Tetrahedron Letters No. 37, pp 3451 - 3454.
© Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/0908-3451$02.00/0

THE "WITTIG REARRANGEMENT" OF α-ALKOXYCARBENES FORMED BY PHOTOREARRANGEMENT OF 1-ALKOXYTRIPTYCENES

Hiizu Iwamura*[1] and Hideyuki Tukada
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Tokyo 113, and The Institute for Molecular Science,
38 Nishigonaka, Myodaiji, Okazaki 444, Japan

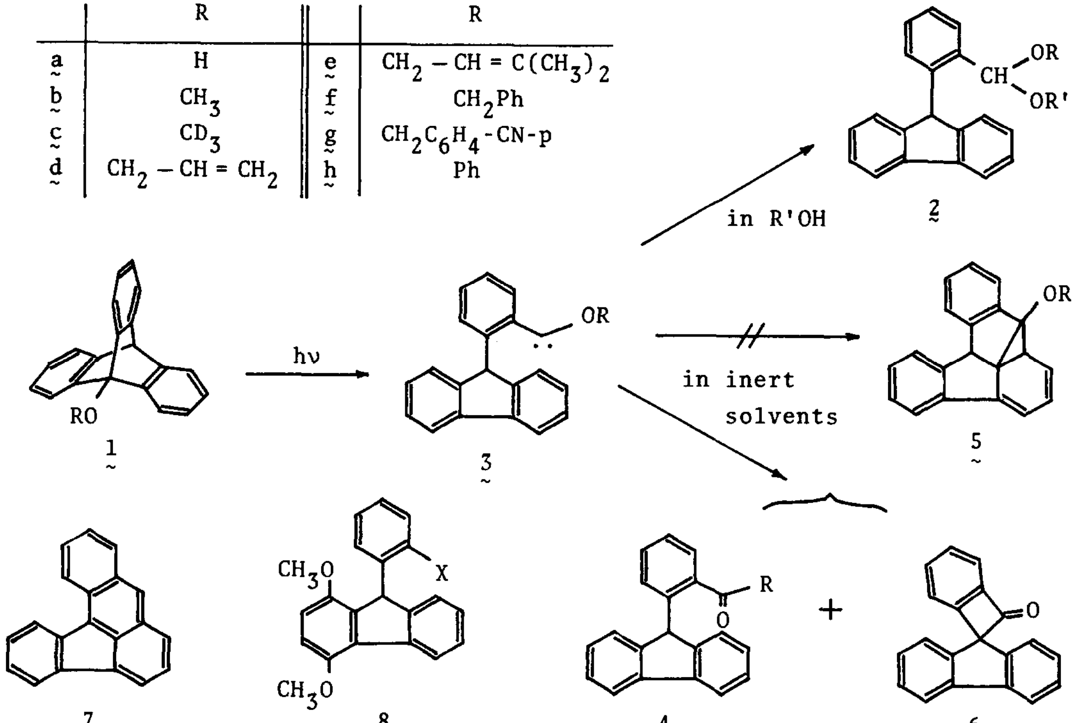
Whereas the nucleophilic nature of α-alkoxycarbenes as indicated by a canonical structure $R'-\overset{-}{C}=\overset{+}{O}-R$ of the resonance hybrid has been demonstrated by the addition reaction to electron-deficient olefins[2] and by the stability of transition metal—carbene complexes,[3] rearrangement and fragmentation reactions appear to be only vaguely understood. We wish to report that the apparently anomalous photoreactions encountered in a wide variety of 1-alkoxytriptycenes provide a good examples of the carbene counterpart of the Wittig rearrangement of α-metallated ethers.[4]

When a 1 – 5 mM solution of 1-alkoxytriptycenes 1 in an alcohol was irradiated for 1.5 hr with a Vycor filtered mercury source in an immersion apparatus, a smooth conversion to the corresponding acetals 2 was achieved. The results are summarized in Table 1. The intermediary formation of alkoxycarbenes 3 followed by OH insertion is thus confirmed. Formation of asymmetric acetals excludes the possibility that acetals 2 might be formed by nucleophilic attack of the solvent molecule to the initially formed benzaldehyde 4a (*vide infra*).[5]

In inert solvents, e.g., cyclohexane and *n*-pentane, the reactions were just as efficient as in alcohols. The photoproducts isolated in good yield (Table 1) were, however, not the expected norcaradienes 5.[6] Aldehyde 4a was obtained almost exclusively from 1-methoxytriptycene 1b.[7,8] The corresponding ketones 4d – 4g were the main photoproducts from 1-allyloxy- and 1-benzyloxytriptycenes 1d – 1g and were often accompanied by a small amount of 4a and spiroketone 6.[8] 1-Phenoxytriptycene 1h formed the exception to the foregoing reaction pattern; benz[a]aceanthrylene 7 together with diphenylacetal 2(R = R' = Ph) were obtained.

These reactions in inert solvents are rationalized as the homolysis and rearrangement of α-alkoxycarbenes 3. Aldehyde 4a appears to be formed by the homolysis of the $O-CH_3$ bond to give the acyl radical followed by abstraction of a hydrogen atom from solvent molecules. An alternative mechanism in which 4a might be produced from methoxycarbene 3b *via* an epoxy or carbonyl ylide intermediate can be ruled out by the lack of a deuterium atom at the formyl position in the product 4a from the methoxy-d_3 compound 1c.[7,9]

	R		R
a	H	e	$CH_2-CH=C(CH_3)_2$
b	CH_3	f	CH_2Ph
c	CD_3	g	$CH_2C_6H_4$-CN-p
d	$CH_2-CH=CH_2$	h	Ph



1 3 2 5

7 8 4 6

The migratory aptitude of the alkyl groups in the above reactions is very reminiscent of the Wittig rearrangement of α-metallated ethers.[4] Thus various benzyl and allyl groups migrate, but the [1,2] shift is reluctant in the simple alkyl and aryl groups in consonant with the diminishing ease of ordinary nucleophilic substitution on group R. Fission to the corresponding ketone and an alkyl anion has been reported as a side reaction in some Wittig rearrangement.[4] Reduced electrophilic reactivity of the α-alkoxycarbenes is considered to be responsible for the occurrence of the Wittig type rearrangement in these carbenes 3 which otherwise might have been intercepted internally by the C = C bond of the aromatic ring to give normal photoisomers 5. In phenoxycarbene 3h, the electron-withdrawing mesomeric effect of the phenyl group appears to counterbalance the reduced electrophilic reactivity of the carbenic center ($Ar-\overset{-}{C}=\overset{+}{O}-Ph$ — $Ar-C-\overset{+}{O}=\overset{-}{Ph}$) and the original photoisomerization pattern is regenerated. Product 7 appears to be formed by elimination of phenol which in

Table 1. Photoproducts of 1-Alkoxytriptycenes

Triptycene	Solvent and/or additive	Photoproducts Isolated yields (%)[a]
1b	CH_3OH	**2**(R = R'=CH_3) 62
1b	*t*-C_4H_9OH	**2**(R = CH_3, R'= *t*-C_4H_9) 43[b]
1b	cyclohexane	**4a** 73; **6** $\leq$ 5; **4b**[c]
1b	cyclohexane + dimethyl fumarate[d]	**4a** 98
1c	cyclohexane	**4a** 73; **6** $\leq$ 5; **4b**[c]
1d	*n*-pentane	**4d** 62; **4a** 4; **6**[c]
1e	*n*-pentane	**4e** 78; **4a** 15; **6**[c]
1f	CH_3OH	**2**(R = CH_2Ph, R'= CH_3) 29[b]
1f	*n*-pentane	**4f** 66; **4a**[c]; **6**[c]
1g	*n*-pentane	**4g** 36; **6** 16; **4a**[c]
1h	cyclohexane	**7** 31; **2**(R = R'= Ph) 29; **4a** $\simeq$ 1
1,2,5-$(OCH_3)_3$	CH_3OH	**8**(X = $CH(OCH_3)_2$) 29; **8**(X = CO_2CH_3) 41
1,2,5-$(OCH_3)_3$	*n*-pentane + ether	**8**(X = CHO) 30[b]

[a] By layer chromatography on silica gel. [b] Although the isolated yield was not necessarily high, no significant n.m.r. signal left unidentified. [c] Not detected. [d] 35 mM in added dimethyl fumarate.

turn will be captured by a second molecule of **3h** to give **2**(R = R'= Ph).

Lastly we note that a [2,3] sigmatropic rearrangement with accompanying allylic inversion did not occur in **3e**. While the [2,3] sigmatropic reaction has been reported for allylthiocarbenes,[10] the identical 9-crotylfluoren-9-ol is obtained either from the 9-crotyloxy- and 9-α-methallyloxyfluorene on treatment with KOH; both [1,2] and [2,3] shifts may take place in the Wittig rearrangement.[4,11]

We conclude that, in contrast to alkylcarbenes in which the hydrogen atom or a group aligned with the vacant pπ orbital of the ambident carbene center migrates preferentially to give olefins and thus the [1,2] shifts have the character of the Wagner-Meerwein rearrangement,[12] the migration in alkoxycarbenes resembles the Wittig rearrangement.

References and Notes

1) Present address: Institute for Molecular Science.
2) A. G. Brook and P. J. Dillon, *Can. J. Chem.*, **47**, 4347 (1969).
3) For a review see D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
4) H. E. Zimmerman in "Molecular Rearrangement," Part 1, P. de Mayo, Ed., Interscience, New York, 1963, p. 345; T. S. Stevens in "Progress in Organic Chemistry," Vol. 7, J. Cook and W. Carruthers, Ed., Butterworths, London, 1968, p. 48.
5) Trapping of the intermediate from 1,2,5-trimethoxytriptycene by methanol to give **8**(X = $CH(OCH_3)_2$) is in marked contrast to 2,5-dimethoxytriptycene in which the OH insertion product of the potential carbene intermediate cannot be found and 5-methoxy derivative of **7** is formed (R. O. Day, V. W. Day, S. J. Fuerniss, and D. M. S. Wheeler, *Chem. Comm.*, 296 (1975)). The difference between the two can be ascribed to the competition of the internal and external reactions.
6) T. D. Walsh, *J. Am. Chem. Soc.*, **91**, 515 (1969); N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, **91**, 516 (1969); H. Iwamura and K. Yoshimura, *ibid.*, **96**, 2652 (1974); H. Iwamura, *Chemistry Lett.*, 5 (1974).
7) H. Iwamura and H. Tukada, *Chemistry Lett.*, 1045 (1976).
8) Satisfactory elemental analyses were obtained for all the compounds described in this communication. The structure of **4a** was confirmed by independent synthesis of the aldehyde through the Kornblum oxidation of 9-(*o*-iodomethylphenyl)fluorene. The aldehyde served as a key intermediate in the preparation of the authentic samples for many other photoproducts obtained in this study. For example, the Jones oxidation of the alcohol obtained by the reaction of benzylmagnesium chloride with **4a** gave **4f**. Spectral properties of the photoproducts will be given in a full paper.
9) For some fragmentary precedents for the cleavage and [1,2] migration of alkoxycarbenes see D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966); R. W. Hoffmann and C. Wunsche, *Chem. Ber.*, **100**, 943 (1967) for dimethoxycarbene. R. W. Hoffmann, R. Hirsch, R. Fleming, and M. T. Reetz, *Chem. Ber.*, **105**, 3532 (1972) for allyloxycarbenes. A. M. Foster and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 608 (1973) for oxacarbenes. However, it is usually the case that the photochemical reactions go in opposite directions; the α-cleavage of small ring ketones leads to the ring-expanded oxacarbenes (P. Yates and R. O. Lutfy, *Accounts Chem. Res.*, **8**, 209 (1975)).
10) J. E. Baldwin and J. A. Walker, *Chem. Comm.*, 354 (1972).
11) J. Cast, T. S. Stevens, and J. Holmes, *J. Chem. Soc.*, 3521 (1960).
12) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968); H. E. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972); A. Nickon, F. Huang, R. Weglein, K. Matsuo, and H. Yogi, *J. Am. Chem. Soc.*, **96**, 5264 (1974).

(Received in Japan 8 June 1978; received in UK for publication 11 July 1978)