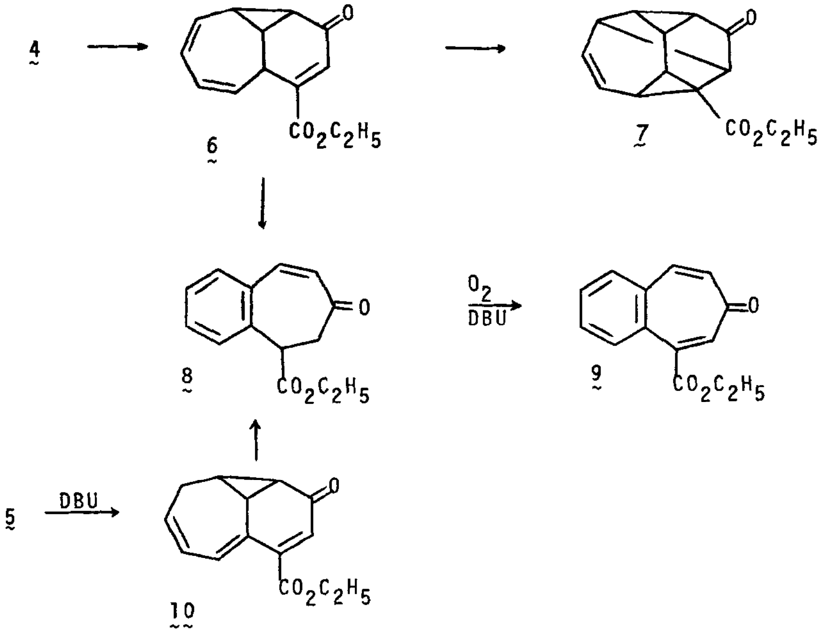


2, R = H

5, R = Br

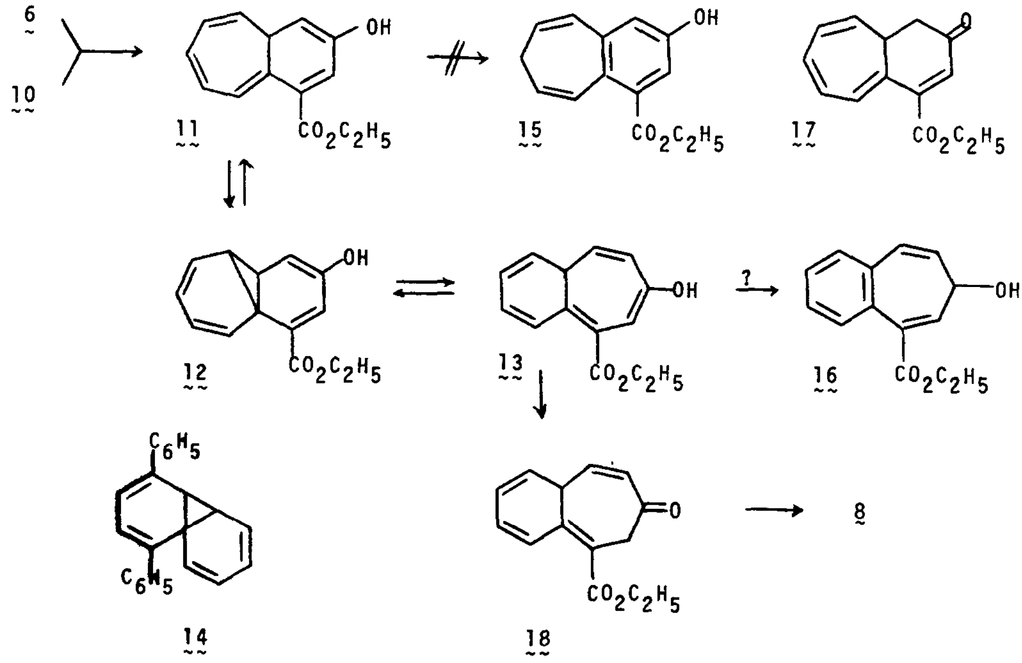


3



Dehydrobromination of 5 with DBU affords an isolable trienone 10 (88%) as an intensely yellow oil; nmr (CCl_4,δ): 5.9-6.4 (4H,m), 4.2 (2H,q,J=7Hz), 1.9-2.4 (4H,m), 1.2 (4H, methyl triplet overlapping a multiplet); ir (neat): 1720, 1667 cm^{-1}; UV (ethanol): λ_{max} 348 nm (5560), 248 nm (31,000); m/e = 230.0948. Prolonged exposure of 10 to DBU under nitrogen results in slow rearrangement to 8 (8 hrs, RT, 90%). Adsorption of the crude product mixture on silica gel and elution with chloroform affords 9 (80%). None of the experiments starting from 5 gives any of the internal Diels-Alder product 7.

The conversion of 4 and 5 into 8 can be explained by way of a common intermediate 11, derived from the trienones 6 and 10 by base-catalyzed enolization. Rapid cycloheptatriene-norcaradiene interconversion would equilibrate 11 with the bis-norcaradiene 12. Subsequent norcaradiene opening in the alternate direction followed by aromatization explains the formation of 8.



Bis-norcaradienes have been implicated as intermediates in several closely related rearrangements.[4] The diphenyl bisnorcaradiene 14 has been detected in solution, and rearranges to a mixture of two diphenyl benzocycloheptatrienes above -10° by norcaradiene opening and 1,5-hydride shift.[5] Thus, ample precedent exists for the skeletal rearrangement which equilibrates 11 and 13. However, it is unusual to find aromatic products derived from only one of these isomers. According to literature precedents, one might expect both 11 and 13 to aromatize by 1,5-hydride shift to 15 and 16, respectively.[4,5]

Although 16 may be a precursor of 8, we prefer to invoke aromatization by base-catalyzed tautomerization rather than by concerted 1,5-hydride shift. This rationale assumes that 11 and 13 may be in equilibrium with the keto esters 17 and 18. Base-catalyzed removal of the highly activated bridgehead proton in 18 should occur with ease (if not violence) and reprotonation α to the ester would account for the formation of 8. Analogous enolization of 17 would not compete because removal of the bridgehead proton does not generate an aromatic ring. There would be more driving force for aromatization of 11 by deprotonation at the bridgehead, but apparently this process is also too slow to play a significant role.

References

1. W. R. Wilber, Ph.D. Dissertation, University of Wisconsin (1974); E. Vedejs, W. R. Wilber, and R. Twieg, submitted for publication.

2. Characterization of 7; nmr (CCl_4,δ): 6.15 (2H,m), 4.1 (2H,m), 3.0 (1H,br.s), 2.4 (1H,d,J=6Hz), 2.2 (2H,br.s), 1.9 (2H,m), 1.5 (1H,t,J=6Hz), 1.24 (3H,t, J=7Hz); ir (neat) 1725-1680 cm^{-1}; exact mass 230.093.

3. H. H. Rennhard, C. DiModica, W. Simon, E. Heilbronner, and A. Eschenmoser, Helv. Chim. Acta, 40, 957 (1957); M. J. Cook and E. J. Forbes, Tetrahedron 24, 4501 (1968); D. J. Bertelli, J. T. Gerig and J. M. Herbelin, J. Amer. Chem. Soc., 90, 107 (1968).

4. C. W. Gruber and M. Pomerantz, Tetrahedron Lett., 3755 (1970); H. Dürr, H. Kober, I. Halberstadt, U. Neu, T. T. Coburn, T. Mitsuhashi, and W. M. Jones, J. Amer. Chem. Soc., 95, 3818 (1973); T. Mitsuhashi and W. M. Jones, Chem. Commun., 103 (1974).

5. H. Dürr, M. Kausch, and H. Kober, Angew. Chem., 86, 739 (1974).