Acetyl Migrations in a Photoexcited βγ-Unsaturated Methyl Ketone: 1,3-Shift in the Excited Singlet State and 1,2-Shift in the Triplet State[1]

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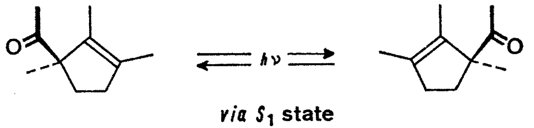
Summary In solution, 3-acetyl-1,2,3-trimethylcyclopent-1-ene (I) undergoes a sigmatropic 1,3-acetyl shift as the major unimolecular reaction in the excited singlet state, and a (thermatically reversible) 1,2-acetyl shift with cyclopropane ring-closure as the predominant triplet state reaction.

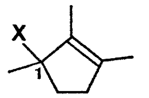
WE report on photochemical results obtained with (*R*)-3-acetyl-1,2,3-trimethylcyclopent-1-ene [(I); $[\alpha]_D^{23}$ + 419° (*c* 3·7, $CHCl_3$); u.v. (iso-octane) λ_{max} 300 nm. (ϵ 151); i.r. (film) 1705 cm.$^{-1}$; n.m.r. ($CDCl_3$) δ 1·15 and 2·04 (two s, 3H each), 1·48 and 1·68 (two s with fine splitting, 3H each); 2,4-dinitrophenylhydrazone, m.p. 163°].[2]† Compound (*R*)-(I) was directly available from the reaction of (*R*)-laurolenic acid[3]‡ with 2 equiv. of methyl-lithium.[4]

U.v. irradiation§ of dilute solutions of the methyl ketone (*R*) (I) in saturated hydrocarbons or benzene results in the formation of complex mixtures of low-yield products. Individual components have not yet been isolated except for one product whose composition and spectral data suggest the structure of a trimethylcyclopentenyl dimer. According to v.p.c. analysis, another of the components is 1,2,3-trimethylcyclopent-1-ene.[7] In the presence of tri-n-butyl stannane (1M in pentane) the proportion of this olefin was slightly increased in the photolysis mixture, and a new product, alcohol (III), was also formed in addition to the previous photoproducts. The rates of formation of these products, including (III), did not change significantly when 1M-naphthalene was added to a parallel run of (*R*)-(I) and stannane.

When the photolysis of a 0·13 M solution of methyl ketone (*R*)-(I) in pentane was interrupted after a consumption of 13% of ketone, the optical rotation of the recovered starting material had dropped from the initial value of $[\alpha]_{436}^{23}$ + 1212° (*c* 1·03) to +1071° (*c* 1·45, both measurements in $CHCl_3$). This photoracemisation accounts for over 32% of the detectable photochemical reaction of (*R*)-(I). That it is due entirely to a 1,3-acetyl migration was demonstrated by the following two photochemical experiments. The trideuteriomethyl compounds (±)-[$^2H_3$]-(VI), 100 ± 1%, and (*R*)-[$^2H_3$]-(VIII), 93 ± 1%, were prepared by methyl Grignard reaction of aldehyde (IV)[5] and oxidation[8] of the resulting two diastereoisomeric alcohols (V), and by hydrogen–deuterium exchange of (*R*)-(I) in tetrahydrofuran–D_2O–NaOD, respectively. Irradiation of an equimolar mixture of (±)-(VI) and (*R*)-(VIII) (each 1·0 M in pentane) and mass spectral analysis of the recovered ketone mixture after interruption of the photolysis at 50% consumption of starting materials established the exclusive presence of [$^2H_3$]-ketones. Scrambling and formation of [$^2H_6$]-ketones had not occurred. Furthermore, the rates of isomerisation of (*R*)-(I) and of (VI) were compared up to about 23% consumption of starting ketones. The conversion of (VI) into (VII) was measured by n.m.r. analysis of the appearance of the methyl signal at δ 1·15. Plots of percentage isomerisation against irradiation time for both runs gave straight lines with identical slopes in the range up to 13% ketone disappearance, and the rates were equal within ±1% in the entire range.

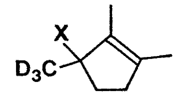


(*R*)-(I) (*S*)-(I)



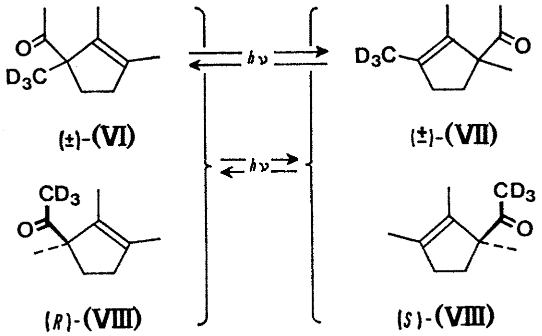
(II) X = H

1(*R*)-(III) X = CH(OH)CH_3



(IV) X = CHO

(V) X = CH(OH)CH_3



The rate of the photoracemisation of (*R*)-(I) was not affected upon the addition of triplet quenchers, 2*M*-penta-1,3-diene and 1 M-naphthalene. Alternatively, sensitisation of (*R*)-(I) in 0·05M acetone solution using 2537 Å radiation gave rise to a new photoisomer (IX) at the expense of both the photoracemisation and the formation of most of the product pattern observed on direct excitation of (*R*)-(I).

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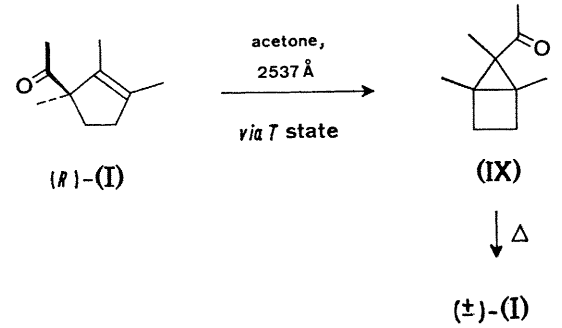
† Satisfactory elemental analyses were obtained for these two new compounds and for ketone (IX). The identification of the remaining new compounds, *i.e.* of alcohol (III) and the deuteriated substances (V), (VI), and (VIII), is based on spectral analysis (i.r., n.m.r., and mass spectra) and on v.p.c. comparison of the deuteriated derivatives with the appropriate non-deuteriated analogues.

‡ The enantiomeric purity of the (*R*)-laurolenic acid ($[\alpha]_D^{23}$ + 185·4 ± 1·1°, liquid) which was used for the preparation of (*R*)-(I), is 96·3 ± 1·4%.[5]

§ Sample solutions for direct irradiation of (I) were degassed by freeze–thaw cycling technique, sealed in Pyrex tubes and stirred magnetically at room temperature. A merry-go-round photoreactor[6] was used, equipped with a 125 w Hg medium pressure lamp which was surrounded by a filter absorbing all wavelengths below 327 nm.

The assignment of constitution (IXa), 5-acetyl-1,4,5-trimethylbicyclo[2,1,0]pentane, is consonant with the spectral data and the optical inactivity of the new product [u.v. (iso-octane) λ_{max} 300 nm. ($\epsilon \sim 80$); i.r. (film) 1705 cm.$^{-1}$; n.m.r. ($CDCl_3$) δ 1·15 (s with fine splitting, 3H), 1·17 (s, 6H), 1·5—2·0 (m, 4H), 2·21 (s, 3H)]. The mass spectrum of (IX) does not differ from that of (I) [prominent peaks at *m/e* 152 (M^+, 1·6%), 109 ($M^+ - COCH_3$, 100%), 81 (17%), 67 (53%), 43 (43%)] except for some negligible differences in relative peak intensities and for the additional fragments $M^+ - 15$ (3%), $M^+ - 28$ (2·5%), and $M^+ - 29$ (3%). The photolytic rearrangement (I) → (IX) was reversed thermally at 200° in a v.p.c. SE-30 column. This thermal isomerisation of (IX) to (I) is novel for a bicyclo[2,1,0]pentanyl ketone, but has precedence in an analogous 1,2-ethoxycarbonyl migration in structurally related ethyl (1),5-(di)-methylbicyclo[2,1,0]pentane-5-carboxylates.[9]**



The results of the direct irradiation experiments with and without triplet quenchers, and of the sensitised photolysis in acetone are evidence that (i) singlet–triplet intersystem crossing in the $\beta\gamma$-unsaturated methylketone (I) is negligible,¶ (ii) reaction modes of the excited singlet state are, *inter alia*, 1,3-acetyl shift, α-cleavage to acetyl and trimethylcyclopentenyl radicals, and reduction to carbinol (upon hydrogen abstraction from stannane), (iii) the predominant triplet reaction is a 1,2-acetyl shift and cyclopropane ring-closure. In several examples products of 1,2- and 1,3-acyl shifts in *cyclic* $\beta\gamma$-unsaturated ketones[10] have been either observed or have been invoked as the intermediates in apparent multi-step transformations. It has been generally assumed that these acyl migrations are preceded by α-fission to allyl-acyl diradicals which then recombine to the appropriate $\beta\gamma$-unsaturated (starting or 1,3-rearranged compounds) or cyclopropyl ketones (1,2-rearrangement and ring closure). Compound (I) is the first $\beta\gamma$-unsaturated methyl ketone which has been found to photorearrange in a similar fashion. At the same time, however, the *aliphatic* nature of (I) sheds doubt on the occurrence of *free radical* intermediates in the rearrangement step. Furthermore, if radical primary products were produced in their electronic ground states, a specific choice between the two reaction paths by excited-state multiplicity of the reactant clearly would be unexpected. Our results suggest that both the 1,2- and the 1,3-acetyl migrations are concerted reaction steps, and that either one or both overall reactions are photochemically-allowed concerted [$\sigma^2 + \pi^2$]-additions.[11] Subsequent to the recent preliminary presentation of our results,[1] Ipaktschi[10b] reported on similar specifically singlet- and triplet-initiated 1,3- and 1,2-acyl migrations in cyclic $\beta\gamma$-unsaturated ketones.

A further result of photochemical interest is, moreover, the reduction of the excited singlet state of ketone (I) to alcohol (III). A similar behaviour is observed with the related aldehyde, 3-formyl-1,2,3-trimethylcyclopent-1-ene, in the presence of tri-n-butylstannane.[1,5] In contrast to these findings, saturated as well as $\alpha\beta$-unsaturated and aryl ketones are known to reduce exclusively in their triplet (n, π^*) state.[12]

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¶ Compound (I) does not exhibit phosphorescence emission at 78°K. in (ether : isopentane : alcohol) upon excitation in its $n \rightarrow \pi^*$ absorption band.

** The thermal isomerisation of 5-acetylbicyclo[2,1,0]pentanes analogous to (IX) → (I) has been found independently (M. J. Jorgenson and A. F. Thacher, *Chem. Comm.*, 1969, 1030). We thank Dr. Jorgenson for this information, prior to publication.

[1] Presented in part at the meeting of the Swiss Chemical Society in Neuchâtel, February 15th, 1969; *cf.* E. Baggiolini, H. P. Hamlow, K. Schaffner, and O. Jeger, *Chimia*, 1969, **23**, 181. For previous paper in this series see R. Imhof, W. Graf, H. Wehrli, and K. Schaffner, *Chem. Comm.*, 1969, 852.

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[4] Method described by C. Tegner, *Acta Chim. Scand.*, 1952, **6**, 782, and references therein.

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[9] M. J. Jorgenson and T. J. Clark, *J. Amer. Chem. Soc.*, 1968, **90**, 2188.

[10] For the most recent reports and leading references see (a) R. K. Murray, jun. and H. Hart, *Tetrahedron Letters*, 1968, 4995; (b) J. Ipaktschi, *ibid.*, 1969, 2153; (c) K. Kojima, K. Sakai, and K. Tanabe, *ibid.*, p. 1925.

[11] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.,

[12] See, *e.g.*, (a) P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 2503; P. Keller, G. Eggart, H. Wehrli, K. Schaffner, and O. Jeger *Helv. Chim. Acta*, 1967, **50**, 2259; R. Simonaitis, G. W. Cowell, and J. N. Pitts, jun., *Tetrahedron Letters*, 1967, 3751; (b) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, 1966, **88**, 1965; (c) G. S. Hammond and P. A. Leermakers, *ibid.*, 1962, **84**, 207; J. A. Bell and H. Linschitz, *ibid.*, 1963, **85**, 528.