

The Competition between Cross-coupling and the Exchange Reaction in the Photoreduction of Aromatic Ketones

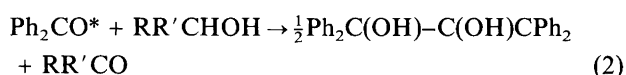
Torben Lund,^a Birger Lundgren^a and Henning Lund^b

^aInstitute of Life Science and Chemistry, Roskilde University Center, DK-4000 Denmark and ^bDepartment of Chemistry, University of Århus, Langelandsgade, DK-8000 Denmark

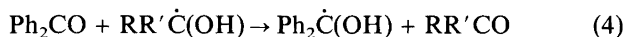
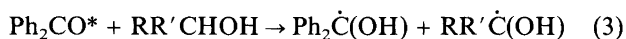
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Four aromatic ketones *K* with different reduction potentials and a series of hydrogen atom donors *AH*₂ with different oxidation potentials of *AH*· were irradiated in pairs and the product composition analyzed. Based on the product analysis the rate *k*_{ex} of the exchange reaction *K* + *AH*· → *KH*· + *A*, was characterized as slow, medium fast or fast, respectively, relative to the radical–radical coupling reactions of *K*· and *AH*·. The results clearly point to the value of a knowledge of the oxidation potential of the *AH*· radicals and the reduction potential of the ketones for the prediction of the outcome of the photoreduction of a ketone by an alcohol or another hydrogen atom donor.

The photoreduction of benzophenone by alcohols is one of the most well-studied photochemical reactions.^{1–5} The reaction is illustrated in most textbooks by the photoreduction of benzophenone by an alcohol, eqns. (1) and (2).^{6,7}



The first step results in the transfer of a hydrogen atom from the alcohol to the triplet excited state of the ketone [eqn. (3)]; this is followed by the transfer of a hydrogen atom from the substituted hydroxymethyl radical to the ground state ketone [eqn. (4)], but in only a few cases is the mechanism discussed in the textbooks.^{8,9}



A simple question might be asked. Why is the cross-coupling product, the mixed pinacol (Ph)₂C(OH)C(OH)(RR') not observed in the reaction? Even though the radicals are formed as a triplet pair some coupling could occur after spin inversion. The problem is not discussed in any textbooks and only very few papers have dealt with this problem.^{10,11}

The general scheme for the photoreduction of ketones (*K*) by hydrogen atom donors (*AH*₂) such as alcohols and alkylbenzenes is shown in Scheme 1.



Scheme 1

In the photoreduction of benzophenone by toluene a statistical ratio (1:2:1) of bibenzyl (A₂H₂), the cross-coupling product (Ph)₂C(OH)CH₂Ph (KHAH) and benzophenone pinacol (K₂H₂) is obtained.^{12–14} How can this difference in the coupling behavior of the 1-hydroxy-1-methylethyl radical (Me₂ĊOH) and the benzyl radical with hydroxydiphenylmethyl radicals (Ph₂ĊOH) be explained? Furthermore, in the photoreduction of acetone by benzhydrol the mixed pinacol (Ph)₂C(OH)C(OH)(CH₃)₂ is observed,¹⁰ whereas this product is not obtained in the photoreduction of benzophenone with 2-propanol. This indicates that the coupling reaction between a hydroxydiphenylmethyl radical

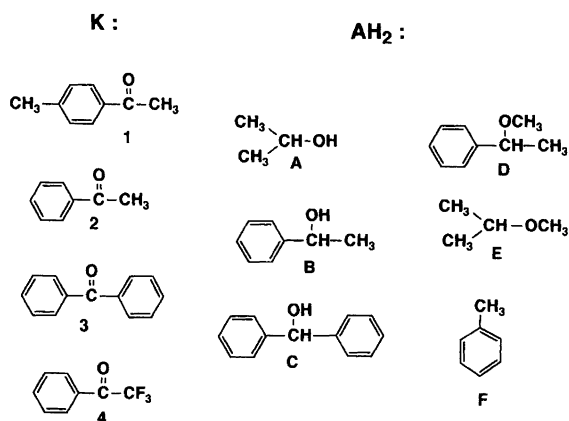


Fig. 1.

and a 1-hydroxy-1-methylethyl radical is not an inherently slow reaction but is comparable in rate to similar coupling reactions. In both photoreductions the same 1-hydroxy-1-methylethyl and hydroxydiphenylmethyl radicals are produced by the initial hydrogen abstraction process [eqn. (6)]. However, the product distribution is different in the two photoreductions.

The rate of the exchange reaction [eqn. (11)] is, as pointed out by Schuster,¹⁵ very important in the determination of the product composition. Apparently the exchange reaction is fast between the 1-hydroxy-1-methylethyl radical and benzophenone and slow in the reactions of the benzyl radical with benzophenone and acetone with hydroxydiphenylmethyl radical compared with the coupling reactions. Even though the importance of the exchange reaction is well recognized^{3-5,15} no attempts have been made to try to rationalize and explain the ob-

served variation in the exchange rates in various types of photo reduction.

The exchange reaction [eqn. (11)] has been suggested to proceed by an electron transfer (ET) from the AH· radical to K coupled with a proton transfer to K^{·-},¹¹ the result being a transfer of a hydrogen atom. The exchange rate constant k_{ex} may therefore be expected to depend on both the oxidation potential of AH· and the reduction potential of the ketone. In order to test this idea four ketones (1-4) 4-methylacetophenone (1), acetophenone (2), benzophenone (3) and α,α,α -trifluoroacetophenone (4) with different reduction potentials and a series of hydrogen atom donors (A-F) 2-propanol (A), 1-phenylethanol (B), benzhydrol (C), methyl 1-phenylethyl ether (D), isopropyl methyl ether (E) and toluene (F) with different oxidation potentials were irradiated in pairs and the product composition analyzed. The oxidation potentials of several hydroxyalkyl radicals and other radicals have recently been obtained by photomodulated voltammetry.^{16,17}

Results and discussion

When the exchange reaction is fast, as in the case of the photoreduction of benzophenone by 2-propanol, the stoichiometric ratio between the ketone (K) and the hydrogen atom donor [the alcohol AH₂] is 2. In order to avoid depletion of K during the photolyses the reactions were performed with a 2:1 molar ratio of K and AH₂. The photolyses were performed in neat mixtures of K and AH₂ and only in the photolysis of benzhydrol (C) were minor amounts of acetonitrile added to obtain a homogeneous solution. The relative product composition of the pho-

Table 1. The product composition of the photolyses (mol %) obtained by GC-FID and HPLC.

Photolysis	start K	start AH ₂	K	AH ₂	A	K ₂ H ₂	KHAH	A ₂ H ₂	Conversion (%)
1A	100	50	60	— ^a	—	20	0	—	40 ^b
2A	100	50	96	—	—	2	0	—	4
3A	100	50	42	—	—	29	0	—	58
4A	100	50	0	—	—	50	0	—	100
1B	64	36	63	31	2	2.0	0.9	0.14	4.9
3B	64	36	24	0	35	20.5	0	0	62
4B	66	34	38.5	15	9	12.8	0	0	39
1C	69	31	68	9.9	0	2.8	4.38	3.7	14
2C	68	32	34	17.3	10.8	10.5	6.5	2.0	40
4C	66	34	7.5	0	25	34	0	0	100
1D	66	34	63.5	30.5	0	0.68	1.18	1.14	3.8
2D	66	34	59.4	35.5	0	0.76	1.00	0.21	3.8
3D	63	37	39	12.5	0	9.5	12.2	2.6	49
4D	64	36	33.6	33.6	5.14 ^c	10.7	4.21	0.73	40
1E	100	76	91	—	—	3.59	0.84	—	8
2E	100	74	95.9	—	—	1.76	0.283	—	3.8
3E	100	50	79	—	—	10.4	0	—	21
4E	100	45	75.4	—	—	12.0	0	—	24
1F	66	34	69	30	0	0.26	0.30	0.076	1.2
2F	66	34	71	27	0	0.26	1.01	0.26	2.3
3F	66	34	61.8	11.2	0	2.04	10.5	0.83	22
4F	67	33	52.9	23.8	0	4.98	5.54	1.10	23

^a Not analysed for. ^b Conversion % = [2 * (%K₂H₂) + %KHAH] / %K(start) * 100%. ^c A = Acetophenone.

tolysis between the ketones **1–4** and the hydrogen atom donors **A–F** is shown in Table 1. The products were identified by GC–MS. The identification of the pinacols from GC–MS is relatively simple. The pinacols show a characteristic ‘doublet’ peak in GC due to the +, – and *meso* forms. Furthermore the two major fragmentation ions in the MS are due to the cleavage of the central C–C bond of the pinacol.

The product distribution is very much influenced by the rate k_{ex} of the exchange reaction [eqn. (11)]. If $k_{ex} \sim 0$ the statistical ratio 1:2:1 between the pinacol from the ketone **K** (K_2H_2), the mixed pinacol (**KHAH**) and the pinacol (A_2H_2) from the alcohol AH_2 is expected when it is assumed that $k_7 = k_8 = k_9$ and $k_{10} \sim 0$. The ketone **A**, obtained from the alcohol AH_2 , is not observed under these conditions. If k_{ex} is very fast only **A** and K_2H_2 are observed while the cross-coupling product **KHAH** and the pinacol A_2H_2 are not found. When k_{ex} is comparable to the rate constants for the couplings (the intermediate case) **A**, K_2H_2 , **KHAH** and A_2H_2 are formed with $[K_2H_2] > [KHAH] > [A_2H_2]$. From the composition of the product mixture of the photoreduction the exchange reaction [eqn. (11)] may therefore be classified as slow, medium fast or fast. The classification (assuming $k_{10} \sim 0$) is summarized in Table 2 and used to classify the product mixtures in Table 1 as shown in Table 3. If the rate of the disproportionation reaction [eqn. (10)] is fast compared with reactions (7)–(9) and (11) it will change the classification shown in Table 3. However, the disproportionation reaction seems important only for the 1-hydroxy-1-methylethyl radical. The 1-hydroxy-1-methylethyl radical may dimerize to pinacol or disproportionate to acetone and 2-propanol [eqn. (10) in Scheme 1]; the ratio of coupling to disproportionation has been measured to be 1:4 at room temperature.¹⁸ The corresponding 1-hydroxy-1-phenylethyl radical [$Ph\dot{C}(OH)CH_3$] and the hydroxydiphenylmethyl radical seem not to disproportionate significantly.^{11,15,19}

For the photoreduction of the medium-fast type in which the exchange reaction, [eqn. (11)] competes with the dimerization reactions, eqns. (7)–(9) the final product composition depends on the concentrations of KH_2 and AH_2 , the light intensity and the photolysis time. This has been shown by Schuster¹⁵ in the photoreduction of [$^2H_{10}$]benzophenone with benzhydrol which is of the ‘medium-fast’ type. In the medium-fast type photoreduction of 4-methylacetophenone (**1**) by 1-phenylethanol (**B**) the time dependence of the product composition has been

Table 2. Classification of the exchange rate based on the photolysis product composition. (Product observed = Yes, not observed = No)

k_{ex}	Relative amounts normally observed			
	A	K_2H_2	KAH₂	A_2H_2
Slow	No	Yes	Yes	Yes
Medium	Yes	Yes	Yes	Yes
Fast	Yes	Yes	No	No

Table 3. The relative mole product compositions of the photolyses. ($K_2H_2 = 100$).

Photolysis	A	K_2H_2	KAH₂	A_2H_2	k_{ex} ^a
1A	–	100	0	–	Fast
2A	–	100	0	–	Fast
3A	–	100	0	–	Fast
4A	–	100	0	–	Fast
1B	100	100	46	7	Medium
3B	171	100	0	0	Fast
4B	70	100	0	0	Fast
1C	0	100	156	132	Slow
2C	103	100	62	19	Medium
4C	74	100	0	0	Fast
1D	0	100	174	168	Slow
2D	0	100	132	28	Slow
3D	0	100	128	27	Slow
4D	48	100	39	7	Medium
1E	–	100	23	–	Slow
2E	–	100	16	–	Slow
3E	–	100	0	–	Fast
4E	–	100	0	–	Fast
1F	0	100	115	29	Slow
2F	0	100	388	100	Slow
3F	0	100	515	41	Slow
4F	0	100	111	22	Slow

^aThe exchange rate k_{ex} is classified as slow, medium or fast according to the criteria in Table 2.

followed (Table 4). In analogy to the results obtained by Schuster¹⁵ the relative concentrations of **2** (**A**), **11** (K_2H_2), **1B** (**KHAH**) and **BB** (A_2H_2) are dependent on the photolysis time and/or the degree of photochemical conversion. After 2 h of photolysis the ratio between **11**, **1B** and **BB** was 1:0.2:0.01 and after 28 h of photolysis the ratio changed to nearly a 1:2:1. One reason for the change in the product distribution is the decrease of the concentration of the ketone **K** which will reduce the importance of the exchange reaction. Furthermore, some secondary photoreduction cannot be excluded in which some of the ketone (**A**) produced in the exchange reaction is excited and photoreduced by 1-phenylethanol with formation of A_2H_2 .

Table 4. The product composition (mol %) of the photolysis of 4-methylacetophenone (**1**) and 1-phenylethanol (**B**) as a function of the photolysis time.

Photolysis time/h	K	AH_2	A	K_2H_2	KAH₂	A_2H_2	Conversion (%)
2	45.8	50.7	0.68	1.23	0.18	0.01	2.6
4	43.5	50.1	0.69	2.23	0.54	0.06	5.0
6	41.5	49.4	0.81	2.76	1.17	0.20	6.7
8	37.7	45.3	2.44	4.44	2.24	0.57	11.1
10	36.8	38.1	2.45	5.97	4.01	1.33	16.0
12	30.7	38.8	3.15	6.55	5.30	2.02	18.4
14	26.4	35.0	2.86	7.64	7.18	3.04	22.5
16	22.7	30.7	2.85	8.56	9.09	4.23	26.2
20	15.5	22.5	1.9	10.1	12.9	7.0	33.1
24	10.9	17.9	1.2	10.8	15.3	8.9	36.9
28	5.5	12.0	0.8	11.8	18.1	11.0	41.7

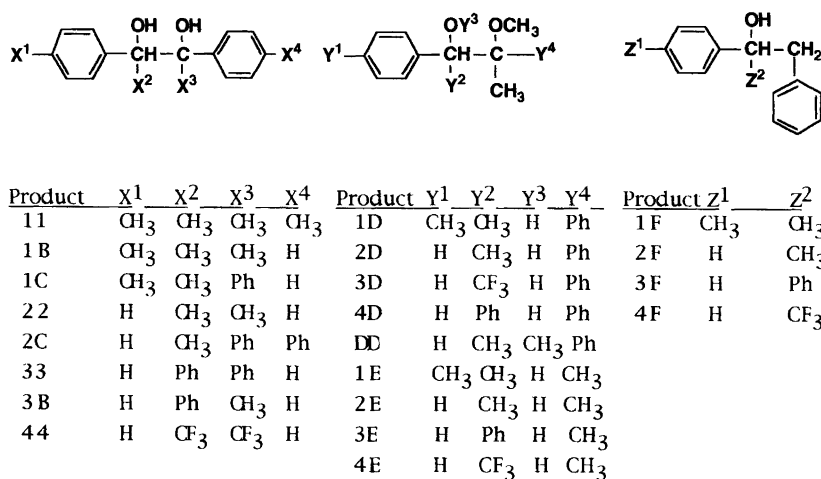
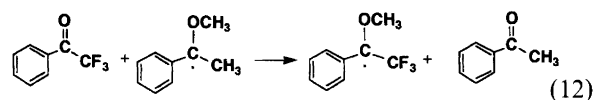


Fig. 2.

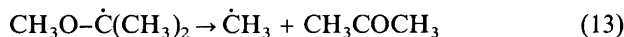
The photoreduction in which the exchange reaction is slow ('slow type') is predicted from Scheme 1 to be more simple than the medium type in the dependence of the product composition on photolysis time. The ratio between the pinacols are expected to be constant during the photolysis. This is demonstrated (see Table 5) in the photoreduction of 4-methylacetophenone (**1**) by benzhydrol (**C**).

The radicals $AH\cdot$ derived from the alcohol hydrogen atom donors **A**, **B** and **C** are oxidized in the exchange reaction [eqn. (11)] to the corresponding ketones, 4-methylacetophenone, acetophenone and benzophenone, respectively. In the photolysis of trifluoroacetophenone (**4**) with the methyl ether **D**, acetophenone and minor amounts of $[(PhC(CF_3)(OCH_3))_2]$ were obtained. This may be formed by an exchange reaction in which a methyl radical is formally transferred to the acetophenone [eqn. (12)]; the mechanism is possibly analogous to that of the exchange reaction [eqn. (11)] in which a hydrogen atom is formally transferred.

The structure of the product, the methylated pinacol $[(PhC(CF_3)(OCH_3))_2]$ (**5**), was identified by independent synthesis by treatment of trifluoroacetophenone pinacol with diazomethane. In the photolysis **3E** and **4E** of benzophenone and trifluoroacetophenone in isopropyl me-



thyl ether no cross-coupling products $KHAH$ or $(CH_3)_2C(OCH_3)-(CH_3O)C(CH_3)_2 (=A_2H_2)$ are observed, and the exchange reaction of the photolysis is therefore characterized as fast. Acetone (=A) is observed by ^{13}C NMR spectroscopy in the photolysis of **3E** and **4E**; however no methylated pinacol ether similar to that described above for ether **D** was detected. It has been suggested²⁰ that the ether radical derived from **E** may fragment according to eqn. (13).



If this fragmentation is much faster than the dimerization reactions it might explain the lack of cross-coupling products. This might mean that the exchange reaction is not involved in the formation of acetone and that the characterization of the exchange reaction in **3E** and **4E** as fast may therefore be misleading.

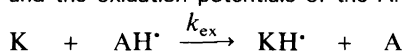
The photoreduction of the ketones **1-4** with toluene is of the slow exchange type. However, the ratio between K_2H_2 , $KHAH$ and A_2H_2 is not the expected 1:2:1 ratio (Table 2). This deviation from the statistical 1:2:1 ratio may be due to the somewhat different coupling rate constants k_7 , k_8 and k_9 .

In the rate-determining step the excited triplet state of the ketone 3K abstracts a hydrogen atom from the donor AH_2 [eqn. (2)] with formation of a triplet radical pair $KH\cdot$ and $AH\cdot$ in a solvent cage. As the radicals are formed as a triplet pair a spin flip must take place to give a singlet pair before coupling occurs. It has been shown¹⁵ that the rate of the spin inversion is generally slow compared with the diffusion out of the solvent cage. The radical coupling therefore predominantly takes place in solution; the spin flipping has, however, been reported to be faster than diffusion in some cases.¹⁰

Table 5. The product composition (mol %) of the photolysis of 4-methylacetophenone (**1**) and benzhydrol (**C**) as a function of the photolysis time.

Photolysis time/h	Product composition (mol %)							Conversion (%)
	K	AH ₂	A	K ₂ H ₂	KAH ₂	A ₂ H ₂		
1.5	61.4	29.0	0	1.80	1.64	1.33	9.5	
3.0	59.2	25.5	0	2.71	2.81	2.15	15.3	
4.5	59.5	24.3	0	2.82	3.00	2.28	16.2	
8.5	54.0	22.66	0	4.27	4.34	3.04	23.3	
10.5	53.0	22.40	0	4.60	4.68	3.33	25.2	
12.5	52.8	22.63	0	2.29	4.61	3.38	20.6	

Table 6. Correlation of the relative rate of the exchange reaction k_{ex} as a function of the reduction potentials of the ketones and the oxidation potentials of the AH^{\cdot} .^a



V/SCE	(-1.11) ^b A	(-1.0) ^c B	(-1.0) ^d C	(-0.45) ^b D	(-0.45) ^b E	(+0.7) ^d F
(-2.19) 1	Fast	Medium	Slow	Slow	Slow	Slow
(-2.14) 2	Fast	X	Medium	Slow	Slow	Slow
(-1.71) 3	Fast	Fast	X	Slow	Fast	Slow
(-1.29) 4	Fast	Fast	Fast	Medium	Fast	Slow

^aHalf-cell reaction: $AH^+ + e^- = AH^{\cdot}$. ^bWayner *et al.* (ref. 17). ^cEstimation based on data in ref. 17 (see the text). ^dWayner *et al.* (ref. 16).

The methylated pinacol **5**, $[(PhC(CF_3)(OCH_3))_2]$, was prepared by the addition of an excess of diazomethane to a solution of trifluoroacetophenone pinacol **44** (100 mg) in CH_2Cl_2 at 0°C. After the addition of diazomethane 20 ml of HBF_4 ether complex (Aldrich) were transferred to the solution. **5**: MS: (m/z , %): 190 (14), 189 (100), 175 (10), 170 (4), 127 (7), 119 (7), 105 (28), 91 (4), 77 (13), 69 (6).

Apparatus. Products were identified by GC-MS carried out on a Hewlett Packard 5890 A gas chromatograph equipped with a 5971A MSD. An HP1 12 m, 0.25 mm internal diameter non-polar GC-column was used, injection temperature 250°C, helium flow 1.0 ml min⁻¹, temperature program 70°C for 2 min to 300°C, rate 10°C min⁻¹.

Benzophenone pinacol decomposed to benzophenone on the injector block. Photolysis mixtures containing benzophenone pinacol was therefore analysed, besides by GC, by HPLC, performed on a RP-18 Nuclosil column with 20% water-80% methanol as the eluent. The detection wavelength was 230 nm.

Photolysis. All photolyses were run on samples in Pyrex tubes which had been degassed by several freeze-thaw cycles. The tube was irradiated by a focused light beam from a Oriel 500 W Hg lamp installed in a Oriel light house. The light passed through a water filter and a Scott 305 nm cut-off filter. In a typical photolysis 2 mmol of ketone were mixed with 1 mmol of the hydrogen atom donor. No solvents were used. However, in order to have a homogeneous solution in the photolysis with benzhydrol (**C**) 0.5 ml of acetonitrile was added. The samples were irradiated from 1-8 h.

Identification of products. MS: (m/z , %): **11**: 209 (5), 137 (4), 136 (40), 135 (100), 134 (4), 121 (15), 119 (11), 91 (15), 65 (6), 43 (100). **1B**: 136 (19), 135 (86), 122 (16), 121 (20), 119 (7), 105 (7), 91 (10), 77 (8), 65 (4), 43 (100). **1C**: 184 (30), 183 (40), 165 (5), 136 (12), 135 (100), 119 (6), 105 (50), 91 (8), 77 (28), 43 (39). **22**: 123 (5), 122 (55), 121 (86), 120 (4), 107 (10), 105 (16), 78 (8), 77 (18), 51 (8), 43 (100). **2C = 3B**: 184 (33), 183 (100), 165 (7), 121 (30), 106 (8), 105 (84), 78 (7), 77 (43), 51 (7), 43 (32). **33**:

Decomposes to benzophenone in the GC injector. **44**: 176 (42), 175 (99), 156 (15), 127 (17), 106 (9), 105 (100), 78 (10), 77 (34), 69 (14), 51 (10). **1D**: 137 (2), 136 (29), 135 (100), 121 (3), 119 (3), 105 (5), 103 (2), 91 (6), 77 (5), 43 (29). **2D**: 136 (9), 135 (100), 105 (6), 103 (2), 91 (3), 78 (2), 77 (7), 51 (2), 43 (10), 32 (2). **3D**: 183 (12), 165 (2), 136 (12), 135 (100), 103 (2), 78 (2), 77 (18), 51 (3), 43 (13). **4D**: 136 (19), 135 (100), 105 (23), 103 (6), 91 (3), 78 (6), 77 (23), 69 (3), 51 (5), 43 (33). **DD**: 135 (15), 122 (70), 121 (100), 120 (6), 107 (12), 105 (26), 78 (13), 77 (20), 51 (8), 43 (71). **1E**: 135 (18), 119 (4), 105 (2), 91 (7), 77 (2), 74 (4), 73 (100), 65 (3), 43 (28), 41 (2). **2E**: 194 (2), 135 (2), 122 (8), 121 (100), 105 (88), 91 (5), 78 (3), 77 (9), 51 (83), 43 (42), 41 (2). **1F**: 194 (2), 122 (6), 121 (100), 105 (10), 92 (10), 91 (15), 77 (11), 65 (6), 63 (3), 51 (4), 43 (41). **2F**: 122 (7), 121 (100), 105 (6), 92 (12), 91 (17), 77 (10), 65 (7), 51 (4), 43 (56). **3F**: 256 (5), 184 (16), 183 (100), 165 (4), 106 (6), 105 (79), 91 (9), 77 (40), 65 (4), 51 (6). **4F**: 175 (42), 127 (7), 105 (56), 93 (7), 92 (100), 91 (68), 77 (18), 69 (7), 65 (13), 51 (7).

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