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OXIDATION OF UNSATURATED TERTIARY AMINES, AMIDES, AND IMIDES BY MOLECULAR OXYGEN CATALYZED BY PALLADIUM COMPLEXES

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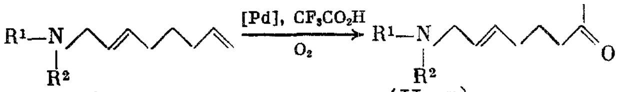
547.333.3

The oxidation of olefins by molecular oxygen in the presence of palladium salts has potential as a route for the synthesis of ketones of various structures [1-5]. On the other hand, there is very little information in the literature on the application of this method to the conversion of unsaturated tertiary amines, amides, and imides into the corresponding carbonyl compounds. This is evidently connected with the fact that amines, added to a $PdCl_2$–CuCl catalyst composition, completely block the oxidation of olefins by molecular O_2 on account of the formation of coordination-saturated complexes of Pd and Cu which are only feebly active in the oxidation of unsaturated compounds.

It might be expected that introduction of protonic acids, capable of bonding with the nitrogen in the initial unsaturated amine, amide, or imide molecule into the palladium catalyst composition would make it possible to oxidize these compounds to the corresponding ketones.

We have established that the presence of a protonic acid in the system, with a ratio amine:acid = 1:3 and amide or imide:acid = 1:1, is a necessary condition for the conversion of the amine, amide, or imide to a ketone. Oxidation by O_2 is carried out in the presence of a $PdCl_2$–CuCl catalyst (Pd:Cu:amine/amide/imide = 1:10:5 to 20) at a temperature of 60-65°C with a reaction time of 6 h in THF as solvent. The highest yields of amino-, amido-, and imidoketones are obtained on oxidation of the unsaturated amine, amide, or imide in the presence of a catalyst and CF_2CO_2H



(Ia-m) (IIa-m)

$R^1 = R^2 = (CH_3)$(a); $R^1 + R^2 = (CH_2)_5$(b); $R^1 + R^2 = (CH_2)_2—O—(CH_2)_2$(c); $R^1 = CH_3$, $R^2 = C_6H_5$(d); $R^1 = COC_6H_5$, $R^2 = C_6H_5$(e); $R^1 = COCH_3$, $R^2 = C_6H_5$(f); $R^1 = COCH_3$, $R^2 = CH_3$(g); $R^1 = COCH_3$, $R^2 = o\text{-}C_6H_4CH_3$(h); $R^1 = COCH_3$, $R^2 = m\text{-}C_6H_4F$(i); $R^1 = COCH_3$, $R^2 = p\text{-}C_6H_4O_2$(j), $R^1 = COH$, $R^2 = H$(k); $R^1 = COH$, $R^2 = C_6H_{13}$(ℓ); $R^1 + R^2 = (COCH_2)_2$(m).

On oxidation of N-methyl-N-(2E,7-octadienyl)aniline (Id), 1,3E-6E-octatriene and methylaniline were formed in addition to (IId), these being the decomposition products of the original amine (Id).

On oxidation of N,N-bis(2E,7-octadienyl) derivatives of methylamine (IIIa) and benzylamine (IIIb), the corresponding mono- and diketones (IVa-c) and (Va-b) were formed:

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TABLE 1. Yields and Properties of Compounds Prepared

Compound	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	Found, %			Empirical formula	Calculated, %			M+
				C	H	N		C	H	N	
(IIa)	89	110(2)	1,4895	71,08	11.18	8.26	$C_{10}H_{19}NO$	71,00	11.24	8.28	169
(IIb)	90	107(2)	1,4849	74,63	11,05	6,64	$C_{13}H_{23}NO$	74.64	11.00	6.69	209
(IIc)	100	121(2)	1,4839	68,22	9,97	6,62	$C_{12}H_{21}NO_2$	68,24	9,95	6,63	211
(IId)	60	150(2)	1,5322	77,91	6,07	9,09	$C_{15}H_{21}NO$	77,92	6,06	9,09	231
(IIe)	78	Chromatographically	1,5649	78,55	7,14	4,32	$C_{21}H_{23}NO_2$	78.50	7,16	4.36	321
(IIf)	100	145(1)	1,5305	74,11	8,13	5,41	$C_{16}H_{21}NO_2$	74,13	8.10	5,40	259
(IIg)	83	115(1)	1,4735	67,08	9,58	7,05	$C_{11}H_{19}NO_2$	67,00	9,64	7,00	197
(IIh)	56	152(1)	1,5253	74,70	8,44	5,15	$C_{17}H_{23}NO_2$	74.72	8,42	5.12	273
(IIi) *	59	159(1)	1,5234	69,25	7,27	5,04	$C_{16}H_{20}NO_2F$	69,31	7,20	5,05	277
(IIj)	60	Chromatographically	1,5721	63,12	6,60	9,18	$C_{16}H_{20}N_2O_4$	63,15	6,57	9.21	304
(IIk)	42	108(1)	1,4881	63,82	8,59	8,27	$C_9H_{15}NO_2$	63.90	8,87	8.28	169
(IIm)	85	148(1)	1,5059	64,52	7,67	6,25	$C_{12}H_{17}NO_3$	64,57	7,62	6.27	223
(IVa)	66	146(1)	1,4771	77,50	11,06	6.35	$C_{17}H_{29}NO$	77.56	11,03	5,32	263
(IVb)	15	Chromatographically	1,4531	81,40	9,71	4,13	$C_{23}H_{33}NO$	81,41	9,73	4.11	339
(IVc)	15	»	1,5514	81,15	9,58	4.37	$C_{22}H_{31}NO$	81.30	9.53	4.30	325
(Va)	34	161(1)	1,4919	73,11	10,37	5,04	$C_{17}H_{29}NO_2$	73,12	10.39	5,01	279
(Vb)	78	Chromatographically	1,5271	77,72	9,32	3,92	$C_{23}H_{33}NO_2$	77,74	9,29	3,94	355
(VIIa)	15	»	1,4810	75,45	10,71	8,82	$C_{20}H_{34}N_2O$	75,47	10,69	8,80	318

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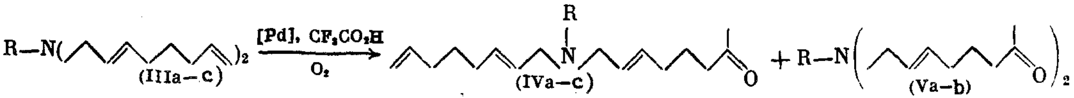
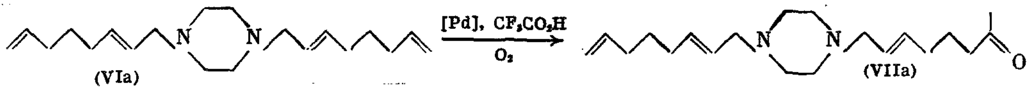
*Found: F 6.85%. Calculated: F 6.82%.



$R = CH_3(a),\ CH_2—C_6H_5(b),\ C_6H_5(c).$

N,N-bis(2E,7-Octadienyl)aniline (IIIc) on oxidation gives only the monoketone (IVc) in 15% yield. N,N'-bis(2E,7-Octadienyl)piperazine (VIa) behaves in a similar way:



EXPERIMENTAL

The initial amines (Ia-d), (IIIa-c), and (IVa), amides (Ie-h, j-l), and imide (Im) were prepared by the methods of [6-8]. Their purity, as determined by GLC, was 99%. GLC analyses were carried out on a Crom-5 chromatograph with flame-ionization detector, 1.2-m column with SE-30, helium carrier gas. Proton NMR spectra were run on a Tesla BS-487B instrument as solutions in CCl_4 with HMDS as internal standard. IR spectra were run on a UR-20 spectrophotometer as thin films or mulls. Mass spectra were recorded on an MX-13-06 instrument with ionization energy 70 eV at 200°C.

Oxidation of Unsaturated Amines, Amides, and Imides. To 85 mmoles of starting material was added 100 ml THF, and CF_3COOH: 26.5 g (255 mmoles) for the amines and 8.8 g (85 mmoles) for amides and imides. The reaction mixture was thoroughly stirred for 3 h at room temperature, or in the case of (Ia, d), (IIIa-c), and (VIa) at 60°C. $PdCl_2$ (1.49 g, 8.5 mmoles) and CuCl (8.36 g, 85 mmoles) were then introduced into the reaction mixture, 5 ml H_2O were poured in and oxygen was bubbled through the mixture at 5 liters/h for 6 h while stirring at 60°C. The reaction mixture was neutralized with $NaHCO_3$, extracted with $CHCl_3$ and the extract was washed with water until the washings were neutral; it was then dried over $MgSO_4$. The solvent was evaporated and the residue distilled in vacuum or chromatographed (silica gel, 40 × 100, 9:1 benzene—methanol eluent). Spectroscopic data for the compounds prepared are given in Table 2 and yields and physicochemical properties in Table 1.

CONCLUSIONS

Oxidation of higher unsaturated tertiary amines, amides, and imides has been carried out using $PdCl_2—CuCl—CF_3COOH$ catalyst system and molecular oxygen, the products being the corresponding amino-, amido-, and imidoketones.

TABLE 2. IR and Proton NMR Spectra of Compounds Prepared

Compound	IR spectra (ν, cm^{-1})				Proton NMR spectra (δ, ppm)							
	$CH=CH_2$	$CH=CH$	$C=O$	aromatic ring	CH_2	$CH_2-C=$	CH_3-CO CH_3-Ph	CH_2-CO	CH_3N	$-N-CH_2-C=$ CH_2-N-Ph	$CH_2=C-$ $CH=CH-$	C_6H_5
(IIa)	–	980, 3030	1720	–	1,55 m	1,91 m	2,01 s	2,21 m	2,35 s	3,08 d	5,56 m	
(IIb)	–	980, 3030	1715	–	1,41 m	1,92 m	2,06 s	2,33 m	–	2,75 d	5,43 m	
(IIc)	–	980, 3030	1715	–	1,51 m	1,83 m	1,95 s	2,26 m	–	2,65 d	5,36 m	
(IId)	–	980, 3030	1715	710, 770, 3010	1,56 m	1,91 m	1,96 s	2,25 m	2,86 s	3,45 m 3,75 d	5,41 m	6,62 m 7,12 m
(IIe)	–	980, 3030	1630, 1710	710, 770	1,51 m	1,82 m	2,0 s	2,16 m	–	2,20 m	5,51 m	7,12 m
(IIf)	–	980, 3030	1660, 1720	710, 770	1,51 m	1,81 m	2,0 s	2,12 m	1,61 s	3,91 d	5,32 m	7,12 m
(IIg)	–	980, 3030	1660, 1710	–	1,53 m	1,81 m	1,96 s	2,30 m	2,03 s 2,75 d	3,75 d	5,40 m	
(IIh)	–	980, 3030	1620, 1710	–	1,51 m	1,81 m	2,00 s 2,21 s	2,36 m	1,66 s	3,81 d	5,41 m	7,22 m
(IIi)	–	980, 3030	1670, 1720	–	1,51 m	1,63 m	2,00 s	2,31 m	1,82 s	3,92 s	5,53 m	7,31 m
(IIj)	–	980, 3030	1670, 1720	–	1,51 m	1,65 m	1,82 s	2,31 m	–	3,95 d	5,49 m	7,55 m
(IIk)	–	980, 3030	1660, 1710	–	1,61 m	1,96 m	2,00 s 2,10 s	2,44 m	–	3,81 d	5,53 m	7,20 s – NH 8,12 m – HCO
(IIm)	–	980, 3030	1715, 1770	–	1,53 m	1,91 m	1,96 s	2,32 m	–	2,53 s 3,86 d	5,36 m	
(IVa)	920	980, 3030	1720 –	–	1,58 m	1,96 m	2,13 s	2,41 m	2,18 s	2,95 d	5,08 m 5,55 m	
(IVb)	920	980, 3030	1715 –	700, 745	1,55 m	1,91 m	2,00 s	2,31 m	–	2,85 d 3,51 s	4,91 m 5,41 m	7,12
(IVc)	920	980, 3030	1715 –	710, 770, 3010	1,55 m	1,83 m	2,00 s	2,25 m	–	3,71 d	4,75 m 5,41 m	6,55 m 6,95 m
(Va)	–	980, 3030	1720 –	–	1,58 m	1,96 m	2,06 s	2,31 m	2,08 s	2,81 d	5,42 m	
(Vb)	–	980, 3030	1715 –	700, 750	1,55 m	1,91 m	2,00 s	2,31 m	–	2,85 d 3,51 s	5,51 m	7,21 m
(VIIa)	920	980, 3030	1715 –	–	1,51 m	1,96 m	2,00 s	2,31 m	2,72 s	3,06 d	4,85 m 5,52 m	

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NEW HYDROCARBONS IN THE SYNTHESIS OF ADAMANTANOIDS

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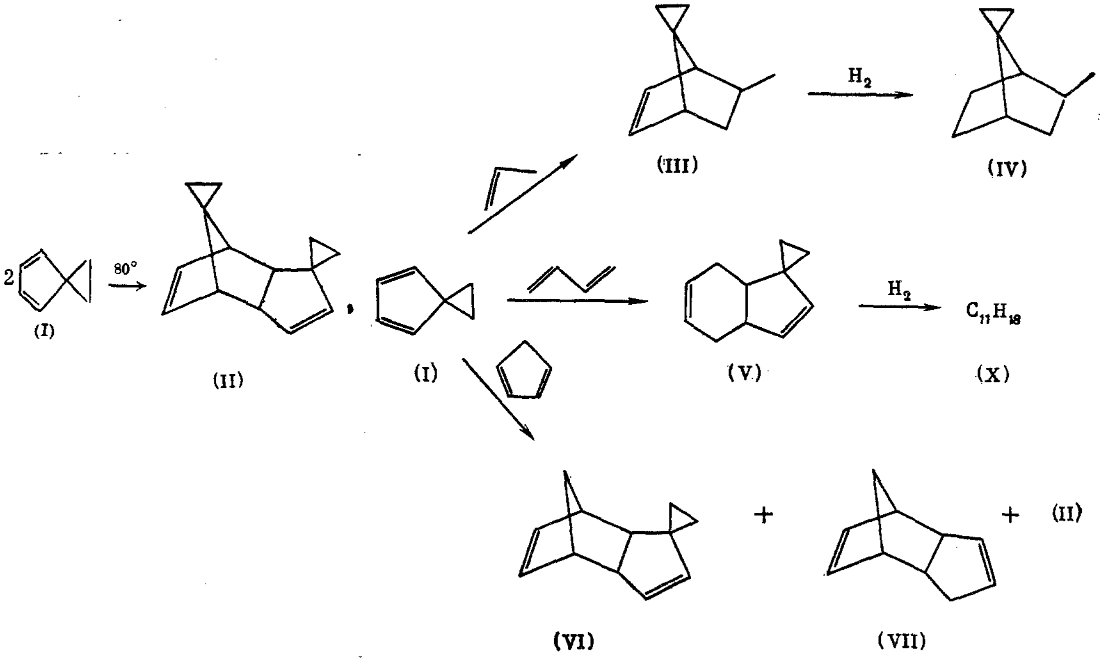
547.315.71:547.518

For obtaining adamantane, diamantane, and their derivatives mainly hydrogenated dimers of cyclopentadiene, norbornadiene, and their derivatives have been used.

In a search for new accessible hydrocarbons capable of being transformed by catalytic skeletal isomerization into adamantane and diamantane, we have investigated thermal and catalytic [2π + 4π]-homo- and codimerization of spiro[2.4]hepta-4,6-diene (I) with propylene, butadiene, and cyclopentadiene.

Considering that thermal dimerization of (I) to dispiro{cyclopropan-5,1'-endotricyclo-$[5.2.1.0^{2,6}]$deka-3,8-dien-10,1''-cyclopropane} (II), which is of interest in the synthesis of cage hydrocarbons, proceeds with very low yields [8], we have tried to carry out a catalytic version of this reaction using Lewis acids. The best results were obtained using the complex $AlCl_3$–dicyclohexyl-18-crown-6 which catalyzes formation of homodimer (II) with yields of 55%.



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