SILVER(I) OXIDE AND SILVER(II) OXIDE INITIATED ALKYLATION OF CYCLOALKANONES WITH ALKENES*

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Cyclopentanone and cyclohexanone were alkylated with 1-octene and 1-decene in the presence of silver(I) or silver(II) oxides under normal pressure at 80 – 130°C to give the corresponding 2-n-alkylcycloalkanones in 68 – 77% yields. Cyclohexene underwent the alkylation less readily and gave generally low yields of the corresponding 2-cyclohexylcycloalkanones. Formation of these products is the first example of a silver(I) oxide initiated alkylation reaction leading to 1 : 1 anti-Markovnikov addition products. The reactions were strongly inhibited by pure oxygen and retarded by a radical inhibitor. Both silver oxides act in these liquid-phase, free-radical chain reactions as heterogeneous initiators. The relative reactivity of cyclopentanone towards 1-octene, as determined by the method of competition reactions, is approximately twice as high as that of cyclohexanone and does not depend under the experiment conditions upon temperature, type of the silver oxide or a ketone to alkene ratio.

The homolytic alkylation of cycloalkanones with terminal alkenes, leading to formation of 2-n-alkylcycloalkanones (1 : 1 adducts), can be initiated by UV-light irradiation[1], cycloalkanone autoxidation[2] and by thermal decomposition of peroxy-compounds[3–8]. The UV-light induced radical addition of cyclohexanone to 1-octene gives, however, 2-n-octylcyclohexanone in only 25% yield[1]. Similarly, the alkylation of cyclopentanone or cyclohexanone with 1-octene initiated by autoxidation in the presence of manganese stearate affords the corresponding 1 : 1 adducts in 48 and 24% yields, respectively[2]. On the other hand, di-tert-butyl peroxide[3,4] (DTBP) and tert-butyl hydroperoxide[8], which both ensure a sufficient supply of the start radicals at higher temperatures, have turned out to be suitable initiators for the addition of cycloalkanones to terminal alkenes, yielding 2-n-alkylcycloalkanones in 50 – 70% and 32 – 62% yields, respectively. We have recently reported on the argentic oxide (AgO)** initiated addition reaction of acetone with 1-alkenes in the liquid

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** On the basis of magnetic behaviour and crystal structure, the argentic oxide[9] (AgO) is now assumed to be rather silver(I)—silver(III) oxide (Ag_2O—Ag_2O_3) (ref.[10]); for simplicity and in accordance with the current literature, the terms argentic oxide, silver(II) oxide and the formula AgO are used throughout this series.

phase leading in one-step process to formation of straight-chain methyl alkyl ketones in 73–83% yields[11,12]. We now find that the addition reaction of ketones with alkenes can be effected also with the more readily accessible silver(I) oxide[13] in place of the argentic oxide. In the present communication the effectiveness of silver(I) oxide and silver(II) oxide as heterogeneous initiators is compared in the anti-Markovnikov type addition reaction of cyclopentanone and cyclohexanone with 1-octene, 1-decene and cyclohexene. Additional data on the possible mechanism of the addition reaction initiated by the silver oxides are also reported.

RESULTS AND DISCUSSION

The alkylation of cyclopentanone and cyclohexanone with 1-octene and 1-decene in the presence of silver(I) oxide or silver(II) oxide gives, under essentially complete alkene consumption and in the absence of any induction period, the corresponding 2-n-octylcycloalkanones (*Ia* and *Ic*) and 2-n-decylcycloalkanones (*Ib* and *Id*) in 68–77% yields (calculated with respect to the charged alkenes) (Tables I and II). The yields of the alkylation reactions are somewhat higher than those (50–70%) obtained in analogous reactions initiated with DTBP (ref.[3]). Cyclohexene undergoes the silver oxide initiated addition less readily and gives only 17 and 5% of the corresponding 2-cyclohexylcycloalkanones *IIIa* and *IIIb*, respectively. The inspection of Table I shows that optimum yields of the 1 : 1 adducts are achieved at a 10 : 1 : 1 initial molar ratio of the ketone to the 1-alkene to silver oxide. In contradistinction to the addition reaction of acetone with alkenes[11], further decrease of the alkene concentration did not affect significantly the yield of the 1 : 1 adducts or the selectivity of the alkylation reaction. An increase in temperature from 80 to 130°C resulted in a decrease in the reaction time from 29–30 to 4–6 h; because of thermal decomposition of silver(I) and silver(II) oxides (see later), a continuous or portionwise addition of the silver oxides was, however, necessary to achieve high yields of the 1 : 1 adducts in the reactions carried out at 120–130°C. All the alkylation reactions leading to 1 : 1 adducts and initiated by silver oxides were accompanied by telomerization as the main side reaction; 15–28% of the alkenes were converted into telomeric high-boiling products (Table I), independently of the temperature or the ketone to alkene molar ratio. Dehydrodimerization of cyclopentanone and cyclohexanone is also taking place to a small extent, yielding a mixture of *meso*- and D,L-bicyclopentyl-2,2'-dione[14] (*IIa*) and of *meso*- and D,L-bicyclohexyl-2,2'-dione[14] (*IIb*), respectively (Table I). Formation of these diketones has not been mentioned in the earlier reported analogous alkylation reactions[1–8]. On the other hand, the products that would arise from the Markovnikov addition, from the attack upon the allylic hydrogen atoms of the alkenes[15] or from the autocondensation of cycloalkanones[16], have not been detected. Also isomerization of the terminal alkenes has not been observed under conditions of the alkylation reaction. Although no differences were observed in the rate or product yields of the silver oxide initiated alkylation reactions performed in contact with air or in nitrogen atmosphere, the reactions have failed to start under 800 Torr of the pure oxygen. However, displacement of oxygen by flushing with nitrogen restored completely the initiating efficiency of the silver oxides and the alkylation reaction started without a distinct induction period, at a normal rate and under immediate deep-brown colouration of the liquid phase and silver-mirror formation. Repeated introduction of the pure oxygen into the reacting suspension led to an instant inhibition of the alkylation reaction and was accompanied by a complete decolourization of the liquid phase. When a small amount of α-naphthol was added as a radical inhibitor to the cyclopentanone–1-octene–silver(I) oxide mixture, the alkylation reaction proceeded at only a fraction of the normal rate until "burning up" of the inhibitor. In the course of the

TABLE I

Alkylation of Cyclopentanone and Cyclohexanone with Alkenes Initiated by Ag_2O and AgO

Ketone	Alkene	Silver oxide	Molar ratio of components[a]	Temperature °C
Cyclopentanone	1-octene	AgO	10/1/0·25	80
		AgO	10/1/1	80
		Ag_2O	10/1/1	80
		AgO[e]	10/1/1	124–130
		Ag_2O[e]	10/1/1	124–130
		AgO[e]	50/1/1	128–130
	1-decene	AgO[e]	10/1/1	130
		Ag_2O	10/1/1	80
		Ag_2O[e]	10/1/1	130
	cyclohexene	AgO	10/1/1	80
Cyclohexanone	1-octene	AgO	10/1/0·25	80
		AgO	10/1/1	80
		Ag_2O	10/1/1	80
		AgO[e]	10/1/1	130
	1-decene	AgO[e]	10/1/1	130
		Ag_2O	10/1/1	80

[a] Ketone/alkene/silver oxide on a 0·0125—0·025 mol alkene scale; [b] yield of 1 : 1 adducts based on charged alkenes and determined by GLC utilizing 2-tridecanone as an internal standard; isolated yields are given in brackets; [c] amount of isomeric bicyclopentyl-2,2′-diones or bicyclohexyl-2,2′-diones in wt.% relative to 1 : 1 adduct formed; [d] amount of high-boiling products

alkylation reaction carried out at 130°C, both silver(I) oxide and silver(II) oxide were converted solely to metallic silver; the inorganic product resulting from the reactions conducted in the presence of silver oxides at 80°C was a mixture of metallic silver and 1–18 wt.% of silver(I) oxide. From these experiments it follows that silver(I) oxide decomposes at substantially lower temperatures than reported by Cotton and Wilkinson[17] (above 160°C) and recently by Nakamori and coworkers[18] (330°C). Preliminary measurements of thermal stability of the silver oxides under the alkylation reaction conditions have shown that by heating silver(II) oxide suspensions in n-heptane at 80°C for 30 h, 35% of the oxide is converted into silver(I) oxide; during heating silver(I) oxide suspensions in n-heptane under identical conditions, 16% of silver(I) oxide is transformed into metallic silver. In both cases n-heptane was recovered unchanged. On heating silver(I) or silver(II) oxide suspensions in 1-oc-

TABLE I
(continued)

Time h	Alkene conversion %	Yield 1 : 1 adduct[b] %	Yield 1,4-dione[c] wt.%	Yield high boiling products[d] wt.%
30	75	58	0·0	—
30	99	75 (69)	1·3	29·2
29	99	77	2·5	—
4	97	70 (61)	2·0	31·1
4	95	— (61)	3·0	30·9
4	95	69	2·6	—
5	80	— (60)	2·4	24·0
29	99	75	2·5	—
5·5	95	— (69)	5·0	26·8
29	42	— (17)	0·5	—
30	38	30	1·5	—
30	88	73 (65)	4·6	24·3
29	96	72	10·0	—
4	89	68 (60)	4·5	26·5
6	93	68 (61)	4·5	27·5
15	90	— (63)	10·0	26·3

in wt.% calcd. from the relation: [high-boiling products (g)] . 100/[high-boiling products (g) + 1 : 1 adduct (g)]; [e] portions of the weighed amount of silver oxides were gradually added to the ketone–alkene mixture in 5–7 min intervals during the reaction; the sole inorganic product formed from AgO or Ag_2O was metallic silver.

tene at 120°C for 4 h led to a complete conversion of the silver oxides into pure metallic silver; the alkene was practically resistant against the action of both silver oxides and only traces of five unidentified substances (less than 1 wt.% in total) were detected by gas–liquid chromatography in the recovered 1-octene.

When silver(II) oxide was reacted with cyclopentanone or cyclohexanone alone at 125°C for 5 h, the 1,4-diones, *i.e.* *IIa* of the unknown stereochemistry and *meso-IIb*, respectively, were isolated, but, in contrast to an analogous nickel peroxide assisted reaction[14], in only 4% and 9% yields (with respect to the charged silver(II) oxide), respectively. The sole inorganic product always produced was metallic silver.

Formation of 2-n-alkylcycloalkanones *Ia*–*Id*, 2-cyclohexylcycloalkanones *IIIa* and *IIIb*, the dimers *IIa* and *IIb* and telomers, a complete inhibition of the alkylation reaction by pure oxygen as well as its retardation by a radical inhibitor strongly support the assumption that the silver(I) oxide and silver(II) oxide initiated alkylation of cycloalkanones with 1-alkenes and cycloalkenes is a free-radical chain reaction wherein both silver oxides act as heterogeneous initiators. To our knowledge, this is the first example of a silver(I) oxide initiated anti-Markovnikov addition reac-

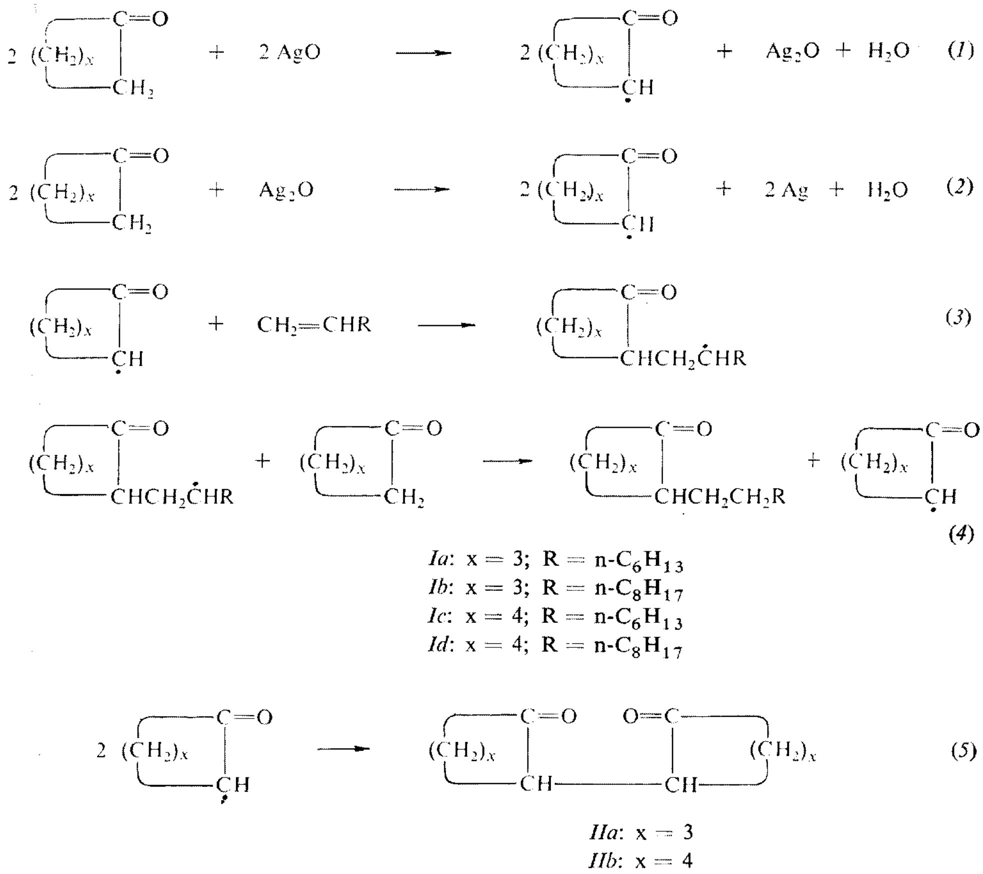
TABLE II

Characterisation of 2-n-Alkylcycloalkanones as Products of Silver Oxide Initiated Alkylation Reactions

1 : 1 Adduct	B.p., °C/Torr (lit.)[a]	Calc./Found		Semicarbazone m.p., °C (lit.)[a]
		% C	% H	
2-n-Octylcyclopentanone[b–f]	98–99/2 (96–97/1·5)	79·53 79·27	12·32 12·16	182·5–184·5 (184·6–185)
2-n-Decylcyclopentanone	115–118/3 (106–108/1)	80·29 80·15	12·58 12·58	182–183 (182·5–183)
2-n-Octylcyclohexanone[d,g–j]	102–103/2 (100–101/1·5)	79·93 79·56	12·46 12·25	109·5–110·5 (109–109·5)
2-n-Decylcyclohexanone	126–128/2 (119–120/1)	80·60 80·44	12·68 12·44	106–106·5 (104·5–105)

[a] Ref.[3]; [b] n_D^{20} 1·4535 (ref.[3] n_D^{20} 1·4530); [c] IR spectrum (neat): $\nu_s(C{=}O)$ 1 740 cm^{-1}; [d] $\nu_s(CH_2)$ 2858; $\nu_s(CH_3)$ 2873; $\nu_{as}(CH_2)$ 2929; $\nu_{as}(CH_3)$ 2959 cm^{-1}; [e] authentic samples[3] of *Ia* showed identical stretching bands; [f] the ratio of absorbances in the IR spectrum, *i.e.* that of 2858 cm^{-1} : : 2873 cm^{-1} as well as that of 2929 cm^{-1}: 2959 cm^{-1} corresponds to 10 : 1; [g] n_D^{20} 1·4619 (ref.[3] n_D^{20} 1·4605); [h] IR spectrum (neat): $\nu_s(C{=}O)$ 1710 cm^{-1}; [i] authentic samples[3] of *Ic* showed identical stretching bands; [j] the ratio of absorbances in the IR spectrum, *i.e.* that of 2858 cm^{-1} : : 2873 cm^{-1} as well as that of 2929 cm^{-1}: 2959 cm^{-1} corresponds to 11 : 1.

tion. The results obtained seem to be best explained by a sequence of the reactions presented in Scheme 1.



Ia: $x = 3$; $R = n\text{-}C_6H_{13}$
Ib: $x = 3$; $R = n\text{-}C_8H_{17}$
Ic: $x = 4$; $R = n\text{-}C_6H_{13}$
Id: $x = 4$; $R = n\text{-}C_8H_{17}$

IIa: $x = 3$
IIb: $x = 4$

SCHEME 1

The chain initiation steps (Eqs. (*1*) and (*2*))* (not detailed at this stage) involve likely an one-electron transfer oxidation of the cycloalkanones by silver oxides to give α-keto radicals. By analogy with the mechanism generally accepted for the

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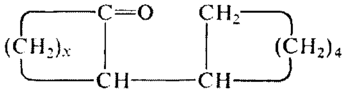
* Provided that the higher silver oxide has the composition corresponding rather to Ag_2O—Ag_2O_3 and that the ketone is oxidized by an one-electron transfer process, the initiation steps (Eqs. (*1*) and (*2*)) should presumably involve a transformation of Ag(I) into Ag(0) and a two-stage conversion of Ag(III) to Ag(II) and Ag(I). The latter transformation is analogous to an one-equivalent change from Pb(IV) to Pb(III) and Pb(II) assumed by Kochi and coworkers[19] in a free-radical oxidative decarboxylation of acids by lead tetraacetate. The experimental evidence available so far does not allow to decide unambiguously between the above (Eq. (*1*)) and this pathway of radical generation in the silver-oxide initiated alkylation reaction.

anti-Markovnikov addition reactions[15], these radicals add rapidly to the 1-alkene, forming thus the secondary cycloalkanoylalkyl radicals (Eq. (*3*)); the interaction of the latter with the cycloalkanones in the radical displacement reaction (Eq. (*4*)) then produces the corresponding 2-n-alkylcycloalkanones *Ia*–*Id*. The same reaction sequence holds also for the formation of 2-cyclohexylcycloalkanones *IIIa* and *IIIb*.



IIIa: x = 3
IIIb: x = 4

Irrespective of the relatively small extent of formation of diketones *IIa* and *IIb* during the alkylation reaction, it appears that mainly the dimerization reactions[15] contribute to chain termination. The formulation of the chain initiation steps (Eqs. (*1*) and (*2*)) is consistent with a transient occurrence of silver(I) oxide in the silver(II) oxide initiated alkylation reactions and with the conversion of silver(I) oxide into metallic silver in the silver(I) oxide initiated reactions. In comparison with organic peroxides[3–8], approximately four to five times higher concentrations of silver oxides are needed for comparable yields of the 1 : 1 adducts to be obtained; therefore, it is evident that the kinetic chain length is quite short in the alkylation of cycloalkanones initiated by silver(I) or silver(II) oxides.

To determine the relative reactivity of cyclopentanone and cyclohexanone in the alkylation reaction with 1-octene, competition experiments were carried out at 80 to 130°C; equimolar mixtures of both ketones were allowed to compete for a limited quantity of the alkene in the presence of the silver oxide (the molar ratio 5–50/1/1) and the molar ratio of the 1 : 1 adduct of cyclopentanone to that of cyclohexanone, which was used to express the reactivity of cyclopentanone relative to cyclohexanone, was followed by gas–liquid chromatographic analysis during the reaction. The value of the molar ratio of the 1 : 1 adducts changed with time but did not depend significantly under the experiment conditions on temperature, the type of the silver oxide or on the ketone to alkene ratio; the data determined at the initial stage (up to 15% alkene conversion) and at the end of the reaction are recorded in Table III. Taking into account decreasing selectivity of the alkylation reaction with increasing reaction time, the molar ratios of the products determined at low alkene conversion during the initial stage of the alkylation appear to be more reliable and show that cyclopentanone is 1·9 to 2·1 times more reactive than cyclohexanone. This reactivity value is somewhat higher than that determined by Nikishin and coworkers[20] (1·52) for the DTBP initiated competition reaction of the above ketones with 1-heptene and than that found by Cazaux and coworkers[21] (1·49) for the benzoyl peroxide initiated competition reaction of the same ketones with β-pinene. In all these competition reactions initiated by organic peroxides[20,21], the relative reactivities of the ketones were calculated from the ratio of the final yields of the corresponding 1 : 1 adducts.

All the silver oxide initiated alkylation reactions occur in a heterogeneous system. Therefore, the question arises whether or which of the discrete steps of the reaction proceed on the surface of silver oxide particles or in the liquid phase of the reaction system. Attempts to elucidate this point as well as further examination of the synthetic utility of this new class of initiating agents will be the subject of forthcoming papers.

EXPERIMENTAL

AgO (ref.[22]) (98·6%) and Ag_2O (ref.[23]) (97·4%) were prepared by standard procedures. 1-Octene, 1-decene, 2-tridecanone (internal standard) (Fluka A.-G.), n-hexadecane (internal standard) (May-Baker Ltd., England), cyclopentanone and cyclohexanone (Lachema, Brno, Czechoslovakia) were commercial products which were fractionated until they were chromatographically pure and redistilled before use. α-Naphthol (Ciech-Gliwice, Poland), used as a radical inhibitor, was of analytical reagent grade purity. Authentic samples of 2-n-octylcyclopentanone (b.p. 106—108°C/3 Torr; n_D^{20} 1·4530) and 2-n-octylcyclohexanone (b.p. 113—115°C/3 Torr; n_D^{20} 1·4612), needed for comparison with our products, were prepared according to Nikishin and coworkers[3].

TABLE III

Competition Reactions of Cyclopentanone and Cyclohexanone with 1-Octene Initiated by Ag_2O and AgO

Mol. ratio of components[a]	Silver oxide	Temperature °C	1-Octene conversion %	Time h	*Ia* : *Ic*[b] mol. ratio	
					initial[c]	final[d]
5/5/1/1	AgO	80	92	13	1·95	1·78
	Ag_2O	80	96	20	1·97	1·71
	AgO	100	90	9	1·92	1·80
	AgO	130	65	4	1·94	1·84
	Ag_2O	130	72	4	1·97	1·74
	AgO[e]	130	83	4	1·93	1·53
	Ag_2O[e]	130	88	4	1·94	1·50
25/25/1/1	AgO	80	90	28	2·09	1·93
50/50/1/1	AgO	80	71	30	2·09	1·92

[a] Cyclopentanone/cyclohexanone/1-octene/silver oxide; [b] the error was ±0·03; [c] measured up to the 15% conversion of 1-octene; [d] measured at the end of the reaction; [e] silver oxides were gradually added into the reaction mixture in 5 min intervals during the reaction.

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Mass spectra were recorded with a JEOL JMS-D100 spectrometer and IR spectra were measured on a Zeiss (Jena) spectrophotometer, model UR-20. Gas-chromatographic analyses were carried out on a Chrom-31 instrument (Laboratorní přístroje, Prague) equipped with a flame-ionisation detector using a steel column (1·5 m × 0·3 mm) packed with 3% SE 30 + 3% Apiezon on Chromaton N-AW-HMDS. The column temperature was 100–180°C. The purity of AgO and its content in the inorganic precipitate resulting from the alkylation and dehydrodimerisation reactions and from determination of the thermal stability of the oxide were determined iodometrically[24]; prior to analysis, the collected inorganic precipitate was washed twice with 25 ml of acetone, dried *in vacuo* and weighed with an accuracy of ±0·2 mg. The Volhard method was used to determine the purity of Ag_2O and its content in the inorganic precipitate from the alkylation reactions and from determination of the thermal stability of Ag_2O: the inorganic precipitate was treated as above and mixed with a 10% aqueous ammonium hydroxide solution. The undissolved metallic silver was filtered off and dried *in vacuo*; the content of Ag^+ in the acidified filtrate was determined by titration with 0·1N ammonium rhodanide. Formation of water during the alkylation reaction was followed by a modified Fisher method.

All the alkylation and dehydrodimerisation experiments as well as determinations of the thermal stability of the silver oxides were carried out under atmospheric pressure in a 50 ml-glass vessel equipped with a magnetical stirrer, a thermometer and a reflux condenser. Inhibition experiments in the presence of pure oxygen were carried out in the same apparatus connected with an oxygen pressure cylinder. No differences in the rate and product yields were found for the alkylation reactions conducted in contact with air or in a nitrogen atmosphere at an intensity of stirring ranging from 200 to 800 rev./min.

Structure determination of the products of the alkylation of the cycloalkanones. A reaction mixture obtained by heating cyclopentanone (10·51 g, 0·125 mol) and 1-octene (1·40 g, 0·0125 mol) in the presence of Ag_2O (2·90 g, 0·0125 mol) under stirring at 80°C for 29 h (conversion of 1-octene 99·5%) was cooled to room temperature, freed of the solid materials (Ag and Ag_2O), mixed with 2-tridecanone (internal standard) and subjected to gas-chromatographic analysis; according to retention times of the authentic compounds, the product present in a low concentration and having shorter retention time was identical with bicyclopentyl-2,2′-dione[14] (*IIa*) (2·5 wt.% based on *Ia*) of unknown stereochemistry and the main product was found to be 2-n-octylcyclopentanone[3] (*Ia*) (77% yield with respect to the charged alkene). The other products of the alkylation reactions were identified in a similar way. The characteristics of 2-n-alkylcycloalkanones and their semicarbazones is presented in Table II. The IR spectra of *Ia* and *Ic* (Table II) were identical with those of authentic compounds. 2-Cyclohexylcyclopentanone[25] (*IIIa*), b.p. 108 to 110°C/13 Torr; M^+ 166 (3·5%) (for $C_{11}H_{18}O$ calculated: M^+ 166) and other ions at *m/e* 123 (1·5), 95 (3), 84 (100), 83 (22), 81 (11), 67 (14·5), 55 (16), 41 (18%); semicarbazone, m.p. 204–206°C (ref.[25] records m.p. 207°C).

General procedure for the alkylation reactions. In a typical experiment, cyclopentanone (21·0 g, 0·25 mol), 1-octene (2·80 g, 0·025 mol) and AgO (3·1 g, 0·025 mol) were stirred (500 rev/min) at 80°C to yield 99% conversion of the alkene after 30 h; the reaction was characterized by the absence of an induction period and by silver-mirror formation on the walls of the reaction vessel and deep-brown colouration of the liquid phase which turned pale yellow at the end of the reaction. The resulting suspension was cooled to 25°C and freed of the precipitated metallic silver and Ag_2O by filtration; the collected precipitate was washed twice with 25 ml of acetone, the filtrates were combined and freed of the acetone and unreacted cyclopentanone by distillation. The residue was fractionated *in vacuo* to give a small fraction (b.p. 98°C/2 Torr) of the diketone *IIa*, 3·40 g of the alkyl ketone *Ia* (69·4% with respect to the charged alkene; b.p. 98 to

99°C/2 Torr) and a residue consisting of higher boiling telomeric products (1·41 g). Other experimental conditions and examples of the alkylation reactions are summarized in Table I. 2-Cyclohexylcyclopentanone (*IIIa*) (17% yield) and 2-cyclohexylcyclohexanone (*IIIb*) (*c.* 5% yield) were isolated in only *c.* 97% purity.

Dehydrodimerisation of cycloalkanones. Bicyclopentyl-2,2'-dione(*IIa*): AgO (6·2 g, 0·05 mol) was gradually added in 5—7 min intervals to cyclopentanone (21·0 g, 0·25 mol) under magnetical stirring at 125°C during 5 h. The precipitated silver was filtered off, the unreacted cyclopentanone was removed by distillation and the residue was distilled *in vacuo* to give 0·31 g of an oily fraction (b.p. 130—140°C/10 Torr), presumably a mixture of the *meso-* and D,L-1,4-dione[14], which partially solidified on standing; separation of the crystalline mass by filtration and its recrystallisation from light petroleum gave the diketone *IIa* of unknown stereochemistry (3·7% on AgO) melting at 66—68°C (ref.[14] m.p. 66—68°C).

meso-Bicyclohexyl-2,2'-dione[26] (*meso-IIb*): AgO (6·2 g, 0·05 mol) was gradually added in 5—7 min intervals to cyclohexanone (24·53 g, 0·25 mol) stirred at 125°C during 5 h. After removal of metallic silver, Ag_2O and the unreacted cyclohexanone, the residue was distilled *in vacuo* to give 0·88 g of an oily fraction, presumably a mixture of the *meso-* and D,L,-1,4-dione[14], b.p. 106—109°C/2 Torr, which solidified partially on standing; recrystallisation of the separated crystalline mass from light petroleum gave the *meso-IIb* 1,4-dione (9·1% on the charged AgO), m.p. 70—72°C (ref.[14] m.p. 72—74°C; ref.[26] m.p. 70°C). The structure of an additional product, formed according to gas-chromatographic analysis (the shorter retention time than that shown by the isomeric diones) in trace amounts, has not been determined.

Competition alkylation experiments. Cyclopentanone, cyclohexanone, 1-octene and AgO or Ag_2O were mixed in a 5—50/5—50/1/1 molar ratio and stirred magnetically at 80—130°C for 4—30 h. Samples were taken from the reaction mixture at fixed time intervals until the reaction ceased and were analysed by gas-liquid chromatography; the *Ia* to *Ic* molar ratios in the reaction mixture were calculated from the chromatographic data by correcting the ratios of the peak heights of *Ia* to *Ic* according to the calibration curve determined for the known mixtures containing the products *Ia* and *Ic* in a molar ratio ranging from 1·49 to 2·21. The chromatograph was calibrated before each analysis by appropriate mixtures of *Ia* and *Ic*. The reaction conditions along with the *Ia* to *Ic* molar ratios determined in the initial stage (up to 15% conversion of 1-octene) and at the end of the alkylation reactions are presented in Table III.

Thermal decomposition of the silver oxides. A magnetically stirred suspension of Ag_2O (2·32 g, 0·01 mol) in n-heptane (10·0 g, 0·1 mol) was heated in contact with air at 80°C for 30 h. The suspension was cooled to 25°C, the inorganic product was filtered off, washed twice with 25 ml of acetone and freed of acetone under reduced pressure at 25°C; its analysis revealed that 16% of Ag_2O was decomposed to metallic silver. The filtrate was freed of acetone and distilled without leaving a residue; no products were detected by gas-chromatographic analysis in the n-heptane recovered. Repeating the above procedure under identical conditions with AgO (1·24 g, 0·01 mol) in n-heptane (10·0 g, 0·1 mol) and analyzing the inorganic product showed that 35% of AgO underwent decomposition to Ag_2O without formation of metallic silver; pure n-heptane was recovered similarly as in the preceding case. Heating of a stirred suspension of Ag_2O (2·32 g, 0·01 mol) in 1-octene (5·6 g, 0·05 mol) under reflux at 120°C for 4 h led, according to the analysis of the insoluble inorganic product, to a complete conversion of Ag_2O to metallic silver. Distillation of the filtrate under normal pressure gave pure 1-octene and 0·036 g (0·6 wt.% on the charged alkene) of a residue; according to gas-chromatographic analysis, the residue was a mixture of approximately equal amounts of five unidentified compounds. When a suspension of AgO (1·24 g, 0·05 mol) in 1-octene (5·6 g, 0·05 mol) was heated under reflux at 120°C for 4 h, AgO was converted completely into metallic silver free of Ag_2O. Distillation of the filtrate under normal pressure gave pure 1-octene and 0·049 g (0·9 wt.% on the charged alkene) of a residue which was identical (gas-chromatographic analysis) with that obtained by thermal decomposition of Ag_2O in 1-octene. All the decomposition reactions, except the decomposition of AgO at 80°C, were characterized by a silver-mirror formation on the reaction vessel walls.

Inhibition of the alkylation reactions. A magnetically stirred suspension of Ag_2O (0·58 g, 0·0025 mol) in cyclopentanone (8·41 g, 0·10 mol), 1-decene (1·40 g, 0·01 mol) and n-hexadecane (0·226 g, 0·001 mol) was heated under a pressure of 800 Torr of pure oxygen at 80°C. According to gas--chromatographic analysis, no 2-n-decylcyclopentanone (*Ib*) was formed even after 6 h of heating. When the apparatus was flushed several times with nitrogen, the liquid phase of the reaction mixture turned deep-brown under immediate formation of a silver mirror on the reaction vessel walls and after 2 h at 80°C, the yield of the alkyl ketone *Ib* reached 15·5% (on the alkene). Repeated contact of the reacting suspension with pure oxygen (800 Torr) caused an instant decolourisation of the liquid phase and the concentration of the alkyl ketone *Ib* in the mixture did not change during another 5 h of heating.

When the above stirred suspension of Ag_2O in cyclopentanone, 1-decene and n-hexadecane was heated in a nitrogen atmosphere in the presence of 0·0144 g (0·1 mmol) of α-naphthol at 80°C, an induction period in the formation of the alkyl ketone *Ib* was observed; after heating for 20 min at the above temperature, only 30% of *Ib* were formed, compared to the reaction carried out in the absence of the inhibitor. Normal alkylation rate was achieved after 40 min at 80°C.

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