

quite different from that of II. At  $-35^\circ$ , there is no significant change in the spectrum, but at higher temperatures the characteristic spectrum of II appears. These changes can also be monitored by hydrolysis experiments. A solution of IV in  $\text{SbF}_5\text{-SO}_2$  kept below  $-50^\circ$  gave upon hydrolysis a single alcoholic product, identified as *endo*-trimethylene-5-*exo*-norbornanol (XI).<sup>8,11</sup> Hydrolysis of a solution of IV in  $\text{SbF}_5\text{-SO}_2$  which had been allowed to warm to  $-10^\circ$  analyzed for 45% 1-adamantanol (III), 35% XI, and four minor products by gas chromatography. When a solution of IV in  $\text{SbF}_5\text{-SO}_2$  had warmed to room temperature, hydrolysis gave 96% 1-adamantanol (III) and 4% of a single second component. Sublimation of the hydrolysate gave essentially pure 1-adamantanol (III), identical in all respects with authentic material.

The rearrangement of 2-*exo*-chloro-*exo*-trimethylene-norbornane (IV) to the 1-adamantyl cation (II) is particularly noteworthy. Heretofore, rearrangements of tricyclic precursors to adamantane and its homologs<sup>2,12</sup> have been confined to hydrocarbons and catalyzed by strong Lewis acids. It has been argued that such systems should be uniquely effective in permitting extremely complex and drastic rearrangements, since carbonium ions can be generated intermolecularly, reversibly, and repeatedly at numerous sites on a molecular framework.<sup>2,12</sup> With compounds such as IV, the site of carbonium ion formation is predetermined, and rearrangements must necessarily proceed by a sequential, intramolecular process which ordinarily limits the rearrangement potential of a given system. The unusual stabilizing effect of  $\text{SbF}_5$  on carbonium ions<sup>3</sup> overcomes this difficulty, and rearrangements as complex as any observed under the most favorable of chemical circumstances are possible. In  $\text{SbF}_5$ , carbonium ions with the greatest over-all stability tend to form, *i.e.*, the most stable carbonium ion *per se*, in a structure with the most stable carbon skeleton. The bridgehead 1-adamantyl cation (II) is not the most stable tricyclic  $\text{C}_{10}\text{H}_{15}$  cation *per se*, but it is present in an extremely stable ring system, and the over-all strain or instability of II is at a minimum.

Unlike sulfuric acid systems, which seem to favor ring opening with formation of stable, allylic cations,<sup>5,7</sup>  $\text{SbF}_5$  preserves the number of rings in the precursor, and side reactions are unimportant.<sup>3</sup> The present results imply that preparative conditions may be found for the conversion of IV or similar compounds into adamantane derivatives in high yields.

**Acknowledgments.**—We wish to thank the Alfred P. Sloan Foundation and the Petroleum Research Foundation for support of this research at Princeton University.

(11) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); D. L. Heywood, B. Phillips, and H. A. Stansbury, Jr., *J. Org. Chem.*, **26**, 281 (1961).

(12) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); P. von R. Schleyer and R. D. Nicholas, *Tetrahedron Letters*, **No. 9**, 305 (1961).

(13) Alfred P. Sloan Research Fellow, 1962–1966.

(14) National Science Foundation Predoctoral Fellow, 1963–1964.

FRICK CHEMICAL LABORATORY  
PRINCETON UNIVERSITY  
PRINCETON, NEW JERSEY 08540  
THE DOW CHEMICAL COMPANY  
EASTERN RESEARCH LABORATORY  
FRAMINGHAM, MASSACHUSETTS 01702

PAUL VON R. SCHLEYER<sup>13</sup>  
RAYMOND C. FORT, JR.<sup>14</sup>  
WILLIAM E. WATTS  
MELVIN B. COMISAROW  
GEORGE A. OLAH

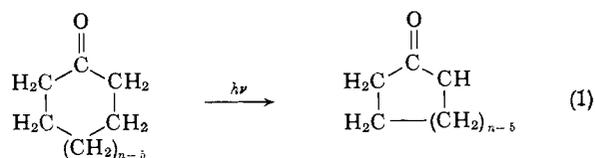
RECEIVED JULY 23, 1964

## A Novel Photoisomerization Reaction of Cyclic Ketones

Sir:

The photochemistry of the cyclic ketones in the liquid phase has not been systematically studied.<sup>1</sup> For two reasons it can be expected that such a study would prove interesting: (i) the reactions of the cyclic ketones in the gas phase (mainly decarbonylation) are subject to pressure quenching<sup>2</sup> so that in the condensed phase these reactions may be superseded by other processes; (ii) the study of light emission from cyclopentanone<sup>3</sup> in the condensed phase shows the presence of a triplet state which is not observed in the gas-phase photochemistry.

In the course of a systematic study of the photolysis of 5-, 6-, 7-, and 8-membered cyclic ketones as pure liquids, a new photoisomerization reaction has been discovered which is interesting both in its complexity and the nature of the excited state from which it originates. The reaction which can be represented by the general equation (1) has been observed when  $n = 6, 7,$



and 8 and in 3-methylcyclohexanone. In cyclooctanone, a variant of this reaction gives 2-propylcyclopentanone as well. 3-Methylcyclohexanone gives mostly, if not entirely, 2,4-dimethylcyclopentanone. In all cases the chief product is a condensed material, while isomeric aldehydes are formed in about the same yield as the ring contracted product.

In cyclohexanone reaction 1, which gives rise to 2-methylcyclopentanone, accounts for 6% of the ketone that is photolyzed. In Fig. 1 the yields of 5-hexenal

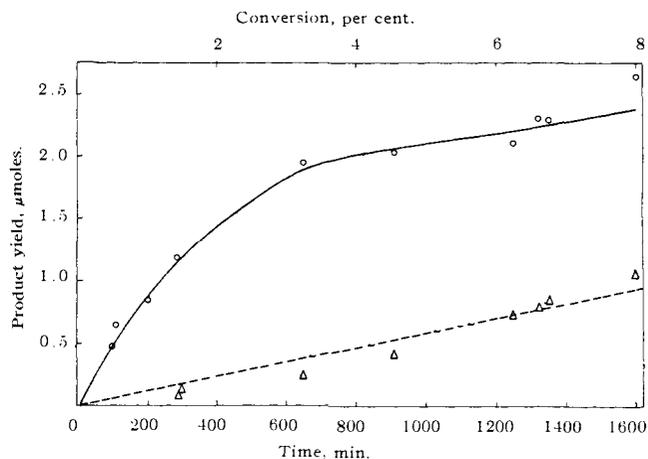


Fig. 1.—Product yields in photolysis of cyclohexanone at 3130 Å. as a pure liquid: open circles, 5-hexenal; open triangles, 2-methylcyclopentanone. Conversion refers to cyclohexanone that had been photolyzed.

and 2-methylcyclopentanone have been plotted as functions of time and per cent conversion. The leveling off in the yield of 5-hexenal may be due to a quenching action by this product on excited cyclohexanone. If

(1) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4344, 4348 (1961).

(3) S. R. La Paglia and B. C. Roquette, *Can. J. Chem.*, **41**, 287 (1963); *J. Phys. Chem.*, **66**, 1739 (1962).

so, the formation of 2-methylcyclopentanone seems to be free from this effect. In solutions of cyclohexanone in cyclohexane, at 3130 Å., the quantum yields for both photoisomers decrease with decreasing concentration. The absolute value for 2-methylcyclopentanone from pure cyclohexanone is of the order of 0.03.

Two aspects of reaction 1 are of considerable interest. One is the mechanism by which the net transfer of a hydrogen atom from the 3 to 2 position or *vice versa* takes place. It seems likely that the process is intramolecular in nature and does not involve long-lived free-radical intermediates, as the addition of about 10% of cyclohexene to a 50% solution of cyclohexanone in cyclohexane caused no change in the rate of formation of 2-methylcyclopentanone. In order to determine whether it is the carbon atom that is  $\alpha$  or  $\beta$  to the carbonyl group that appears in the methyl group in the product, the photolysis of cyclohexanone-2,2,6,6- $d_4$  is being investigated.

A second interesting point is the identity of the excited state which gives rise to reaction 1. Since the formation of 5-hexenal is capable of being quenched (by itself) while the formation of 2-methylcyclopentanone is not, it seems reasonable to suggest that these two reactions occur from two different electronic states of cyclohexanone. The failure to observe reaction 1 in the gas phase is not contrary to this suggestion as this reaction might easily have gone unobserved if its quantum yield in the vapor phase is as small as it is in the liquid. A more direct approach based on the emission of radiation to identify the excited states in the condensed phase is also under investigation.

**Acknowledgment.**—The authors are grateful to Drs. E. B. Whipple, R. L. Hinman, and D. Arnold of the Union Carbide Research Institute for the determination of the n.m.r. spectra.

IBM WATSON RESEARCH CENTER  
YORKTOWN HEIGHTS, NEW YORK

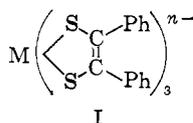
S. CREMER  
R. SRINIVASAN

RECEIVED AUGUST 6, 1964

**Tris(*cis*-1,2-stilbenedithiolato)vanadium(VI) or  
Tris(dithiobenzil)vanadium(0).  
A Novel Vanadium Complex<sup>1</sup>**

Sir:

We report here the characterization of a remarkable new vanadium complex, which is one member of a series of six-coordinate complexes with the general formula I with  $n = 0, 1, \text{ or } 2$ , and  $M = V, Cr, Mo, \text{ or } W$ .



$W$ .<sup>2</sup> Analytical and solution molecular weight data establish the correctness of I for the  $n = 0$  complexes.<sup>3</sup>

(1) Acknowledgment is made to the National Science Foundation for support of this research.

(2) R. B. King, *Inorg. Chem.*, **2**, 641 (1963), has reported the related complexes  $Mo[S_2C_2(CF_3)_2]_3$  and  $W[S_2C_2(CF_3)_2]_3$ .

(3) The  $n = 0$  complexes of V, Cr, Mo, and W were previously formulated as  $M(S_2C_2Ph)_3$  on the basis of analytical results that were found to be in error [G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964)]. *Anal. Calcd.* (found): for  $C_{12}H_{10}S_6V$ : C, 64.82 (64.79); H, 3.89 (3.87); S, 24.73 (24.34). For  $C_{12}H_{10}S_6Cr$ : H, 3.89 (4.03); S, 24.69 (24.64). For  $C_{12}H_{10}S_6Mo$ : C, 61.28 (61.04); H, 3.68 (3.76); S, 23.38 (23.2); mol. wt., 823.1 (763). For  $C_{12}H_{10}S_6W$ : C, 55.36 (55.58); H, 3.33 (3.43). In addition, the complexes with  $M = Re, Ru, \text{ and } Os$  appear to be tris and not bis as previously reported.

Reduction of the  $n = 0$  complexes ( $M = Cr, Mo, \text{ or } W$ ) with  $NaBH_4$  in diglyme gives the  $n = 1$  complexes, which are reoxidized by air to the neutral materials. For  $M = Mo$ , two reversible polarographic waves are observed in DMF.

The odd-electron (I) systems have  $S = 1/2$  and show characteristic e.s.r. spectra. The  $V(S_2C_2Ph)_3$  complex shows an eight-line e.s.r. spectrum in  $CHCl_3$  solution, with  $\langle g \rangle = 1.992$ . The substantial isotropic hyperfine splitting of  $61.6 \pm 0.3$  gauss due to  $^{51}V$  ( $I = 7/2$ ) strongly suggests that the unpaired electron is in a metal-based molecular orbital.<sup>4</sup> For comparison, the  $M(S_2C_2Ph)_3^-$  complexes ( $M = Cr, Mo, \text{ or } W$ ), in which the unpaired electron is in the next higher MO, show characteristic  $\langle g \rangle$  values and electron-nucleus hyperfine splittings as follows:  $M = Cr$ ,  $\langle g \rangle = 1.996$ ,  $\langle a \rangle(^{53}Cr) = 19.0 \pm 0.5$  gauss;  $M = Mo$ ,  $\langle g \rangle = 2.011$ ,  $\langle a \rangle(^{95,97}Mo) = 11.2 \pm 0.4$  gauss;  $M = W$ ,  $\langle g \rangle = 1.992$ . The relative metal/ligand character of the two MO's in question is suggested by the normalized isotropic hyperfine splittings in the V ( $n = 0$ ) and Cr ( $n = 1$ ) complexes. The normalized splittings of 42 gauss/nm. for  $V(S_2C_2Ph)_3$  and 60 gauss/nm. for  $Cr(S_2C_2Ph)_3^-$  indicate that the higher MO has somewhat more metal character in the first-row complexes.<sup>5</sup>

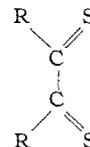
The  $V(S_2C_2Ph)_3$  complex has special significance in the problem of formulation of the ground states of bis and tris complexes containing bidentate, unsaturated sulfur-donor ligands.<sup>6</sup> The stability of  $V(S_2C_2Ph)_3$  makes it clear that the oxidation-state formalism which requires  $R_2C_2S_2^{2-}$  and high-oxidation-state metals cannot be applied consistently to these complexes, since the formalism in the V ( $n = 0$ ) case would call for V(VI).<sup>7</sup> It would be unreasonable to suggest that the metal is effectively  $3p^5$  in this complex. Further,  $V(S_2C_2Ph)_3^{7a}$  cannot be the first example of a complex of this type in which the ligand is oxidized,

(4) The unpaired electron, although "metal-based," is almost certainly delocalized through the ligand system, since the  $^{51}V$  splitting is considerably less than in  $VO(H_2O)_5^{2+}$  [ $\langle a \rangle(^{51}V) = 118$  gauss; R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960)]. In fact, the  $^{51}V$  splitting in  $V(S_2C_2Ph)_3$  compares favorably with the splitting in  $V(CN)_6^{4-}$  [ $\langle a \rangle(^{51}V) = 60$  gauss; J. M. Baker and B. Bleaney, *Proc. Phys. Soc.*, **A66**, 952 (1952)], where some delocalization through the CN<sup>-</sup> system is expected.

(5) The  $^{53}Cr$  splitting in  $Cr(S_2C_2Ph)_3^-$  is larger than the splitting in  $Cr(CN)_6^{3-}$  observed in  $K_3[Co(CN)_6]$ . For  $Cr(CN)_6^{3-}$ ,  $\langle a \rangle(^{53}Cr) = 15.8$  gauss [K. D. Bowers, *ibid.*, **A65**, 860 (1952)].

(6) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, in press.

(7) The conventional oxidation-state formalism allows two limiting descriptions of complexes of such ligands. In the first, the metal is assigned a high oxidation state and is considered to be bonded to the ligand  $R_2C_2S_2^{2-}$ . In the second, the metal is assigned a low oxidation state, and the ligand is represented as  $R_2C_2S_2$ .



It is clear that for  $R = Ph$  (and presumably for other R's as well), neither limiting formulation satisfactorily describes the full range of bis and tris complexes of the ligand. The first formalism requires V(VI) in  $V(S_2C_2Ph)_3$ , while the second requires M(-1) and M(-2) in the anionic complexes, which is not appealing in any case and is certainly unreasonable in the bis complexes with  $M = Ni$ . It should also be noted that the  $R_2C_2S_2$  formulation requires Ni(0) in  $Ni(S_2C_2Ph)_2$ , in which case we would expect a tetrahedral  $NiS_4$  arrangement. However, there is evidence that the complex is planar [G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962)]. Structural work now in progress [M. R. Truter] should decide the issue.

(7a) NOTE ADDED IN PROOF.—The  $V(S_2C_2Ph)_3$  complex has independently been characterized by A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki; private communication from Dr. R. H. Holm.