Table I. Variation of Isomer Distribution[a] in Sodium Hydroxide Solution at 50°

Entry	Compd	Time, min	% **1**	% **3**	Wt **1** + **3** recovered,[b] g
1	**1**	10	43	57	1.7
2	**1**	20	41	59	1.4
3	**1**	40	43	57	1.2
4	**1**	60	41	59	1.0
5	**3**	15	41	59	0.8[c]

[a] Analysis by integration of nmr curves. [b] Entries 1–4 were obtained by removing 10-ml aliquots from a solution of 10.0 g (0.085 mole) of β,γ-sulfolene in 47 ml of 2 *N* sodium hydroxide. The weights recorded are those of the chloroform extracts of these basic solutions. Combining the water layers of the four aliquots followed by treatment with dimethyl sulfate provided 5.7 g of ether arising from alcohol **5**. These results account for 88% of the material used. [c] Recovered ~0.8 g of the sulfolene mixture from a run in which 1.0 g of **3** was used.

tivity are the inductive effect of the sulfone group, the state of hybridization of the carbon atom, and 3d-orbital stabilization of the transition state leading to **4**. Since the 3d-orbital factor could also be operative, and possibly more effectively, in the transition state leading to the allylic species **2**,[14] inductive and hybridization effects are favored as an explanation for the rapid vinyl proton abstraction.

Acknowledgment. Technical assistance by Mr. J. Ward and Mr. M. Beisner, assistance with nmr by Dr. J. J. McLeskey, and the continued interest of Dr. W. I. Lyness are gratefully acknowledged.

(14) H. P. Koch and W. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

Charles D. Broaddus
The Procter & Gamble Company, Miami Valley Laboratories
Cincinnati, Ohio 45239
Received May 9, 1966

Azoalkenes as Intermediate Compounds in the Formation of Osazones from α-Acetoxy Ketones

Sir:

The formation of phenylazoalkenes from the alkaline decomposition of phenyltosylhydrazones was reported in a recent paper[1] and the mechanism shown in Figure 1 (left) was suggested.[1]

This "push-pull" system can proceed in either direction; the treatment of the α-acetoxycyclohexanone phenylhydrazone (II; obtained from the reaction between α-acetoxycyclohexanone (III) and phenylhydrazine) with LiH in warm benzene leads to the formation within a few minutes of 1-(phenylazo)cyclohexene (I) in a quantitative yield (Figure 1, right). The formation of I from II occurs spontaneously, even in the cold. If II is dissolved in methanol or another solvent, the colorless solution rapidly becomes yellow and thin-layer chromatography of this solution shows that variable amounts of I are being formed.[2]

Compound I has been isolated in significant amounts (35–50%).

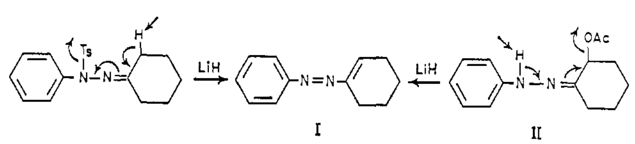

Figure 1.

The formation of II (mp 87–90°, infrared: 3300 and 1720 cm^{-1}. *Anal.* Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.60; H, 7.75; N, 11.40) from the reaction of α-acetoxycyclohexanone (III) with 1 mole of phenylhydrazine is very rapid.[3] If III is allowed to react with an excess of phenylhydrazine in benzene or in methanol and the mixture maintained at room temperature for several hours, the 1,2-cyclohexanedione bisphenylhydrazone (IV)[4] is obtained.

The formation of osazones from α-hydroxy ketones is a well-known reaction which has been studied intensively.[5] The formation of osazones from α-halo or α-acetoxy ketones has been reported occasionally, but its mechanism has not yet been elucidated.[2b] To obtain information about the formation of osazones from α-acetoxy ketones we allowed III to react with phenylhydrazine under different experimental conditions. The course of the reaction was followed by means of thin-layer chromatography. There was an immediate formation of II, which was then rapidly transformed into I. If an excess of phenylhydrazine was present, I was first transformed into compound V, which then formed the osazone IV. The three compounds, I, IV, and V, were isolated from the reaction mixture.

If II is allowed to react with phenylhydrazine under certain conditions, V precipitates[6] as a white yellowish solid, and on standing in the reaction mixture is slowly converted to IV. The analytical data (mp 133–34°; infrared: 3300 and 1640 cm^{-1}; ultraviolet: maximum at 208 mμ (ϵ 23,000); 252 mμ (ϵ 19,000); 276 mμ (ϵ 20,000). *Anal.* Calcd for $C_{18}H_{22}N_4$: C, 73.43; H, 7.53; N, 19.03. Found: C, 73.43; H, 7.53; N, 19.12) and the nmr spectrum of V[7] suggest that its structure is that of a phenylhydrazone of 2-(β-phenylhydrazine)-cyclohexanone (Figure 2). The formation of V can be explained if one assumes a 1:4 addition of phenylhydrazine to the conjugated system of I[8] (Figure 2). To verify this conclusion, we treated I with 1 mole of phenylhydrazine in a concentrated methanolic solution in the cold; V precipitated from the solution in high yield (70–80%).

The transformation of V into IV implies an oxidation. In order to obtain information about this step of the reaction, a series of experiments was undertaken. In neutral solutions V is relatively stable. It remains

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(1) L. Caglioti, P. Grasselli, and G. Rosini, *Tetrahedron Letters*, 4545, (1965).

(2) For the formation of aryl- and alkylazoalkenes from analogous reactions see (a) B. T. Gillis and J. D. Hagarty, *J. Am. Chem. Soc.*, **87**, 4575 (1965); (b) F. Ramirez and A. F. Kirby, *Ibid.*, **75**, 6026 (1953); (c) J. van Alphen, *Rec. Trav. Chim.*, **64**, 305 (1945).

(3) Full details of this work will be given elsewhere.

(4) G. J. Bloink and K. H. Pausacker, *J. Chem. Soc.*, 1328 (1950).

(5) I. Dijong and F. Micheel, *Ann.*, **684**, 216 (1965); M. M. Shemjakin, V. I. Mamind, K. M. Ermolaev, and E. M. Bamdas, *Tetrahedron*, **21**, 2775 (1965), and references.

(6) At this stage, V could be isolated in a yield of 60–70%.

(7) The spectrum shows a large absorption between δ 1.3 and 2.3 (7 H), a triplet (1 H) at δ 4.38 ($CH_2C(N)H$), a one-proton signal at δ 2.75 attributed to the allylic H_{eq} ($J_{gem} \cong 13$ cps, $J_{eq,ax} \cong J_{eq,eq} \cong$ 3 cps); the allylic H_{ax} is at a higher field overlapped by the methylene absorption. The –N*H*–N*H*–Ph group lies at δ 3.1–3.9 (2 H, broad); the =NN*H*Ph is obscured by the aromatic protons (δ 6.5–7.5).

(8) For 1:4 additions on analogous system see H. Beyerand and G. Badicke, *Ber.*, **93**, 826 (1960).

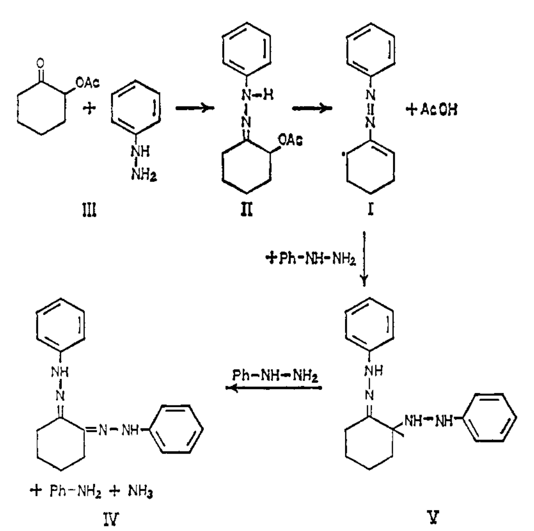

Figure 2.

stable when phenylhydrazine is added and does not seem to be affected by the presence of air. If AcOH is added to a solution of V in methanol or in benzene, IV is formed rapidly. This does not depend upon the presence of an oxygen atmosphere.[9]

This reaction was followed carefully by thin-layer chromatography. It was observed that immediately after the addition of AcOH the 1-(phenylazo)cyclohexene (I) was formed, together with increasing amounts of IV. The yield of IV was 40–42%. The azoalkene I was slowly transformed into other compounds.

If AcOH is added to a mixture of V and excess phenylhydrazine in benzene, IV is formed rapidly. No formation of I is observed.

In this case the yield is over 80%. Ammonium acetate and aniline are also obtained in significant amounts. Oxygen does not take part in this reaction also.[9]

The experiments reported above can be explained if it is assumed that in the presence of AcOH V reacts with phenylhydrazine, leading to aniline, NH_3, and IV. In the absence of phenylhydrazine, a part of V decomposes to phenylhydrazine and I (this reaction can be explained as the reverse of a 1, 4 addition of phenylhydrazine to the phenylazoalkene). The phenylhydrazine thus formed reacts with V leading to the formation of the osazone.

The presence of acetic acid seems to be a critical factor in the formation of this osazone. The reaction of I with excess phenylhydrazine leads to the formation of V, which on standing is not transformed into IV. If AcOH is added to the reaction mixture, however, the osazone is promptly formed. If II or III is used as the starting material for the reaction, the osazone is formed; it should be noted that in both cases 1 mole of AcOH is formed during the conversion of II into I.

The isolation of I, II, IV, and V from the reaction between α-acetoxycyclohexanone and phenylhydrazine, the thin-layer chromatographic examination of the variation with time of the relative amounts of these compounds in the reaction mixture, the significant yields obtained in the conversion of II into I, of I into V, and of V into IV, the thin-layer chromatographic examination of the relative rates of the conversions of I into V and then into IV, and of V into IV under equivalent conditions, allow us to conclude that the formation of osazones from α-acetoxy ketones and phenylhydrazine takes place according to the sequence presented in Figure 2.

Work is in progress to elucidate the mechanism of the conversion of V into IV.

Acknowledgment. We are indebted to Dr. R. Mondelli for the interpretation of the nmr spectrum, and to Dr. G. Valentini for the analytical determinations.

L. Caglioti, G. Rosini, F. Rossi
Istituto di Chimica Organica della Università di Camerino
Camerino, Italy

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[9] During the transformation of V into IV oxygen is not absorbed from the atmosphere. A certain quantity of oxygen is absorbed if IV is present in the solution; at the same time, IV is transformed into its degradation products.

A Rhenium-to-Rhenium Triple Bond

Sir:

Recent studies of polynuclear (metal atom cluster type) complexes of rhenium(III) have led to the discovery and description of a Re(III)–Re(III) quadruple bond.[1–3] This bond, which occurs in the $Re_2X_8^{2-}$ (X = Cl, Br, SCN) species and also in the $XRe(O_2CR)_4ReX$ molecules,[4,5] is composed of a σ bond, two orthogonal π bonds, and a δ bond.[3,7] It is the latter, whose strength in $Re_2Cl_8^{2-}$ is estimated at ≤50 kcal/mole (about ≤14% of the total Re–Re bond energy), which restricts the $Re_2X_8^{2-}$ species to their remarkable eclipsed rotomeric configuration.[8] The Re–Re quadruple bond has a length of 2.25 ± 0.01 A.[2,8–10] This may be compared to the lengths of the Re–Re bonds in various Re_3X_9 species, where the bond order[13,14] is 2, which are, on the average, 2.48 A.[15–20]

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(1) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(2) F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

(3) F. A. Cotton, *ibid.*, **4**, 334 (1965).

(4) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

(5) W. R. Robinson, unpublished studies in which a structure identical with that[6] of $Mo_2(O_2CCH_3)_4$, except for the addition of coordinated chloride ions at each end along the fourfold molecular axis, has been proved for $Re_2(O_2CC_6H_5)_4Cl_2$. The Re–Re distance is ~2.21 A, but this is subject to slight change upon further refinement.

(6) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

(7) C. B. Harris, Ph.D. Thesis, Massachusetts Institute of Technology, 1966, has carried out a semiquantitative extended Hückel calculation from which the numerical estimate of bond strength is derived.

(8) This configuration has been found for the $Re_2Cl_8^{2-}$ ion also in the pyridinium[9] and collidinium[10] (2,4,6-trimethylpyridinium) salts, in the $Re_2Br_8^{2-}$ ion,[11] and in the $Tc_2Cl_8^{3-}$ ion.[12]

(9) V. G. Kuznetzov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1963). However, further refinement[10] of the structure using the published F_{obsd} values leads to slight changes in bond distances, bringing Re–Re to 2.25 ± 0.01 A.

(10) Unpublished work of W. R. Robinson.

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(20) M. Elder and B. R. Penfold, *Nature*, **205**, 276 (1965).