Green Chemistry Module for Organic Chemistry

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Topic: Atom Economy

A Measure of the Efficiency of a Reaction

Efficiency of a Reaction

- Percentage yield

Theoretical yield = (moles of limiting reagent)(stoichiometric ratio; desired product/limiting reagent)(MW of desired product)

Percentage yield= (actual yield/theoretical yield) X 100

Table 1 **Reagents Table**

Reagent	MW	Weight Used (g)	Theoretical Moles Needed	Moles Used	Density	Bp (°C)
1 C_4H_9OH	74.12	0.80	0.0108	0.0108	0.810	118
2 NaBr	102.91	1.33	0.0108	0.0129		
3 H_2SO_4	98.08	2.0	0.0108	0.0200	1.84	

Table 2 **Desired Product Table**

Compound	MW	Theoretical Yield (Moles)	Theoretical Yield (Grams)	Actual Yield (Grams)	% Yield	Density	Bp (°C)
4 C_4H_9Br	137.03	0.011	1.48 (100%)	1.20	81	1.275	101.6

$$\underset{1}{CH_3CH_2CH_2CH_2OH} + \underset{2}{NaBr} + \underset{3}{H_2SO_4} \longrightarrow \underset{4}{CH_3CH_2CH_2CH_2Br} + \underset{5}{NaHSO_4} + \underset{6}{H_2O}$$

Equation 1a

$CH_3CH_2CH_2CH_2OH$ +	$NaBr$ +	H_2SO_4	$\longrightarrow$	$CH_3CH_2CH_2CH_2Br$ +	$NaHSO_4$ +	H_2O
1	2	3		4	5	6
0.08g	1.33	2.0		1.48 g (theoretical yield)		
0.0108mole	0.0129	0.0200		0.0108 mole (theoretical yield)		

Compound 1 is the limiting reagent

Suppose the actual yield is 1.20 g of compound 4.

Percentage yield= (actual yield/theoretical yield) X 100

= (1.20 g/1.48 g) X 100 = 81%

Atom Economy in a Substitution Reaction

Equation 1b

$$\underset{1}{H_3C{-}CH_2{-}CH_2{-}CH_2{-}OH} + \underset{2}{Na{-}Br} + \underset{3}{H_2SO_4} \longrightarrow \underset{4}{H_3C{-}CH_2{-}CH_2{-}CH_2{-}Br} + \underset{5}{NaHSO_4} + \underset{6}{H_2O}$$

Table 3 **Atom Economy of Equation 1**

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 C_4H_9OH	74	4C,9H	57	HO	17
2 NaBr	103	Br	80	Na	23
3 H_2SO_4	98	—	0	2H,4O,S	98
Total 4C,12H,5O,BrNaS	275	4C,9H,Br	137	3H,5O,Na,S	138

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (137/275) X 100 = 50%

1 2 3 4 5 6

Table 4 Experimental Atom Economy of Equation 1: Based on Actual Quantities of Reagents Used

Reagents Formula	Weight of Reagent (FW X moles used)	Utilized Atoms	Weight of Utilized Atoms (FW X moles)	Unutilized Atoms	Weight of Unutilized Atoms (FW X moles)
1 C_4H_9OH	74.0 X .0108 = .80	4C,9H	57 X .0108= .62	HO	17 X .0108=.18
2 NaBr	103 X .0129= 1.33	Br	79.9X .0129=1.03 79.9X .0108=~~0.86~~ excess 0.17	Na	23 X .0129=.30 excess ~~0.17~~ subtotal 0.47
3 H_2SO_4	98 X .0200= 2.0	—	0.00	2H,4O,S	98.1 X .0200=1.96
Total 4C,12H,5O,BrNaS	4.13	4C,9H,Br	1.48	3H,5O,Na,S	2.61

% Experimental Atom Economy = (mass of reactants utilized in the desired product/total mass of all reactants) X 100
= (theoretical yield/total mass of all reactants) X 100
= (1.48 g/4.13 g) X 100 = 36%

% Yield X Experimental Atom Economy

% Yield X Experimental Atom Economy = (actual yield/theoretical yield) X (mass of reactants utilized in the desired product/total mass of all reactants) X 100

%PE ·EAE= (actual yield/theoretical yield) X (theoretical yield/total mass of all reactants) X 100 = (actual yield/total mass of all the reactants) X100

= (1.20 g/4.13 g) X 100 = 29%

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, innocuous when used.

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

6. Energy requirements should recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

10. **Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.**
11. **Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.**
12. **Substances and the form of a substance used in a chemical process should chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.**

Atom Economy in Elimination Reactions

- Equation 2

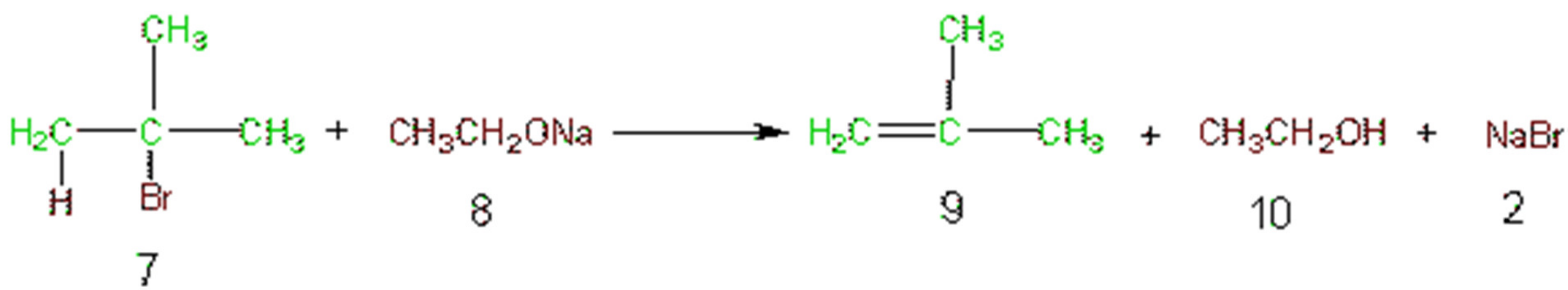
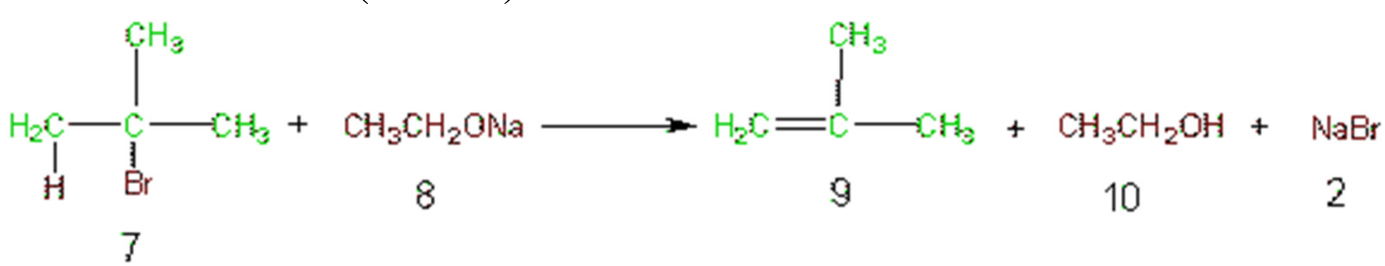


Table 5 Atom Economy Equation 2

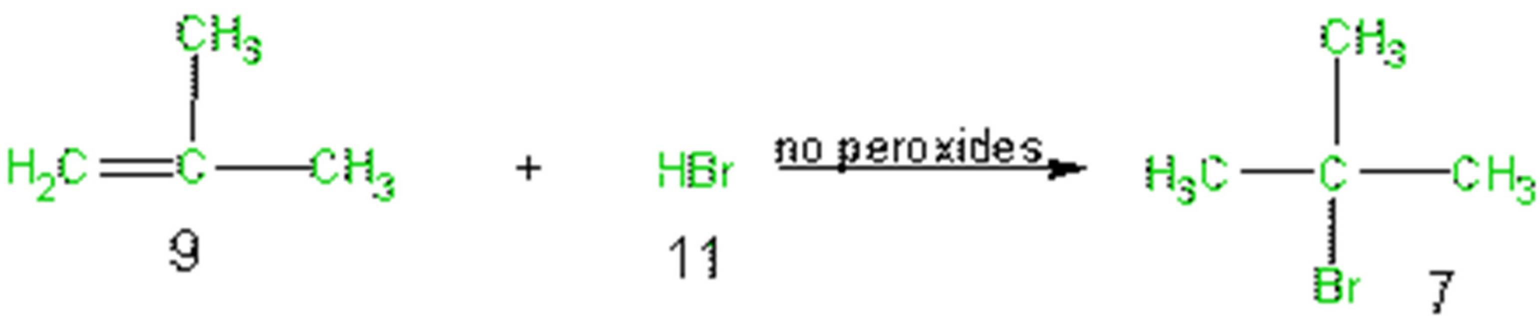
Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
7 C_4H_9Br	137	4C,8H	56	HBr	81
8 C_2H_5ONa	68	—	0	2C,5H,O,Na	68
Total 6C,14H,O,Br,Na	205	4C,8H	56	2C,6H,O,Br,Na	149

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (56/205) X 100 = 27%



Atom Economy in Addition Reactions

- Equation 3



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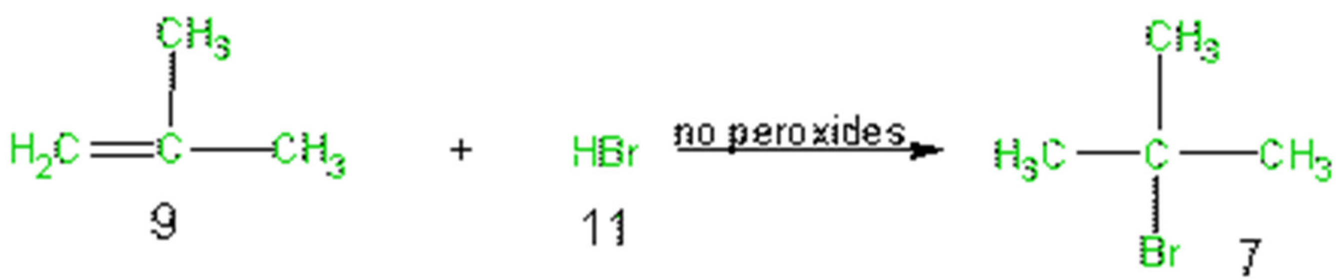
11
7

Table 6 Atom Economy **Equation 3**

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
9 C_4H_8	56	4C,8H	56	___	0
11 HBr	81	HBr	81	___	0
Total 4C,9H,Br	137	4C,9H,Br	137	___	0

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (137/137) X 100 = 100%



Atom Economy in Rearrangement Reactions

- Equation 4

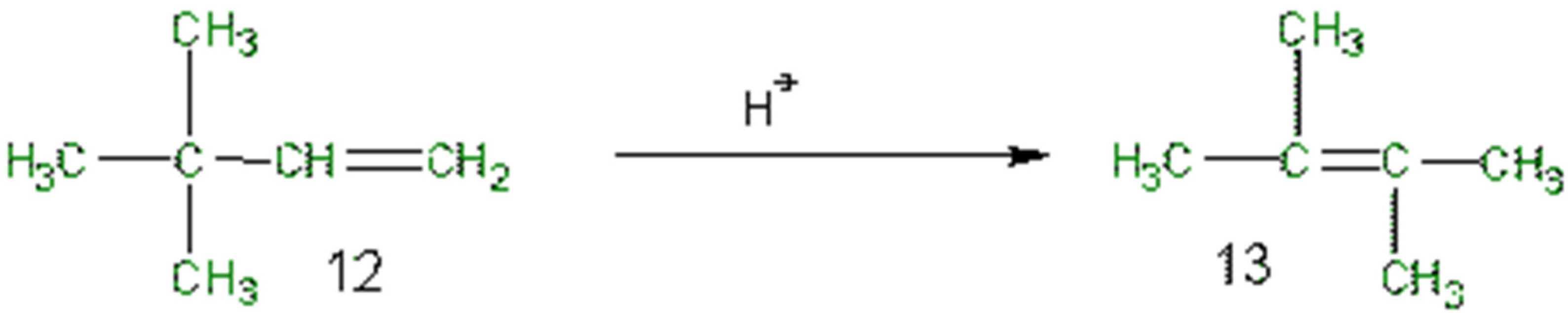
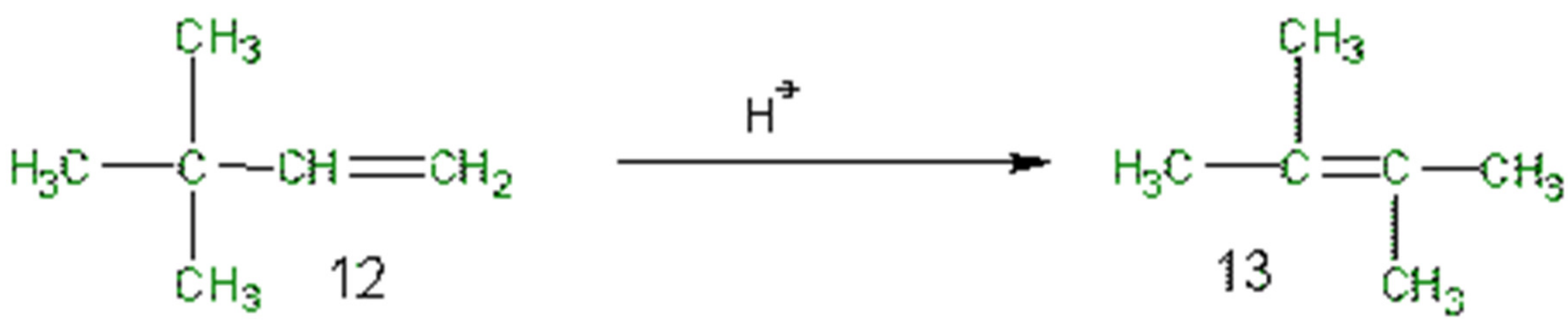


Table 7 Atom Economy Equation 4

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
12 C_6H_{12}	84	6C,12H	84	—	0
Total 6C,12H	84	6C,12H	84	—	0

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (84/84) X 100 = 100%



Scheme 1 Atom Economy in The Clorohydrin Route to Ethylene Oxide

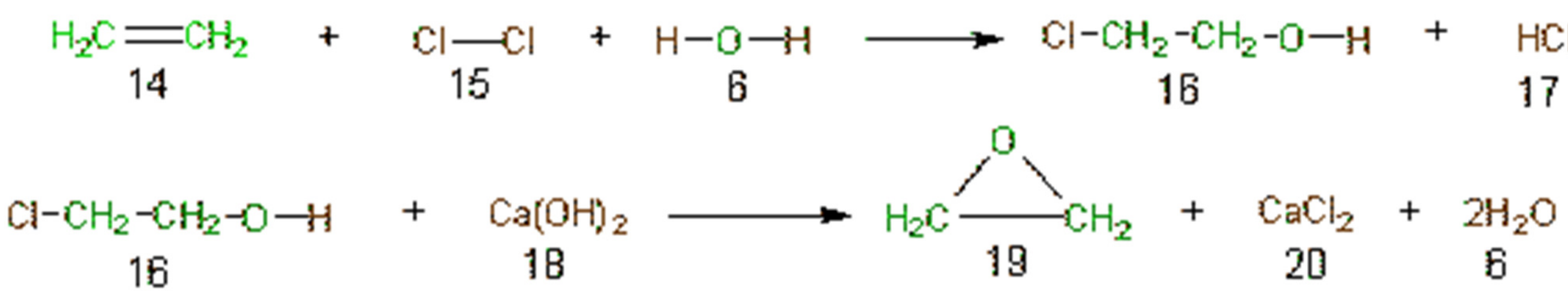


Table 8 Atom Economy of Scheme 1, The Clorohydrin Route to Ethylene Oxide

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
14 C_2H_4	28	2C,4H	28	—	0
15 Cl_2	71	—	0	2Cl	71
6 H_2O	18	O	16	2H	2
18 $Ca(OH)_2$	72	—	0	Ca,4H,2O	72
Total 2C,8H,3O,Ca,2Cl	189	2C,4H,O	44	6H,2O,Ca,2Cl	145

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100

= (44/189) X 100 = 23%

Scheme 2 Atom Economy in The Catalytic Route to Ethylene Oxide

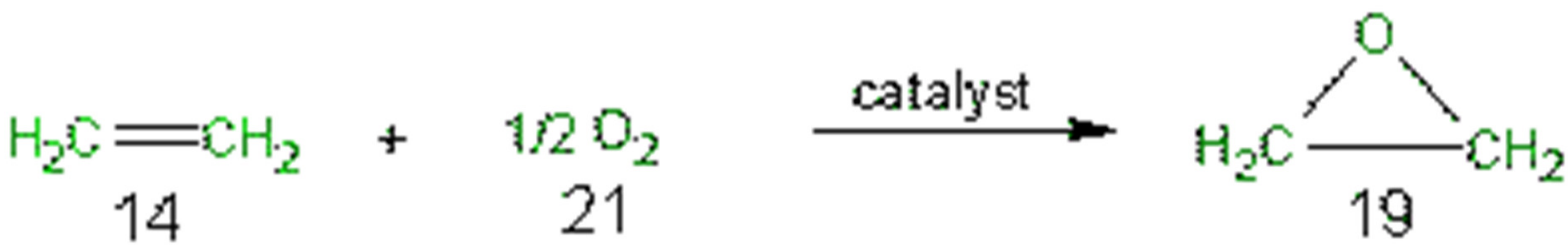
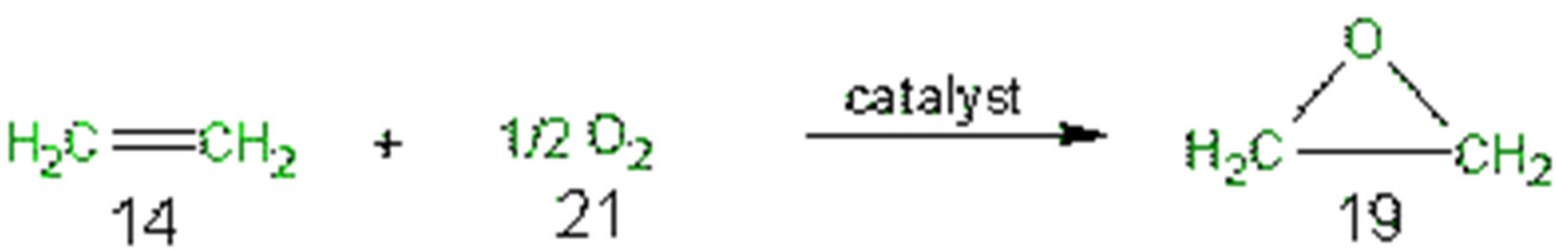


Table 9 Atom Economy of Scheme 2, The Catalytic Route to Ethylene Oxide

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
14 C_2H_4	28	2C,4H	28	—	0
21 1/2 O_2	16	O	16	—	0
Total 2C,4H,1O1	44	2C,4H,O	44	—	0

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (44/44) X 100 = 100%



The Boots Synthesis of Ibuprofen

Scheme 3, Atom Economy

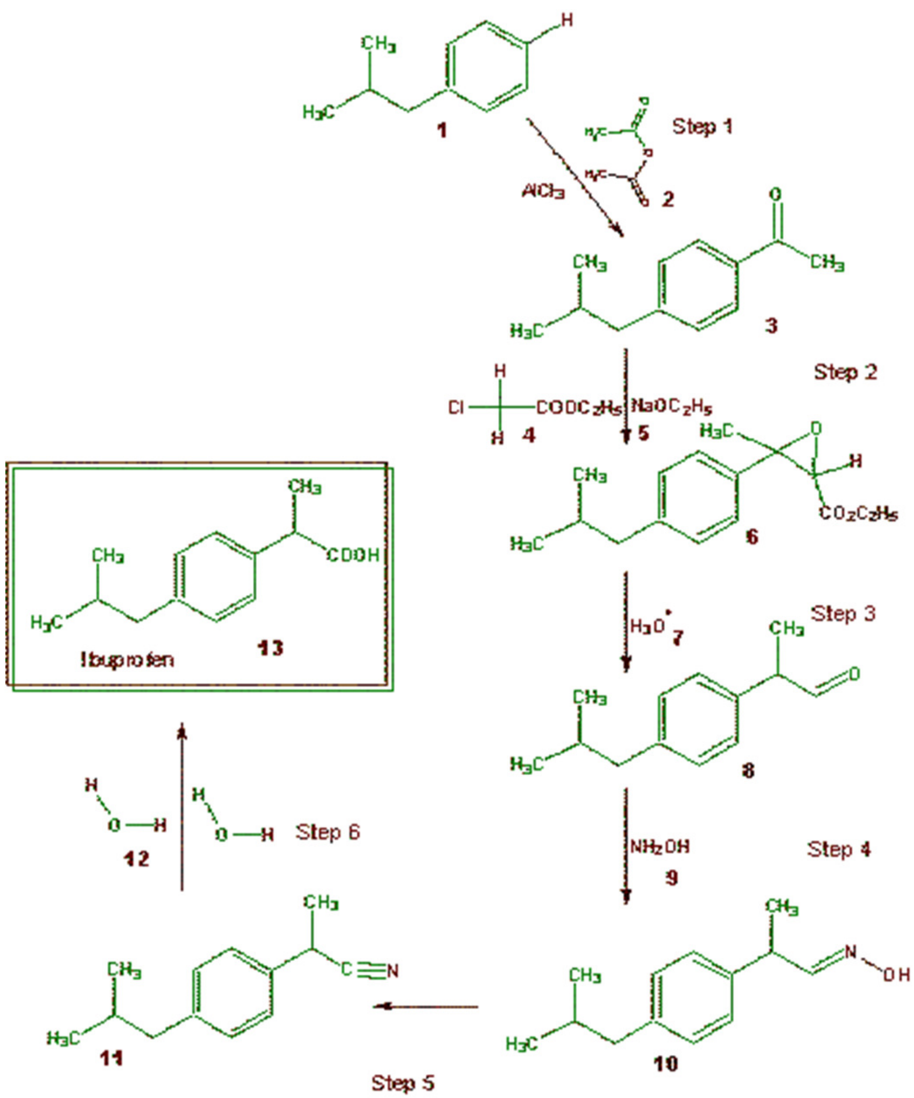


Table 10 Atom Economy of Scheme 3, the Boots Company Synthesis of Ibuprofen

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 $C_{10}H_{14}$	134	10C,13H	133	H	1
2 $C_4H_6O_3$	102	2C,3H	27	2C,3H,3O	75
4 $C_4H_7ClO_2$	122.5	C,H	13	3C,6H,Cl,2O	109.5
5 C_2H_5ONa	68	—	0	2C,5H,O,Na	68
7 H_3O	19	—	0	3H,O	19
9 NH_3O	33	—	0	3H,N,O	33
12 H_4O_2	36	H,2O	33	3H	3
Total 20C,42H,N,10O, Cl,Na	514.5	Ibuprofen 13C,18H,2O	Ibuprofen 206	Waste Products 7C,24H,N,8O, Cl,Na	Waste Products 308.5

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (206/514.5) X 100 = 40%

The BHC Synthesis of Ibuprofen

Scheme 4, Atom Economy

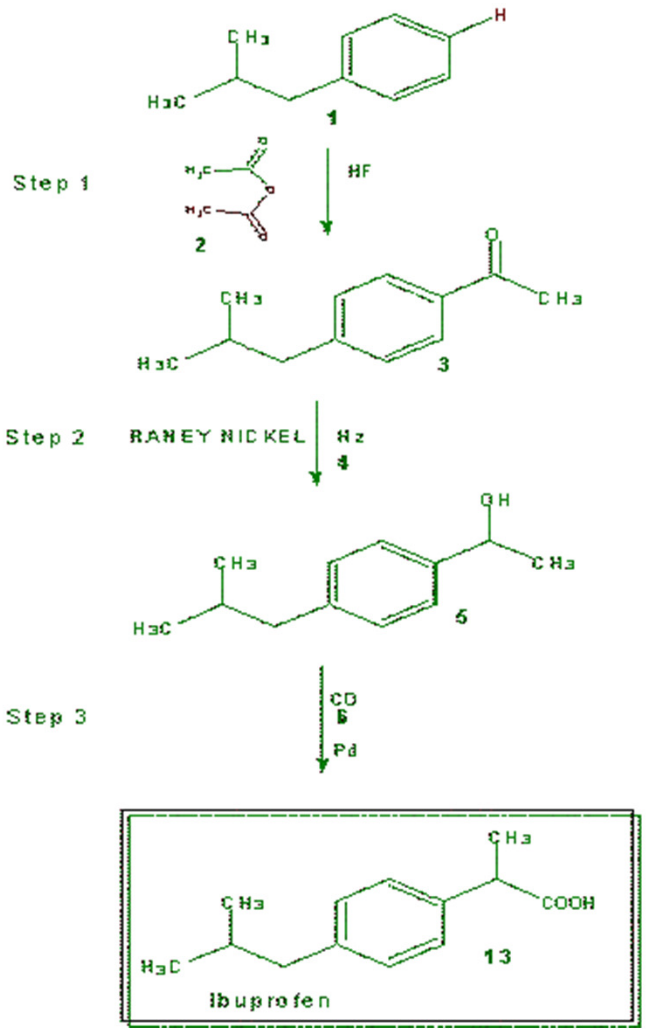


Table 11 Atom Economy of Scheme 4, the BHC Company Synthesis of Ibuprofen

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 $C_{10}H_{14}$	134	10C,13H	133	H	1
2 $C_4H_6O_3$	102	2C,3H,O	43	2C,3H,2O	59
4 H_2	2	2H	2	——	0
6 CO	28	CO	28	——	0
Total 15C,22H,4O	266	Ibuprofen 13C,18H,2O	206	Waste Products 2C,3H,2O	60

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (206/266) X 100 = 77%