Efficient Synthesis of Bicyclo[5.3.0]decatrienones and of 2-Tetralones *via* Rhodium(II) Acetate-catalysed Cyclisation of α-Diazoketones derived from 3-Arylpropionic Acids

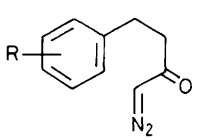
M. Anthony McKervey,* Sarbajna M. Tuladhar, and M. Fiona Twohig

Department of Chemistry, University College, Cork, Ireland

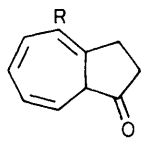
Rhodium(II) acetate-catalysed cyclisation of α-diazoketones derived from 3-arylpropionic acids produces bicyclo[5.3.0]decatrienones or 2-tetralones depending on the substitution pattern of the aryl ring; the former products are transformed into the latter by catalytic amounts of trifluoroacetic acid.

Recent work indicates that a number of catalysed reactions of α-diazocarbonyl compounds which traditionally have been brought about by copper salts can be improved on substantially through the use of rhodium(II) carboxylates,[1] a case in point being the discovery[2] that $Rh_2(OCOCF_3)_4$ is a very efficient catalyst for producing regiospecific cycloheptatriene carboxylates from benzene and diazoesters in contrast to the classical Buchner procedures[3] which yield complex mixtures of regioisomers. In seeking to develop a general synthetic entry into the bicyclo[5.3.0]decane series with functionality in both rings for eventual total synthesis of perhydroazulene sesquiterpenes we have investigated catalytic reactions of α-diazoketones derived from 3-arylpropionic acids.† 1-Diazo-4-phenylbutan-2-one (**1**), the parent member of the series, had been found already to cyclise to bicyclo[5.3.0]decatrienone (**9**) in 40—50% yield when exposed to copper(I) chloride in hot bromobenzene.[4] We now find that (a) the transformation of (**1**) into (**9**) can be brought about essentially quantitatively in minutes by catalytic amounts of rhodium(II) acetate in dichloromethane, (b) substituents on the benzene ring in (**1**) exert significant directive effects on the course of the reaction, and (c) the reaction provides the basis of a new efficient catalytic synthesis of 2-tetralones.

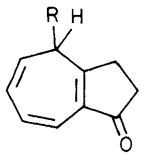
Dropwise addition (*ca.* 20 min) of a dichloromethane solution of (**1**) to a solution of rhodium(II) acetate [*ca.* 1 mg per 100 mg of (**1**)] in dichloromethane under reflux produced trienone (**9**) (99%), which was chromatographically (t.l.c.) and spectroscopically (n.m.r.) homogeneous. While brief exposure of (**9**) to triethylamine caused the expected shift of one olefinic bond to afford the isomeric trienone (**11**),[4a] an unexpected rearrangement to 2-tetralone (**20**) was discovered when (**9**) was left in prolonged contact with silica gel. The latter change could be brought about more efficiently by treating (**9**) with a drop of trifluoroacetic acid (TFA). This two-step synthesis of 2-tetralone was easily executed as a one-pot procedure by sequential treatment of diazoketone (**1**) with catalytic amounts of rhodium(II) acetate and TFA whereupon (**20**) was obtained in 95% yield (87% after distillation).



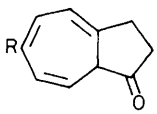
(**1**) R = H
(**2**) R = 4-Me
(**3**) R = 4-OMe
(**4**) R = 4-OAc
(**5**) R = 2-Me
(**6**) R = 2-OMe
(**7**) R = 3-OMe
(**8**) R = 3-OAc



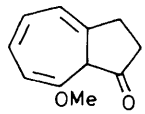
(**9**) R = H
(**10**) R = Me



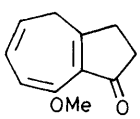
(**11**) R = H
(**12**) R = Me



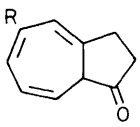
(**13**) R = Me
(**14**) R = OMe
(**15**) R = OAc



(**16**)

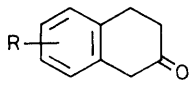


(**17**)

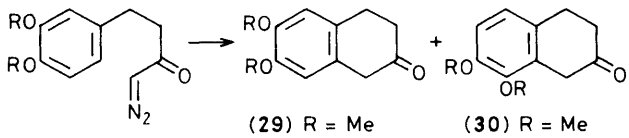


(**18**) R = OMe
(**19**) R = OAc

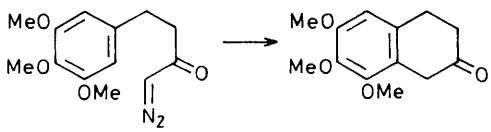
† The diazoketones were obtained in high yield from the appropriate acyl chloride and diazomethane.



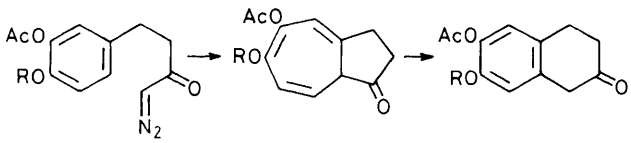
(**20**) R = H
(**21**) R = 7-Me
(**22**) R = 7-OMe
(**23**) R = 7-OAc
(**24**) R = 5-Me
(**25**) R = 8-OMe
(**26**) R = 6-OMe
(**27**) R = 6-OAc



(**28**) R = Me
(**31**) R—R = CH_2
(**29**) R = Me
(**32**) R—R = CH_2
(**30**) R = Me



(**33**)
(**34**)



(**35**) R = Me
(**36**) R = Ac
(**37**) R = Me
(**38**) R = Ac
(**39**) R = Me
(**40**) R = Ac

Application of the catalytic sequence to a series of related diazoketones with substituents on the aromatic ring produced the following observations. The 4-methyl, 4-methoxy, and 4-acetoxy derivatives, (**2**), (**3**), and (**4**), on exposure to rhodium(II) acetate quantitatively furnished the respective trienones (**13**),[4a] (**14**), (**15**),†‡ which could be further transformed *in situ* into 7-methyl-2-tetralone[5] (**21**) (84%), 7-methoxy-2-tetralone[6] (**22**) (88%), and 7-acetoxy-2-tetralone (**23**) (90%), respectively, on brief exposure to TFA. The 2-methyl and 2-methoxy derivatives (**5**) and (**6**) exhibited contrasting behaviour. Whereas the former afforded trienone (**10**) (99%)§ and, following TFA treatment, 5-methyl-2-tetralone[5] (**24**) (86%), indicating that cyclisation had occurred on the side of the benzene ring away from the substituent, the 2-methoxy derivative (**6**) cyclised towards the substituent to produce trienone (**16**) (98%), which was transformed into the isomeric trienone (**17**) (70%) by triethylamine and into 8-methoxy-2-tetralone[7] (**25**) (84%) by TFA. The repulsive effect of an *ortho*-methyl group on the direction of cyclisation may be steric in origin, whereas an *ortho*-methoxy group, through co-ordination, may attract the putative complexed carbenoid intermediate.

The directive effect of a *meta*-methoxy substituent was rather more striking for the product isolated from diazoketone (**7**) and rhodium(II) acetate was 6-methoxy-2-tetralone[8] (**26**) (86%), and not the ring expanded trienone (**18**). This pattern was repeated in three other cases in which the diazoketone precursor possessed at least one alkoxy substituent *meta* to the reacting side chain. Thus, the 3,4-dimethoxy derivative (**28**) cyclised to afford an 80 : 20 mixture of tetralones (**29**)[9] and (**30**) (96%), the 3,4-methylenedioxy derivative (**31**) similarly produced tetralone (**32**)[10] predominantly (97%), and the 3,4,5-trimethoxy derivative (**33**) gave 6,7,8-trimethoxy-2-tetralone (**34**) in excellent yield (89%). However, the system reverted to the earlier pattern of producing ring expanded trienones when the *meta*-substituent was acetoxy as in diazoketones (**8**), (**35**), and (**36**), which on exposure to rhodium(II) acetate gave trienones (**19**), (**37**), and (**38**), respectively, in >90% yield; addition of TFA completed the synthesis of tetralones (**27**) (77%), (**39**) (65%), and (**40**) (95%), from these trienones.

The foregoing observations demonstrate the efficacy of rhodium(II) catalysis in intramolecular Buchner procedures for the production of bicyclo[5.3.0]decane derivatives. Furthermore, the process can now be extended to include an efficient catalytic synthesis of 2-tetralones of value as synthetic intermediates. It seems reasonable to suppose that the cyclisation mechanism involves formation of an unstable norcaradienone intermediate whose fate is determined by substituent effects: in the absence of an electron donating group at the *meta*-position electrocyclic ring opening produces the kinetically favoured trienones; a *meta*-methoxy group, on the other hand, promotes the alternative bond breaking terminating in tetralones. Conversion of the kinetic trienones into tetralones by TFA implies the existence of an equilibrium between trienones and norcaradienones with acid-promoted leakage of the latter to tetralones.

Received, 10th October 1983; Com. 1339

‡ All new compounds gave satisfactory analytical and/or mass spectrometric data. Structures are supported by i.r. and ^1H and ^{13}C n.m.r. spectra.

§ This was confirmed by n.m.r. analysis of the corresponding conjugated trienone (**12**) produced by treatment of (**10**) with Et_3N.

References

1 M. P. Doyle, W. H. Tamblyn, and V. Bagheri, *J. Org. Chem.*, 1981, **46**, 5094; M. A. McKervey and P. Ratananukul, *Tetrahedron Lett.*, 1982, 2509; A. Demonceau, A. F. Noels, A. J. Hubert, and P. Teyssie, *J. Chem. Soc., Chem. Commun.*, 1981, 688; T. N. Salzmann, R. W. Ratcliffe, B. G. Christensen, and F. A. Bouffard, *J. Am. Chem. Soc.*, 1980, **102**, 6161.

2 A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot, and P. Teyssie, *J. Org. Chem.*, 1980, **45**, 695.

3 V. Dave and E. W. Warnhoff, *Org. React.*, 1970, **18**, 217; S. D. Burke and P. A. Greico, *ibid.*, 1979, **26**, 361.

4 (a) L. T. Scott, M. A. Minton, and M. A. Kirms, *J. Am. Chem. Soc.*, 1980, **102**, 6311; (b) A. Constantino, G. Linstrumelle, and S. Julia, *Bull. Soc. Chim. Fr.*, 1970,, **907**, 912.

5 J. J. Sims, M. Cadogan, and L. H. Selman, *Tetrahedron Lett.*, 1971, **14**, 951.

6 M. D. Soffer, J. C. Cavagnol, and H. E. Gellerson, *J. Am. Chem. Soc.*, 1949, **71**, 3857.

7 D. W. Johnson and L. N. Mander, *Aust. J. Chem.*, 1974, **27**, 1277, obtained this tetralone in 20% yield by treating diazoketone (**7**) with $Et_2O{\cdot}BF_3$.

8 J. H. Burckhalter and J. R. Campbell, *J. Org. Chem.*, 1961, **26**, 4232.

9 A. S. Horn, C. J. Grol, D. Dijkstra, and A. H. Mudder, *J. Med. Chem.*, 1978, **21**, 825.

10 M. Kanao, T. Hashizume, Y. Ichikawa, K. Irie, and S. Isoda, *J. Med. Chem.*, 1982, **25**, 1358.