CONCLUSIONS

1. The basic principles governing the cyclocodimerization of norbornene with allyl compounds have been elucidated for their reaction in the presence of a three-component catalyst system, $\mathrm{Ni(acac)_2{-}P(OR)_3{-}AlR'_3}$ (or $\mathrm{MgR''_2}$); a highly selective method has also been developed for the introduction of a methylenecyclobutane fragment to a norbornene hydrocarbon derivative.

2. A new Ni complex has been prepared; it appears to be the catalyst which is active for the cyclocodimerization of norbornene with allylic compounds.

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OXIDATION OF UNSATURATED LINEAR AND CYCLIC HYDROCARBONS BY MOLECULAR OXYGEN CATALYZED BY COMPLEXES OF TRANSITION METALS

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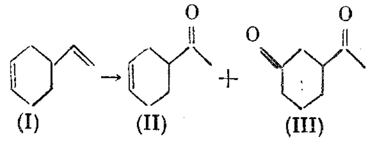
UDC 542.943.7:547.318:547.518

In the continuation of investigations on the oxidation of higher polyunsaturated compounds, and also with the object of developing effective and selective methods of the functionalization of olefins, we studied the oxidation of linear and cyclic hydrocarbons by molecular O_2 catalyzed by the $\mathrm{PdCl_2{-}CuCl}$ system [1]; the hydrocarbons contain one or several double bonds with varying geometry.

Derivatives of cyclohexene, norbornene, norbornadiene (NBD), quadricyclane, 1E,5Z-cyclodecadiene, methylenetricyclane, bismethylenetricyclane, methyldeltacyclene, and 1,5E,9-decatriene were selected as the objects of investigation. The 1:10 system of $\mathrm{PdCl_2{-}CuCl}$ as the solution in THF was utilized as the catalyst; this permitted the adequate ease of separation of the reaction products from the catalyst, and the isolation of the highest yields of the carbonyl compounds.

The oxidation of 4-vinyl-1-cyclohexene (I) with oxygen at 60°C leads to the formation of 4-acetyl-1-cyclohexene (II) and 3-acetylcyclohexanone (III) in the ratio of 96:4 and a total yield of 90%.



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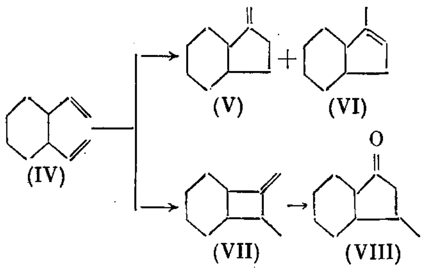
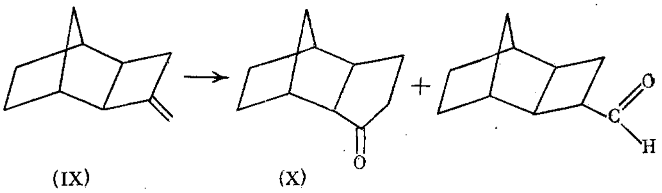
Under analogous conditions, 1,2-cis-divinylcyclohexene (IV) yielded a 60% yield of 3-methylbicyclo$[4.3.0^{2,4}]$octan-1-one (VIII) and a mixture of unsaturated C_{14} hydrocarbons with a system of conjugated double bonds. The latter are the products of the isomerization of the double bonds in 1,2-divinylcyclohexane under the action of the complexes of Pd and Cu.


(IV) (V) (VI) (VII) (VIII)

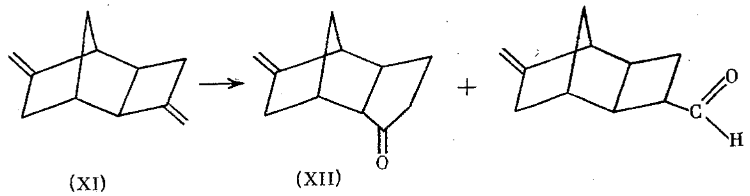
It can be assumed that, in the conditions of the reaction, (IV) is initially converted to the indan derivatives (V) and (VI) or 7-methylene-8-methylbicyclo[4.2.0]octane (VII), the oxidation of which gives (VIII).

The reaction of methylenecyclopentane and 1-methylcyclopentene with O_2 was investigated to test this assumption. It was found that the indicated derivatives of cyclopentane were fully recovered unchanged from the reaction independently of the reaction conditions and the concentration of the catalyst. The formation of insignificant amounts of methylcyclopentene is only observed in the case of methylenecyclopentane. According to [2], methylenecyclobutane is readily oxidized to cyclopentanone under the action of stoichiometric amounts of the $PdCl_2$-CuCl complex as a solution in DMF. The results obtained and the data of [2] permitted the proposition of the intramolecular catalytic dimerization of cis-1,2-divinylcyclohexane to (VII), which is converted to (VIII) in the presence of O_2.

The investigation of the oxidation of tricyclic hydrocarbons containing methylenecyclobutane fragments showed that 3-methylenetricyclo$[4.2.1.0^{2,5}]$nonane (IX), which was obtained according to [3], is readily converted to an 85% yield of tricyclo$[5.2.1.0^{2,6}]$decan-3-one (X).


(IX) (X)

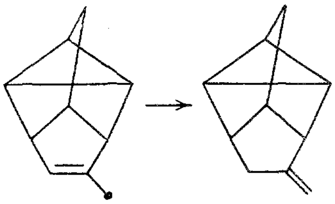
Similarly, O_2 reacts with 3,7-dimethylenetricyclo$[4.2.1.0^{2,5}]$nonane (XI) forming 8-methylenetricyclo$[5.2.1.0^{2,6}]$decan-3-one (XII) with a yield of 50%.


(XI) (XII)

Formyl derivatives (the content in the reaction mixture is $\leqslant 2\%$) are formed together with (X) and (XII).

Therefore, the oxidation of hydrocarbons with methylene-cyclobutane fragments to cyclopentanone derivatives, which is effected by O_2 and is catalyzed by Pd complexes, has a general character and can serve as an effective method for the isolation of cyclopentanones of the given structure.

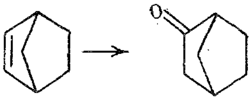
In contrast to the tricyclic olefins referred to, 8-methyltetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$non-8-ene (XIII) [4] is practically entirely converted to the thermodynamically more stable 8-methylenetetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$nonane (XIV) in the conditions of the oxidation.



(XIII) (XIV)

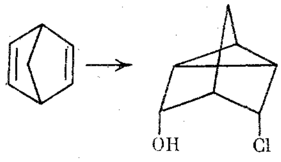
It can be seen that, independently of the structure of the initial olefin, the double bond of the methylcyclopentane ring does not undergo oxidation by O_2; this is also the case for the simple methylcyclopentene.

We also investigated the oxidation of cycloolefins with disubstituted double bonds. Bicyclo[2.2.1]hept-2-ene (XV) gives bicyclo[2.2.1]heptan-2-one (XVI) quantitatively.



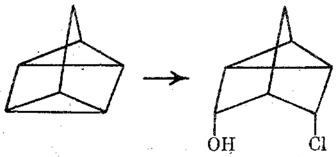
(XV) (XVI)

The oxidation of bicyclo[2.2.1]hepta-2,5-diene (XVII) to 2-hydroxy-6-chlorotricyclo-$[2.2.1.0^{3,5}]$heptane (XVIII) (yield 10–15%) proceeds unusually; the mechanism of the reaction is unclear for the present. Under the conditions selected, a significant part of (XVII) is isolated in the form of stable complexes with Pd and Cu ions which are not active in the oxidation reaction.



(XVII) (XVIII)

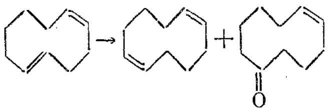
Meanwhile, quadricyclane (XIX), which is a valence isomer of NBD, is very readily and rapidly oxidized to (XVIII) with a yield of 60%.



(XIX) (XVIII)

In contrast to NBD, the oxidation of quadricyclane evidently proceeds in the coordination sphere of Pd, passing the stage of the formation of the free NBD. However, the appearance of NBD in the reaction mixture and the precipitation of a copious residue in the form of complexes with ions of Pd and Cu are observed on the 50% conversion of quadricyclane.

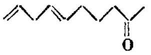
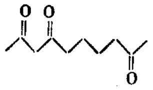
Taking 1E,5Z-cyclodecadiene (XX) as an example, the influence of the geometry of the double bond on its activity in the oxidation, catalyzed by $PdCl_2$-CuCl, was investigated.



(XX) (XXI) (XXII)

Under the conditions described, (XX) gives 1Z,6Z-cyclodecadiene (XXI) and 5Z-cyclodecen-1-one (XXII) quantitatively in the ratio of 3:2. In the absence of O_2, 1E,5Z-cyclo-

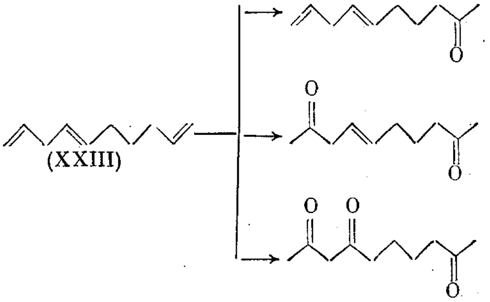
TABLE 1. Oxidation of 1,4E,9-Decatriene Using O_2, H_2O_2, NiO_2, NaOCl, Ag_2O, MnO_2, and $KMnO_4$ in the Presence of the $PdCl_2$–CuCl Catalyst [THF, $PdCl_2$ (0.0085 mole), CuCl (0.085 mole), olefin (0.085 mole), 60°C, 6h]

Oxidant	Molar ratio of oxidant: olefin	Total yield, %	Composition of the reaction products, %		
					
$KMnO_4$	1 : 1	48	100	–	–
NiO_2	1 : 1	54	100	–	–
NaOCl	1 : 1	94	100	–	–
Ag_2O	1 : 1	51	100	–	–
	2 : 1	25	100	–	–
H_2O_2	1 : 1	87	65	35	–
	2 : 1	100	30	70	–
	3 : 1	100	–	30	70
MnO_2	1 : 1	87	70	30	–
	2 : 1	64	100	–	–
	3 : 1	46	100	–	–
	1 : 1	56[a]	100	–	–
	1 : 1	68[b]	100	–	–
	1 : 1	100[c]	35	65	–
O_2	–	55	90	10	–
	–	100[d]	70	30	–
	–	100[e]	3	97	–

[a] Temperature of the reaction is 20°C.
[b] Temperature of the reaction is 40°C.
[c] Duration of the reaction is 7 h.
[d] Duration of the reaction is 12 h.
[e] Duration of the reaction is 18 h.

decadiene is completely converted to (XXI). The results obtained indicate that the Z-isomers are less active than the E-isomer in the oxidation. In fact, all the attempts to oxidize 1Z,6Z-cyclodecadiene were unsuccessful.

We tried to apply the given method for the selective introduction of the CO group into linear hydrocarbons containing several double bonds of varying type.


(XXIII)
(XXIV)
(XXV)
(XXVI)

For example, 6E,9-decadien-2-one (XXIV) is formed exclusively in 55% yield by the reaction of 1,4E,9-decatriene (XXIII) with O_2 for 6 h at 60°C. The increase of the reaction time to 18 h leads to the 3:97 ratio of (XXIV) and 4E-decen-2,9-dione (XXV) in the total yield of 100%. We did not manage to perform the oxidation of the internal disubstituted double bond using O_2. Only the monoketone (XXIV) is formed with high selectivity in the case of the other oxidants ($KMnO_4$, MnO_2, NiO_2, Ag_2O, H_2O_2). The oxidation can only be directed in favor of the preferential formation of the triketone (XXVI) in the case of the application of excess H_2O_2.

EXPERIMENTAL

Linear and cyclic unsaturated hydrocarbons of 99% purity, which were obtained according to the methods of [5-12], were utilized in the work. The products were analyzed on a

TABLE 2. Properties of the Compounds Obtained

Compound	bp, °C (p, mm of Hg stem)	n_D^{20}	Found, %			Empirical formula	Calculated, %		
			C	H	Cl		C	H	Cl
(II)	45(1)	1.4715	77,44	9.65		$C_8H_{12}O$	77.42	9,67	–
(III)	94(1)	1.4759	68.55	8.59		$C_8H_{12}O_2$	68.57	8,57	
(VIII)	55(1)	1,4750	78.91	10.50		$C_{10}H_{16}O$	78,94	10.52	
(X)	78(1)	1.4978	79.92	9.30		$C_{19}H_{14}O$	80,00	9,33	
(XII)	81(1)	1,5189	81,42	8,66		$C_{11}H_{14}O$	81,48	8,64	
(XVI)	55(2)	1.4964	90.90	9,09		$C_{10}H_{12}$	90,50	9.01	
(XVIII), (XX)	70(1)	1,5178	58,30	6.27	24,31	$C_7H_{19}C_{10}$	58,33	6,25	24.30
(XXII)	78(1)	1.4931	78.90	10.55		$C_{10}H_{16}O$	78,94	10,52	
(XXIV)	61(1)	1.4610	78.89	10,48		$C_{10}H_{16}O$	78,94	10.52	
(XXV)	73(1)	1.4635	71.40	9.49		$C_{10}H_{16}O_2$	71,43	9,52	
(XXVI)	mp 51–52°	–	65.21	8.67		$C_{10}H_{16}O_3$	65,21	8.69	

"Khrom-41B' chromatograph with a flame ionization detector, a 1.2 m column with SE-30, and N_2 as the gas carrier. The PMR spectra were obtained on a "Tesla BS-487B" instrument with the solutions in CCl_4 and the internal standard of HMDS. The IR spectra were recorded on a UR-20 spectrophotometer using a film or mineral oil. The mass spectra were recorded on an MX-13-06 instrument with 70 eV as the energy of the ionizing electrons, and 200°C as the temperature of the ionization chamber.

The General Method for the Oxidation of Unsaturated Linear and Cyclic Hydrocarbons by Molecular O_2 in the Presence of Pd Complexes. To 1.5 g of $PdCl_2$ (0.0085 mole) and 8.36 g of CuCl (0.085 mole) in 50 ml of the solvent were added 5 ml of H_2O and 0.085 moles of the unsaturated hydrocarbon. A stream of O_2 was bubbled at the rate of 5 liters/h through the reaction mass, or the required amount of the appropriate oxidant was introduced (Table 1). The mixture was stirred for the required time at 60°C. At the completion of the reaction, the catalyzate was diluted with $CHCl_3$ and washed with 5% HCl (threefold with 100 ml portions) followed by H_2O until the neutral reaction of the washings was obtained. The organic layer was dried with $MgSO_4$. The data of the elemental analysis and the physicochemical constants are presented in Table 2.

4-Acetyl-1-cyclohexene (II). The IR spectrum (ν, cm^{-1}) is as follows: 720 (cis-CH=CH) and 1715 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.5 multiplet (2H, CH_2), 2.01 singlet (3H, $CH_3C=O$), 2.2 multiplet (4H, $CH_2C=$, 1H, CHC=O), and 5.5 multiplet (2H, CH=CH). M^+ 124.

3-Acetylcyclohexanone (III). The IR spectrum (ν, cm^{-1}) is as follows: 1720 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.5 multiplet (4H, CH_2), 2.01 singlet (3H, $CH_3C=O$), 2.1 multiplet (4H, $CH_2C=O$), and 2.6 multiplet (1H, HCC=O). M^+ 140.

3-Methylbicyclo[4.3.0^{2,4}]octan-1-one (VIII). The IR spectrum (ν, cm^{-1}) is as follows: 1730 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.03 doublet (3H, CH_3C, J = 6 Hz), 1.25 multiplet (1H, CH), 1.6 multiplet (8H, CH_2; 1H, CH), 2.0 multiplet (2H, $CH_2C=O$), and 2.4 multiplet (1H, HCC-O). M^+ 152.

Tricyclo[5.2.1.0^{2,6}]decan-3-one (X). The IR spectrum (ν, cm^{-1}) is as follows: 1730 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.08-1.6 multiplet (8H, C^5H_2, C^8H_2, C^9H_2, $C^{10}H_2$), 1.76-2.15 multiplet (3H, C^1H, C^6H, C^7H), and 2.40 multiplet (3H, $>C^2HC=O$, $C^4H_2C=O$). M^+ 150.

8-Methylenetricyclo[2.5.1.0^{2,6}]decan-3-one (XII). The IR spectrum (ν, cm^{-1}) is as follows: 890, 3080 ($>C=CH_2$), and 1735 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.0-1.60 multiplet (4H, C^4H_2, $C^{10}H_2$), 1.70-2.10 multiplet (5H, C^1H, C^7H, C^6H, C^9H_2), 2.45 multiplet (3H, $C^4H_2C=O$, $>C^2HC=O$), and 4.65 multiplet (2H, $C^{11}H_2$). M^+162.

8-Methylenetetracyclo[4.3.0.0^{2,4}0^{3,7}]nonane (XIV). The IR spectrum (ν, cm^{-1}) is as follows: 920 and 3080 ($CH_2=CH$). The PMR spectrum (δ, ppm) is as follows: 0.87-1.22 multiplet (3H, C^2H, C^3H, C^4H), 1.5 (2H, C^5H_2), 1.8 multiplet (1H, C^1H), 2.05 multiplet (1H, C^6H), 2.25 multiplet (2H, C^9H_2), 2.35 multiplet (1H, C^7H), and 4.65 doublet (2H, CH_2—C). M^+ 132.

Bicyclo[2.2.1]heptan-2-one (XVI). The structure was confirmed by comparison with the known compound [13].

2-Hydroxy-6-chlorotricyclo[2.2.1.0^{3,5}]heptane (XVIII). The IR spectrum (ν, cm^{-1}) is as follows: 3400 (OH). The PMR spectrum (δ, ppm) is as follows: 1.30 multiplet (2H, C^4H_2), 1.43 multiplet (2H, C^3H, C^5H), 1.88 multiplet (2H, C^7H_2), 3.4 singlet (1H, C^1H), 3.8 multiplet (1H, $>C^6HCl$), 3.88 multiplet (1H, $>C^2OH$), and 4.5 multiplet (1H, $>C^2H$). M^+ 144.

1Z,6Z-Cyclodecadiene (XXI). The physicochemical constants of (XXI) agree with the data of [14].

5Z-Cyclodecen-1-one (XXII). The IR spectrum (ν, cm^{-1}) is as follows: 1731 (>C=O) and 720 (cis-CH=CH). The PMR spectrum (δ, ppm) is as follows: 1.4 multiplet (6H, CH_2), 1.7 multiplet (4H, $CH_2C=C$), 2.06 multiplet (4H, $CH_2C=O$), and 5.3 multiplet (2H, CH=CH). M^+ 152.

6E,9-Decadien-2-one (XXIV). The IR spectrum (ν, cm^{-1}) is as follows: 920, 3080 ($CH=CH_2$), 980 (trans-CH=CH), and 1720 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.5 multiplet (2H, CH_2), 1.9 multiplet (2H, $CH_2C=$), 2.0 singlet (3H, $CH_3C=O$), 2.3 multiplet (2H, $CH_2C=O$), 2.9 doublet (2H, $=CCH_2C=$), 4.8-5.1 multiplet (2H, $>C=CH_2$), and 5.4 multiplet (3H, CH=CH, CH=C). M^+ 152.

4E-Decen-2,9-dione (XXV). The IR spectrum (ν, cm^{-1}) is as follows: 980 (trans-CH=CH) and 1720 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.5 multiplet (2H, CH_2), 1.9 multiplet (2H, $CH_2C=$), 2.0 singlet (6H, $CH_3C^2=O$, $CH_3C^9=O$), 2.3 multiplet (2H, $CH_2C=O$), 2.8 multiplet (2H, $O-CCH_2C=$), and 5.03 multiplet (2H, CH=CH). M^+ 168.

Decane-2,4,9-trione (XXVI). The IR spectrum (ν, cm^{-1}) is as follows: 1715 (>C=O). The PMR spectrum (δ, ppm) is as follows: 1.79 multiplet (4H, CH_2), 2.05 singlet (3H, $CH_3C^9=O$), 2.1 singlet (3H, CH_3C^2O), 2.3 multiplet (4H, $CH_2C=O$), and 2.5 multiplet (2H, $O{-}C^2CH_2C^4{=}O$). M^+ 184.

CONCLUSIONS

1. The catalytic system of $PdCl_2$—CuCl permits the selective oxidation by oxygen in the THF solution of mono-, bi-, and tricyclic olefins, as well as 1,4E,9-decatriene, to high yields of carbonyl compounds.

2. The Z double bond in the cyclic olefins possesses significantly less activity than the E-isomer in the oxidation by oxygen.

3. The $PdCl_2$—CuCl system in combination with H_2O_2, NiO_2, $KMnO_4$, NaOCl, or the oxides of silver and manganese can be utilized as an effective reagent for the selective oxidation of linear polyenes to carbonyl compounds.

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