# A [3,3]-Sigmatropic Shift in Diels–Alder Adducts of Fulvenes: an Example of a Reverse-Claisen Rearrangement

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PREVIOUSLY we reported that the reaction of fulvenes with *cis*-hex-3-ene-2,5-dione resulted in the formation of dihydropyrans[1] of structure (I) rather than the expected adducts (II). Evidence is now presented that the dihydropyrans (I) are the thermal transformation products of the Diels–Alder adducts (II)† which consequently require milder conditions for their preparation. Shorter reaction periods or lower temperatures have generally been effective and compounds of both types have now been isolated for a variety of 6- and 6,6′-substituted fulvenes (*e.g.* dimethyl-, diphenyl-, methylphenyl- and *p*-methoxyphenylfulvene). Thus, an equimolar solution of diphenylfulvene and the ketone when refluxed in ether for 20 hr. gave (II; $R^1 = R^2 = Ph$) in 23% yield whereas (I; $R^1 = R^2 = Ph$) was obtained in 35% yield by boiling the reactants in benzene (5½ hr.). Similarly, when *p*-methoxyphenylfulvene and the ketone were refluxed in ether for 30 hr. a mixture of (I; $R^1 = p\text{-MeOC}_6H_4$, $R^2 = H$) (15%) and (I; $R^1 = H$, $R^2 = p\text{-MeOC}_6H_4$) (30%) was formed which could be separated by column chromatography; refluxing for 6½ hr. produced mainly (II; $R^1 = H$, $R^2 = p\text{-MeOC}_6H_4$) in 15% yield. The *endo*-diacetylnorbornene adduct (II; $R^1 = R^2 = Ph$) smoothly rearranged, without apparent dissociation, on boiling for ½ hr. in 80—100° light petroleum to give, in excellent yield, a product identical to the dihydropyran (I; $R^1 = R^2 = Ph$) prepared as described. This transformation could be observed directly in ethanol solution at 45° by following the change in the u.v. spectrum. Over a period of about 24 hr., the diphenylethylene

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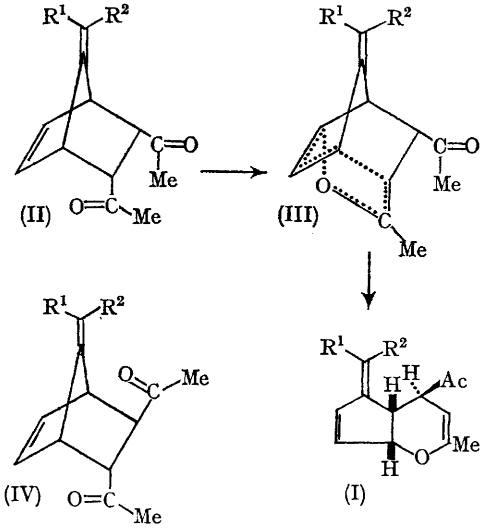
† Chemical and spectroscopic evidence is in full agreement with the structural assignment for these adducts and n.m.r. spectroscopy confirms the *endo*-stereochemistry of the acetyl groups in (II).

absorption of (II; $R^1 = R^2 = Ph$) $\lambda_{max}$ 247·5 nm., ($\epsilon$ 17,700) was completely replaced by the diphenylbutadiene absorption, $\lambda_{max}$ 288 nm. ($\epsilon$ 17,700) present in (I; $R^1 = R^2 = Ph$). The rearrangement gave good first order kinetics ($k = 3{\cdot}46 \times 10^{-5}$ sec.$^{-1}$) and all spectra passed through a pure isosbestic point at 263·5 nm. The presence of this feature implies that no significant dissociation occurs during rearrangement and excludes from the reaction pathway any long-lived intermediate.

*cis-endo*-2,3-Diacetyl-7-isopropylidenenorborn-5-ene (II; $R^1 = R^2 = Me$) rearranges even more rapidly to the dihydropyran (I; $R^1 = R^2 = Me$) (Table). The negative entropy of activation, the small solvent effect and the results reported above for the diphenyl adduct (II; $R^1 = R^2 = Ph$) are consistent with an intramolecular transformation occurring *via* a cyclic transition state (III), and are typically those observed for no-mechanism reactions.[2] This conversion of a $\gamma\delta$-unsaturated ketone into an allyl vinyl ether by a [3,3]-sigmatropic shift[3,4] is an example of the rarely documented reverse-Claisen rearrangement.[5]



The known ease with which many Diels–Alder adducts of fulvenes dissociate in solution[6] makes this change of special interest; however, the corresponding adducts prepared from 6,6′-dimethyl- and diphenyl-fulvenes and *trans*-hex-3-ene-2,5-dione (IV; $R^1 = R^2 = Me$ or Ph) do dissociate under similar conditions rather than rearrange. These observations may probably be accounted for by the greater thermodynamic stability of the *trans*-adducts (IV) [*cf.* the *cis*-adducts (II)] whereas the expected product of their rearrangement should be less stable than the dihydropyrans (I), because of increased non-bonded interactions.

*Kinetic data* for rearrangement of* (II; $R^1 = R^2 = Me$)

| $T°$ | Ethanol $k \times 10^5$ (sec.$^{-1}$) | Cyclohexane $k \times 10^5$ (sec.$^{-1}$) |
|---|---|---|
| 30 | 7·25 | — |
| 32·5 | — | 1·83 |
| 35 | 13·0 | 2·53 |
| 40 | 23·4 | 4·5 |
| 45 | 39·9 | 8·65 |
| $\Delta E\ddagger$ (kcal. mole$^{-1}$) | 21·0 | 24·3 |
| $\Delta S\ddagger$ 308·1 (e.u.) | −5·8 | −10·5 |
| log $A$ | 11·96 | 10·94 |

* Two runs were made for each determination; good first-order kinetics were observed.

*cis-endo*-2,3-Diacetylnorbornene is relatively very stable and shows no tendency to dissociate or rearrange at temperatures below 100°. Thus, the ease with which the fulvene adducts (II) undergo this transformation is best interpreted in terms of the greater strain associated with the trigonal carbon atom C-7 [7,8] and the extension of conjugation due to the developing butadiene system. This involvement of the exocyclic system is supported by the fact that the adduct (II; $R^1 = p\text{-MeOC}_6H_4$, $R^2 = Me$) rearranges approximately twice as fast as (II; $R^1 = Ph$, $R^2 = Me$).

(*Received, March 27th*, 1968; *Com.* 385.)

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[3] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2511; *ibid.*, 1965, **87**, 4389.

[4] This rearrangement involves a transition state which must have similar geometry to that postulated in the Woodward and Katz rearrangement of substituted dicyclopentadienes, (R. B. Woodward and T. J. Katz, *Tetrahedron*, 1959, **5**, 70).

[5] M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, 1965, **48**, 1985; M. F. Ansell and V. J. Leslie, *Chem. Comm.*, 1967, 949. See also E. Vogel, *Angew., Chem. Internat. Edn.*, 1963, **2**, 6.

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[8] Similar acceleration has been observed in rearrangement of dicyclopentadiene-8-one when compared to 8-hydroxydicyclopentadienes; R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.* (*C*), 1967, 1382.