Tetrahedron Letters,Vol.25,No.29,pp 3051-3054,1984 0040-4039/84 $3.00 + .00
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THE PHOTOINDUCED ADDITION OF ACETONE TO 1,7-DIMETHYLTRICYCLO[4.1.0.0^{2,7}]HEPTANE. HYDROGEN ATOM ABSTRACTION FROM AN ACTIVATED METHYL GROUP

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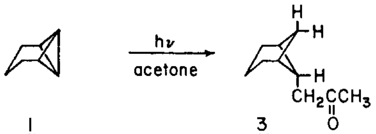
Summary: Activation of a bridgehead methyl group by the bicyclo[1.1.0]butyl moiety resulted in hydrogen abstraction by a photogenerated acetonyl radical, followed by a radical chain addition process.

Recently, we have described several examples of the addition of photogenerated radicals across the C1-C3 bond of the bicyclo[1.1.0]butyl moiety.[1,2] These additions, which are exemplified by the conversion of 1 and 2 into 3 and 4, respectively, were shown to proceed by a radical chain process.[2] These radical chain processes were photoinitiated through the conversion of an appropriate ketone into the corresponding radical, which resulted from hydrogen atom loss from the α-position. We now wish to report a new type of radical chain process which formally involves the addition of acetone to a methyl group activated by the C1-C3 bond of the bicyclo[1.1.0]butyl group.



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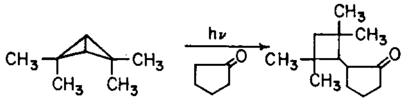

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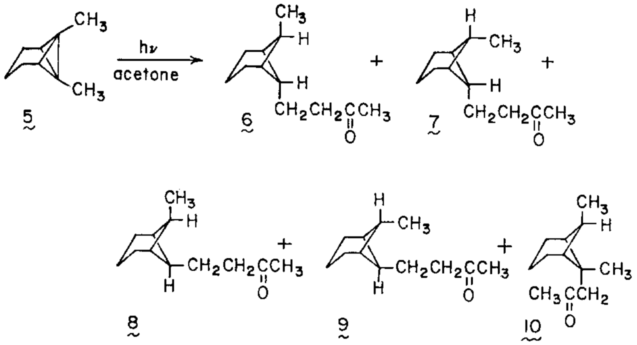
Irradiation of a solution of 1,7-dimethyltricyclo[4.1.0.0^{2,7}]heptane (**5**) in acetone in a Pyrex vessel under argon for 61 h with a bank of sixteen 300-nm lamps gave 18% of a 54:20:14:6:6 mixture of **6**, **7**, **8**, **9**, and **10**, respectively.[3,4] These five isomeric compounds were separated by preparative vapor phase chromatography on a 20% FFAP on 45/60 Chromosorb P column.

Compound **10**, which was the first to elute, was readily identified by its 300 MHz ^{1}H NMR: ($CDCl_3$) δ 2.57 [1 H, m (unresolved q of t, J = 6.8 Hz, J = 6.0 Hz)],[5] 2.53 (2 H, s), 2.12 (3 H, s), 1.95 - 2.00 (2 H, m), 1.75 - 1.85 (3 H, m), 1.45 - 1.75 (3 H, m), 1.22 (3 H, s), 0.95 (3 H, d, J = 6.8 Hz). Comparison of these data with those of 3, and with those of the products from the photoinitiated addition of acetone to 1-methyltricyclo[4.1.0.0^{2,7}]heptane, left little doubt that this was the product which would result from the addition of the acetonyl radical across the C1-C7 bond of **5**. We had anticipated that this would be the major product instead of a very minor component of the mixture, as was observed.

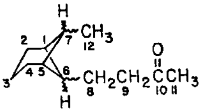


Compounds **6**, **7**, **8**, and **9** were shown to be stereoisomers by a combination of NMR spectroscopy and mass spectrometry.[6] All four of these compounds gave very similar cracking patterns in the mass spectrometer. A combination of ^{13}C NMR and ^{1}H NMR established: (a) that no rearrangement of the bicyclo[3.1.1]heptyl skeleton had occurred, (b) that a hydrogen had been added to C7 of **5**, (c) that a hydrogen had been added to C1 of **5**, and (d) that a hydrogen of the methyl group at C1 had been replaced by the acetonyl moiety (vide post). Thus, the major task involved the assignment of correct stereochemistry to each of the four stereoisomers.

Table 1 lists the ^{13}C NMR spectral data for the four isomeric ketones. This data provided evidence for a preliminary assignment of structure. Particularly indicative were the similarities of the methyl groups attached to C7 of **6** and **8**, and of C8 of **6** and **7**. Unequivocal evidence for the structural assignments was obtained through extensive decoupling of the ^{1}H NMR spectra at 300 MHz.[7] Of particular significance was the coupling of the hydrogens at C6 and C7 with those at C1 and C5. When H6 and H7 are arranged as in **9**, the coupling is known to be close to zero, while when the arrangement of these protons are as shown in **6**, the coupling is 5-7 Hz.[8] For **6**, H6 was a triplet of triplets at δ 1.84 ($J_{1,6} = J_{5,6}$ = 5.6 Hz, $J_{6,8}$ = 7.7 Hz), and H7 was a quartet of triplets at δ 2.03 ($J_{1,7} = J_{5,7}$ = 5.6 Hz, $J_{7,12}$ = 6.5 Hz). For **7**, H6 appeared as a triplet of triplets at δ 2.32 ($J_{1,6} = J_{5,6}$ = 5.9 Hz, $J_{6,8}$ = 6.8 Hz), and H7 showed a quartet centered at δ 1.92 ($J_{7,12}$ = 6.9 Hz). Similar analysis of **8** showed H6 as a triplet at δ 1.82 ($J_{6,8}$ = 7.9 Hz) and H7 as a quartet of triplets at δ 2.47 ($J_{1,7} = J_{5,7}$ = 6.2 Hz, $J_{7,12}$ = 6.9 Hz). Compound **9** represented an unusual situation in that W-form coupling[9] existed between H6 and H7. As a result, H6 appeared as a triplet of doublets at δ 1.46 ($J_{6,7}$ = 4.6 Hz, $J_{6,8}$ = 8.1 Hz); H7, whose resonance was centered at δ 1.68, was obscured as part of a complex multiplet. Decoupling of the H7 resonance confirmed the indicated coupling ($J_{6,7}$ = 4.6 Hz, $J_{7,12}$ = 7.4 Hz).

The five products identified above constituted approximately 90% of the volatile material from the irradiation.[4] Mechanistically, the formation of **6** - **9** requires the removal of a

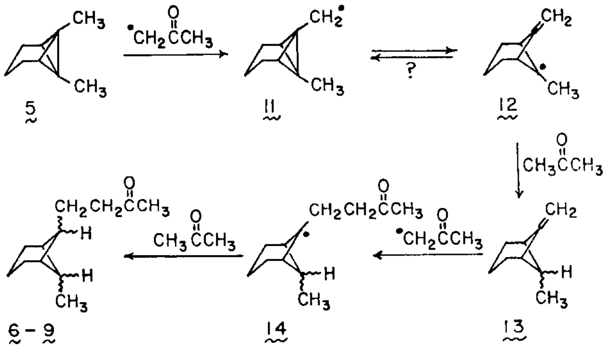
Table 1. ^{13}C NMR Shifts and Multiplicities for Isomers **6** - **9**



Position	**6**	**7**	**8**	**9**
1,5[a]	38.85 (d)	40.41 (d)	39.71 (d)	42.00 (d)
2,4[b]	19.53 (t)	23.98 (t)	23.99 (t)	33.01 (t)
3[c]	13.95 (t)	14.46 (t)	14.33 (t)	15.31 (t)
6	39.80 (d)[d]	37.07 (d)[e]	40.96 (d)[d]	45.19 (d)[f]
7	34.26 (d)[d]	34.67 (d)[e]	32.69 (d)[d]	39.33 (d)[f]
8	21.42 (t)	21.30 (t)	25.16 (t)	28.28 (t)
9	42.58 (t)	41.64 (t)	42.92 (t)	42.97 (t)
10	209.41 (s)	209.39 (s)	209.55 (s)	209.40 (s)
11	29.91 (q)	29.91 (q)	30.00 (q)	29.97 (q)
12	11.38 (q)	16.69 (q)	11.74 (q)	19.81 (q)

(a) This set of doublets was assigned to C1 and C5 on the basis of an intensity *ca.* twice that of either of the other doublets. (b) This set of triplets was assigned to C2 and C4 on the basis of an intensity *ca.* twice that of either of the other triplets. (c) Assigned by analogy to the position of C3 in a large series of derivatives of bicyclo[3.1.1]heptane.[1] (d) Assigned on the basis of their correspondence to C6 and C7 of **7**. (e) Assigned on the basis of selective decoupling of H7. (f) These were *tentatively* assigned on the assumption that both C6 and C7 were shifted downfield as a result of the steric interaction of the two pseudoaxial groups attached to C6 and C7.

hydrogen from one of the methyl groups. A reasonable (but unproven) mechanism would involve initial hydrogen abstraction from **5** by a photogenerated acetonyl radical,[1,2] which would produce **11**. Current understanding[10] of cyclopropylcarbinyl radicals suggests that **11** should open rapidly



to give **12**.[11] Acetone could serve as a hydrogen atom source which would permit the conversion of **12** into **13** with regeneration of the acetonyl radical. Addition of the acetonyl radical to **13** would be expected to produce **14**. Hydrogen abstraction from acetone by **14** would then yield **6 - 9** and regenerate the requisite acetonyl radical.

The difference in behavior between **5** and **1** (or the 1-monomethylated version of **1**) is intriguing. It is not clear whether the formation of **6 - 9** is the result of inhibition of the formation of **10** due to the steric effect of the second methyl group, special activiation of one of the methyl groups by the methyl substituted bicyclobutyl moiety, or a combination of these two factors. What is apparent is that, of all of the hydrogens on **5**, the hydrogens on the methyl group are specifically activated. This suggests that **11** may not be a discrete intermediate and that hydrogen atom removal from **5** may lead directly to **12**.

Acknowledgement. We are indebted to the National Science Foundation for Grant CHE81-14772, which supported the investigation and Sohio and Amoco for fellowships to J.L.S.

References and Footnotes

1. Gassman, P. G.; Smith, J. L. J. Org. Chem. **1983**, 48, 4438.
2. Gassman, P. G.; Carroll, G. T. J. Org. Chem., in press.
3. Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.
4. The remainder of **5** was converted into higher molecular weight, non-volatile material.
5. Coupling constants were determined by multiple decoupling experiments.
6. In addition, all four compounds showed a carbonyl absorption in the IR in the region from 1717-1730 cm^{-1}.
7. In certain instances EuFOD was used as a shift reagent in order to separate overlapping resonances.
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11. It is not known in this example whether **12** is formed in a concerted manner (vide post) or whether **11** and **12** form a hybrid structure. The bishomoallylic nature of **12** may play a dramatic part in its formation.

(Received in USA 24 April 1984)