

TABLE I  
THE INFLUENCE OF IODINE ON THE YIELDS OF CARBON  
DIOXIDE

Solvent <sup>a</sup>	Ac <sub>2</sub> O <sub>2</sub> , <sup>b</sup> mole l. <sup>-1</sup>	I <sub>2</sub> , mole l. <sup>-1</sup>	H <sub>2</sub> O, ml.	CO <sub>2</sub> , <sup>c</sup> %	Time, <sup>d</sup> hr.	Temp., °C.
Cyclohexene	0.056			57.7	45	80
Cyclohexene	.056			60.0	37	80
Cyclohexene	.050			65.4	40	80
Cyclohexene	.051	0.208	12	31.4	45	75
Cyclohexene	.056	.198	10	22.8	45	75
Cyclohexene	.056	.198	10	25.0	37	75
Cyclohexene	.050	.176	12	23.8	40	73
CCl <sub>4</sub>	.051			100.0 <sup>f</sup>	49	75
CCl <sub>4</sub>	.040			80.8	51	75
CCl <sub>4</sub>	.042			87.5	69	71
CCl <sub>4</sub>	.039			84.3	54	73
CCl <sub>4</sub>	.039			82.7	54	73
CCl <sub>4</sub>	.043			79.9	53	74
CCl <sub>4</sub>	.050	.190	10	25.3	43	67
CCl <sub>4</sub>	.040	.160	10	33.2	61	68
CCl <sub>4</sub>	.051	.143	12	28.4	49	69
CCl <sub>4</sub>	.040	.142	12	37.7	51	69
CCl <sub>4</sub>	.042	.042	7	54.4	69	70
CCl <sub>4</sub>	.043	.045	10	52.9	53	70

<sup>a</sup> 300–400 ml. <sup>b</sup> Prepared as the solid, dissolved in the solvent and titrated by the method of Wagner, Smith and Peters.<sup>7</sup> <sup>c</sup> The carbon dioxide was swept out of the apparatus by a slow stream of carbon dioxide-free nitrogen, through an ice trap, a Dry Ice trap, concentrated sulfuric acid, magnesium perchlorate and absorbed on Ascarite. <sup>d</sup> The time during which the solution boiled gently and the time of last weighing of Ascarite tube; the Ascarite tube was weighed periodically and weighing was discontinued when the carbon dioxide evolution had appeared to cease. <sup>e</sup> Temperature of solution. <sup>f</sup> We cannot account for this result.

vided data from the decomposition of O<sup>18</sup>-labeled acetyl peroxide in cyclohexene, which led them to rule out the possibility that the acetoxy radical is exclusively responsible for cyclohexyl acetate formation. Martin and Drew<sup>3</sup> prefer a molecular collision mechanism. They note, however, that their evidence does not rule out the possibility that the Shine and Slagle<sup>1</sup> mechanism may be operating simultaneously with their own, but they quote the earlier works<sup>2,4</sup> as making it seem unlikely that cyclohexene would trap acetoxy radicals before they decompose to methyl radicals and carbon dioxide.

While we are not able to comment at length at this stage on Martin and Drew's work it is necessary for us to point out that one of the corroborating pieces of evidence, the single experiment of Walling and Hodgdon, may lead to the wrong inference about the effect of iodine and water on the decomposition of acetyl peroxide.

For some time now we have been using Hammond's technique<sup>5</sup> with solutions of acetyl peroxide. Our results with cyclohexene were so consistently in accord with an acetoxy radical intermediate that we felt obliged to investigate carbon tetrachloride solutions, too. Our data, given in Table I, show that there is a very marked drop in carbon dioxide in the presence of iodine and water, in both the cyclohexene and carbon tetrachloride solutions. It is apparent that the amount of carbon dioxide liberated in the presence of iodine depends on the relative concentration of the iodine. The data point up the known difference between acetyl peroxide and benzoyl peroxide, since in the latter case an equimolar concentration of iodine will give a nearly quantitative yield of benzoic acid.<sup>5</sup>

(7) C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

In spite of this difference, it is evident that iodine affects the acetyl peroxide decomposition markedly. In connection with the result of Walling and Hodgdon there is a small error in their calculations which, when corrected, shows that the yield of carbon dioxide obtained by them in the presence of approximately equimolar iodine was not almost quantitative but was 83%. Our data show that in carbon tetrachloride alone acetyl peroxide decomposes to give between 80–100% of the theoretical carbon dioxide. Induced decomposition in this system has been demonstrated by Edwards and Mayo<sup>8</sup> and by Ross and Fineman.<sup>9</sup> The former isolated 16% of methyl acetate from 0.1 M solutions at 76°.

Thus, it is faulty to use<sup>6</sup> the experiment of Walling and Hodgdon to show "completely negative results" in attempts at trapping acetoxy radicals, and the ruling out<sup>6</sup> of acetoxy radicals in solution reactions is, at this stage, precipitate.

At a later date we shall submit in full our work on this and similar systems, and also our kinetic data for decompositions in solution.

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(8) F. G. Edwards and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1265 (1950).

(9) S. D. Ross and M. A. Fineman, *ibid.*, **73**, 2176 (1951).

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# LITHIUM-AMMONIA REDUCTION OF $\alpha,\beta$ -UNSATURATED KETONES. II. FORMATION AND ALKYLATION OF A $\beta$ -CARBANION INTERMEDIATE

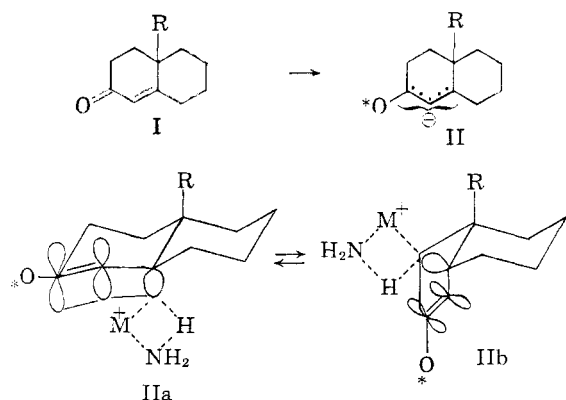
Sir:

In order to explain the stereochemical results obtained in the reduction of  $\alpha,\beta$ -unsaturated ketones such as I with lithium in ammonia solution we suggested<sup>1</sup> recently that an intermediate  $\beta$ -carbanion (*cf.* II) is involved in which only those conformations are permitted which allow continual overlap of the developing p-orbital on carbon with the p-orbitals of the enol double bond. Of the three possible conformations for the protonation transition state this requirement is only met by IIa and IIb (the oxygen atom marked with a star is either  $\cdot\text{O}$  or  $\text{M}^+ - \text{O}$  depending on whether  $\beta$ -protonation takes place after addition of one or two electrons) and the actual product obtained is that corresponding to that one of the two permitted conformations with the lowest energy (a *trans* decalone in this particular situation).

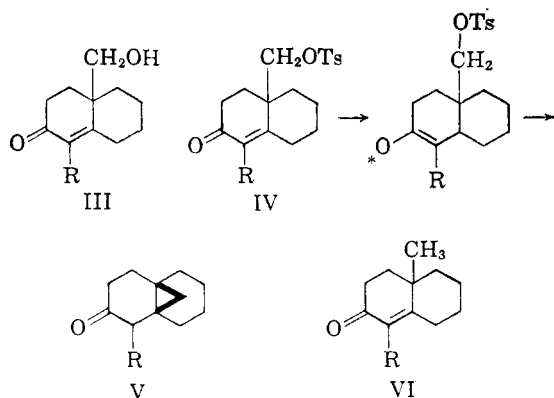
Implicit in this mechanistic picture are several assumptions: (a) the  $\beta$  carbon actually acquires carbanion character without the necessary concerted addition of a proton from ammonia; (b) the  $\beta$ -carbanion can be neutralized (for instance by a proton from ammonia) from either direction, *i.e.*, transition states of conformation related to IIa and IIb must be in equilibrium.

We now have obtained evidence which strikingly confirms both assumptions: The unsaturated keto tosylate IV, R = H, was prepared by the reaction

(1) G. Stork and S. D. Darling, *J. Am. Chem. Soc.*, **82**, 1512 (1960).



of 10-hydroxymethyl- $\Delta^{1,9}$ -2-octalone-2-dioxolane<sup>2</sup> (III, R = H), with toluenesulfonyl chloride in pyridine followed by deketalization with methanolic hydrochloric acid on the steam-bath for fifteen minutes. The tosylate IV thus obtained had m.p. 102–104° after recrystallization from hexane–ethyl acetate (calcd. for  $C_{15}H_{22}O_4S$ : C, 64.65; H, 6.63. Found: C, 64.67; H, 6.80). Addition of lithium to a solution of IV in tetrahydrofuran and dry liquid ammonia, then addition of ammonium chloride and isolation, gave a 45% yield of V, R = H, b.p. (bath) 75–78° (0.4 mm.). This gave, under mild conditions, the corresponding orange 2,4-dinitrophenylhydrazone, m.p. 155–157°;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  366 m $\mu$ ,  $\epsilon$  20,400. (Calcd. for  $C_{17}H_{20}N_4O_4$ : C, 59.29; H, 5.85. Found: C, 58.91; H, 5.74.) The structure of V follows from its infrared spectrum which shows a saturated carbonyl group,



from the n.m.r. spectrum which shows the expected proton resonance at  $\tau \cong 9.7$  and by the acid catalyzed rearrangement of V on heating with aqueous acetic acid containing sulfuric acid. The rearrangement converted V completely into an  $\alpha,\beta$ -unsaturated ketone, as shown by infrared spectra, and the product was identified as 10-methyl- $\Delta^{1,9}$ -octalone (VI, R = H) by mixed melting point of its 2,4-dinitrophenylhydrazone, m.p. 168–169°, with a sample made from authentic material (reported<sup>3</sup> m.p. 169°).

In a similar fashion the tosylate of IV (R =  $\text{CH}_3$ )<sup>4</sup> m.p. 81–82° (calcd. for  $C_{19}H_{24}O_4S$ : C, 65.50;

H, 6.94. Found: C, 65.33; H, 6.88) was reduced with lithium in anhydrous ammonia to give around 50% of V, R =  $\text{CH}_3$  identified as its 2,4-dinitrophenylhydrazone, m.p. 125–127°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  363 m $\mu$ ,  $\epsilon$  23,100 (calcd. for  $C_{18}H_{22}O_4N_4$ : C, 60.32; H, 6.19; N, 15.63. Found: C, 60.70; H, 6.31; N, 15.58). The structure of V, R =  $\text{CH}_3$ , was confirmed as before by its n.m.r. spectrum which showed again the presence of the cyclopropane hydrogens in addition to the split methyl peak. Rearrangement of V, R =  $\text{CH}_3$ , with acid as above transformed it into the expected 1,10-dimethyl- $\Delta^{1,9}$ -2-octalone (VI, R =  $\text{CH}_3$ ) identified as its 2,4-dinitrophenylhydrazone, m.p. 199–200° undepressed by an authentic specimen.<sup>5</sup>

(5) F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952).

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# CARBONYL AND HYDRIDO-CARBONYL COMPLEXES OF IRIUM BY REACTION WITH ALCOHOLS. HYDRIDO COMPLEXES BY REACTION WITH ACID Sir:

Evidence has been presented recently<sup>1</sup> that iridium halides react with triphenylphosphine (or related ligands) in alcohols to yield hydrido complexes,  $[\text{IrHX}_2\text{L}_3]$ , and, at higher temperatures,  $[\text{IrH}_2\text{XL}_3]$ , rather than simple adducts which might be expected from these environments. We now find that on further treatment of these reaction mixtures the interaction with the solvent proceeds to give hydrido-carbonyl and carbonyl complexes, the subjects of the present communication. The new types of iridium compounds (see Table I) are diamagnetic, non-electrolytes and stable in air.

TABLE I

Compound	Color	M.p., °C. (dec. in vac.)	Infrared spectrum (cm. <sup>-1</sup> ) <sup>a</sup> $\nu_{\text{Ir-H}}$ $\nu_{\text{C=O}}$
$[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$	Lemon yellow	323–325	... 1944
$[\text{IrBr}(\text{CO})(\text{Ph}_3\text{P})_2]$	Yellow	318–320	... 1947
$[\text{IrHCl}_2(\text{CO})(\text{Ph}_3\text{P})_2]$	White	315–320	2245 <sup>b</sup> 2030
$[\text{IrHBr}_2(\text{CO})(\text{Ph}_3\text{P})_2]$	Light yellow	348–351	2230 2030
$[\text{IrHCl}_2(\text{CO})(\text{Ph}_3\text{As})_2]$	Light yellow	249–252 <sup>c</sup>	2200 2020

<sup>a</sup>  $\pm 5$  cm.<sup>-1</sup>, halocarbon mull. <sup>b</sup> Deuteride, 1603 cm.<sup>-1</sup>;  $\nu_{\text{Ir-H}}/\nu_{\text{D-H}} = 1.40$ ; calcd., 1.41. <sup>c</sup> In air.

$[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$  has been synthesized from  $\text{IrCl}_3 \cdot (\text{H}_2\text{O})_x$  or  $(\text{NH}_4)_2\text{IrCl}_6$ , triphenylphosphine (10–20 moles) and these alcohols (temperature, time and yield refer to best results): aqueous 2-( $\beta$ -methoxyethoxy)-ethanol, 190°, 2 hr., 86%; ethylene glycol, 190°, 7 hr., 75%; diethylene glycol, 240°, 2 hr., 76%; triethylene glycol, 270°, 4 hr., 83%. (Anal. Calcd. for  $\text{IrClP}_2\text{C}_{37}\text{H}_{30}\text{O}$ : Ir, 24.6; Cl, 4.5; P, 7.9; C, 57.0; H, 3.9; O, 2.05. Found: Ir, 25.0; Cl, 4.1; P, 8.2; C, 57.6; H, 4.1; O, 2.2.) Preliminary studies of the mechanism of this peculiar reaction indicate that hydrogen is liberated as one of the by-products. The compound has been obtained also, although in low yield, by treating the reactants with aqueous *butanal* at 70° for 2 hr.

The presence of a coordinated CO is shown by the characteristic strong absorption in the infrared spectrum. Carbon monoxide is given off on pyro-

(1) L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961).

(2) L. S. Minckler, A. S. Hussey and R. H. Baker, *J. Am. Chem. Soc.*, **78**, 1009 (1956).

(3) E. C. duFeu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).

(4) J. Tsuji, Ph.D. Thesis, Columbia University, 1960.