Synthetic Methods and Reactions; 98[1]. Improved Solid Super Acid (Nafion-H) Catalyzed Rupe Rearrangement of α-Ethynyl Alcohols to α,β-Unsaturated Carbonyl Compounds

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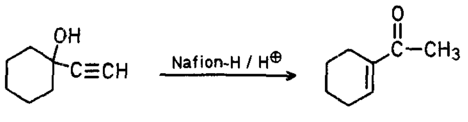
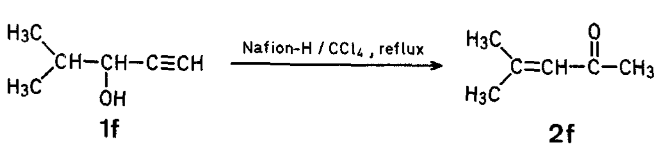
α,β-Unsaturated ketones are versatile intermediates in organic synthesis[2-5]. One of the most feasible routes to α,β-unsaturated carbonyl compounds is the acid catalyzed rearrangement of alkynyl tertiary alcohols (Rupe reaction)[6-9]. The major drawback of the Rupe reaction is that the formed α,β-unsaturated products can readily undergo subsequent acid-catalyzed polymerization[10] and that substantial amounts of side products, e.g. vinylacetylenes and aldehydes are also formed[11]. Consequently, the method is generally less than satisfactory.

We now report a significant improvement of the Rupe-rearrangement of α-acetylenic tertiary alcohols **1** to the corresponding α,β-unsaturated ketones **2** using Nafion-H[12], a solid superacidic perfluorinated resinsulfonic acid catalyst. The method provides good yields with little or no by-products formed, easy work-up for the isolation of the products and ready regeneration of the catalyst without loss of activity. The results are summarized in Table, are better than or comparable to those obtained using mercury-impregnated Dowex-50 resin (see Table and Ref.[14]).



1b **2b**



1f **2f**

1-Acetylcyclooctene (2e):

A mixture of 1-ethynylcyclooctanol (3.04 g, 20 mmol) and Nafion-H (1 g) in tetrachloromethane (30 ml) is refluxed till completion of the reaction (14 h), as monitored by T.L.C. (silica gel plates with benzene as an eluent) and/or by G.L.C. analysis (condition: glass capillary column 25 ft × 0.25 nm i.d., OV 101; 100 °C). The solid resinsulfonic acid is then filtered off, and the solvent is evaporated. The crude product is purified by distillation giving 1-acetylcyclooctene (**2e**); yield: 2.67 g (88%); b.p. 105–107 °C/10.5 torr. Physical and spectral characteristics are identical with those of an authentic sample.

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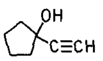
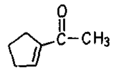
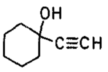
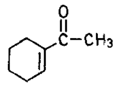
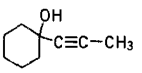
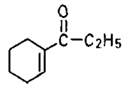
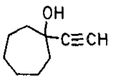
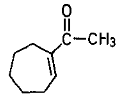
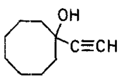
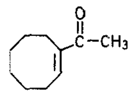
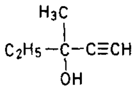
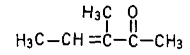
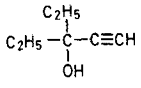
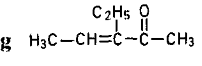
Table. Nafion-H Catalyzed Rupe Rearrangement

α-Ethynyl alcohol		α, β-Unsaturated carbonyl compound		Reaction time [h]	Yield[a] [%]	b.p. [°C]/torr	
						found	reported
1a		**2a**		15	60 (50)[b]	58°/10	67°/16[13]
1b		**2b**		15	84 (87)[c]	92°/20	96–98°/22[14]
1c		**2c**		17	75 (—)	97–99°/15	—[d]
1d		**2d**		10	78 (<47)[b]	105°/20	90–97°/17[13]
1e		**2e**		14	88 (—)	105–107°/12	108°/12[15]
1f	 $C_2H_5-C(CH_3)(OH)-C\equiv CH$	**2f**	 $H_3C-CH=C(CH_3)-C(=O)-CH_3$	16	83 (—)[e]	62–63°/50	62–65°/50[11]
1g	 $C_2H_5-C(C_2H_5)(OH)-C\equiv CH$	**2g**	 $H_3C-CH=C(C_2H_5)-C(=O)-CH_3$	16	80 (84)[c]	73–75°/50	147–153°/760[14]

[a] Yield of isolated product of purity ≥96% (G.L.C.); I.R. and ^{1}H-N.M.R. spectra of isolated products were in accord with those of authentic samples. Values in brackets are yields previously reported.

[b] Reflux in 90% formic acid.

[c] Reflux in 90% acetic acid in the presence of mercury impregnated Dowex-50 resin.

[d] ^{1}H-N.M.R. ($CDCl_3$): $\delta = 1.05$ (t, 3H, $J = 7$ Hz); 1.65 (br, 4H); 2.25 (br, 4H); 2.60 ppm (br, 3H); cf. Ref.[16].

[e] Reflux in formic acid gave a mixture of the ketone, the vinylic acetylene, and the aldehyde.

3-Methyl-3-pentene-2-one (2f):

A mixture of 3-methyl-1-pentyn-3-ol (**1f**; 2.94 g, 30 mmol) and Nafion-H catalyst (1 g) in tetrachloromethane (30 ml) is heated to reflux till the reaction is completed (16 h), as monitored by T.L.C. The catalyst is filtered off and the solvent is evaporated. The crude product is further purified by distillation which affords 3-methyl-3-pentene-2-one; yield: 2.35 g (80%); b.p. 60–63 °C/50 torr. Physical and spectral characteristics are identical with those of an authentic sample.

Regeneration of Nafion-H Catalyst:

The used catalyst after filtration is washed with tetrachloromethane. Repeating the preparation of 3-methyl-1-pentyne-3-ol with the regenerated catalyst gave identical results with those using freshly activated catalyst.

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[1] For part 97, see: G. A. Olah, S. C. Narang, A. G. Luna, *Synthesis*, submitted.

[2] H. O. House, *Modern Synthetic Reactions*, 2nd Edn., W. A. Benjamin, New York, 1972, pp. 492–628.

[3] J. ApSimon, *The Total Synthesis of Natural Products*, Vol. I–III, Wiley-Interscience, New York, 1973.

[4] J. d'Angelo, *Tetrahedron* **32**, 2979 (1976).

[5] A. J. Waring in *Comprehensive Organic Chemistry*, Vol. I, J. F. Stoddart Ed., Pergamon Press, Elmsford, New York, 1979, pp. 1017–1104.

[6] H. Rupe et al., *Helv. Chim. Acta* **9**, 672 (1926); **11**, 449, 656, 965 (1928).

[7] R. Heilmann, R. Glenat, *Ann. Chim. (Paris)* **8**, 175 (1963).

[8] S. Swaminathan, K. V. Narayanan, *Chem. Rev.* **71**, 429 (1971).

[9] L.-I. Olsson, A. Claesson, C. Bogentoft, *Acta Chem. Scand.* **27**, 1629 (1973).

[10] M. F. Ansell, J. W. Hancock, W. J. Hickinbottom, *J. Chem. Soc.* **1956**, 911.

[11] R. W. Hasbrouck, A. D. A. Kiessling, *J. Org. Chem.* **38**, 2103 (1973).

[12] Nafion 501 as the potassium salt was obtained from the DuPont Co.

[13] I. Heilbron, E. R. H. Jones, J. B. Toogood, B. C. L. Weedon, *J. Chem. Soc.* **1949**, 1827.

[14] M. S. Newman, *J. Am. Chem. Soc.* **75**, 4740 (1953).

[15] N. Jones, H. T. Taylor, E. Rudd, *J. Chem. Soc.* **1961**, 1342.

[16] B. M. Trost, M. J. Bogdanowicz, *J. Am. Chem. Soc.* **95**, 5311 (1973).

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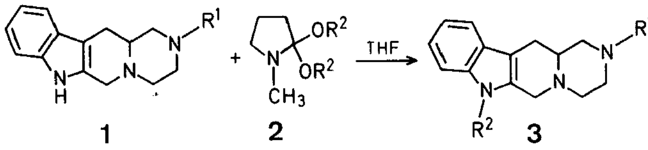
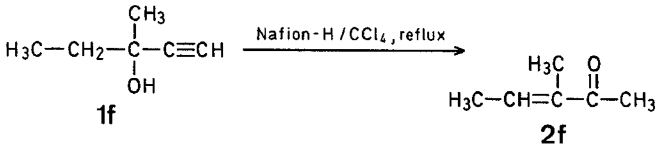
S. K. Agarwal, A. K. Saxena, N. Anand, *Synthesis* **1981** (6), 465-466:
The formula scheme (p. 465) should be:

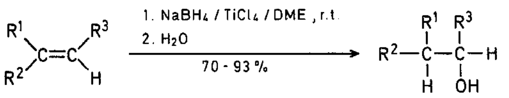


G. A. Olah, A. P. Fung, *Synthesis* **1981** (6), 473-474:
The reaction scheme **1f**→**2f** should be:



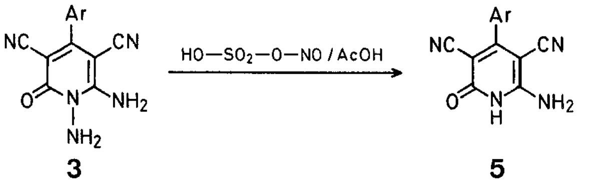
2f

Abstract 6127, *Synthesis* **1981** (6), 498:
The formula scheme **1**→**2** should be:

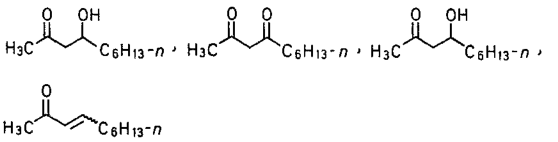


1 2

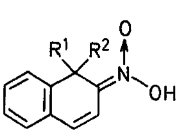
J. L. Soto, C. Seoane, P. Zamorano, F. J. Cuadrado, *Synthesis* **1981** (7), 529-530:
The reaction scheme **3**→**5** (p. 529) should be:



A. B. Smith, III, P. A. Levenberg, *Synthesis* **1981** (7), 567-570:
The heading for Table 1 (p. 567) should be Oxidation of 4-Hydroxy-2-decanone (**3a**) under various conditions. The structure given in the first column of Table 1 should be, respectively:

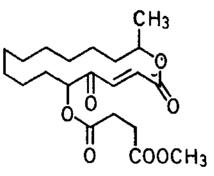


G. Bartoli, M. Bosco, A. C. Boicelli, *Synthesis* **1981** (7), 570-572:
The structure of products **4aa-cd** (p. 571) should be:



4aa-cd

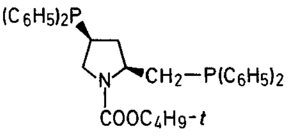
Y.-H. Lai, *Synthesis* **1981** (8), 585-604:
The structure of compound **31** (p. 588) should be:



31

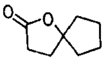
M. R. H. Elmoghayar, M. K. A. Ibraheim, A. H. H. Elghandour, M. H. Elnagdi, *Synthesis* **1981** (8), 635-637:
The title compounds **5** are thiazolo[3,2-*a*]pyridine derivatives.

A. Kleemann, J. Martens, M. Samson, W. Bergstein, *Synthesis* **1981** (9), 740-741:
The structure of compound **6** should be:



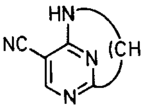
(–)-BPPM (**6**)

Abstract 6236, *Synthesis* **1981** (11), 922:
The structure of product **3** should be:

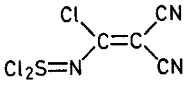


3

F. Freeman, *Synthesis* **1981** (12), 925-954:
The structures of compounds **162** and **163** (p. 937) should be:



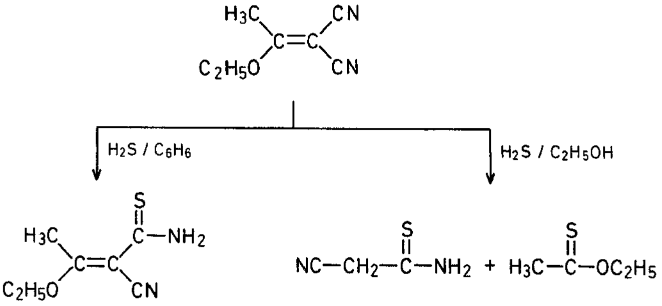
162



163

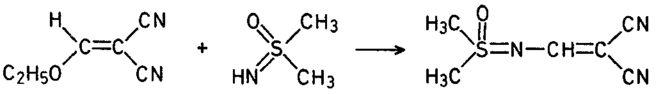
The text of the first paragraph starting on p. 943 (right-hand column) should be: Hydrogen sulfide reacts with 1-ethoxyethylidenemalononitrile, the methyl homolog of **9**, to give different products depending on the solvent used[293].

The following formula scheme should be:



256 **257** **258**

The first formula scheme on p. 944 (right-hand column) should be:

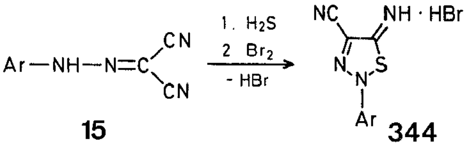


9 **275** **276**

The last sentence on page 946 (left-hand column) should be: An analogous reaction with cyclopentadiene leads to the 2-azabicyclo[2.2.1]heptene (**299**) and with cyclohexadiene to 2-azabicyclo[2.2.2]octene (**301**) derivatives[317].

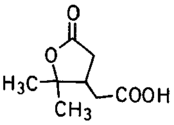
The correct names for compounds **336** and **337** (p. 949) are 5-hydroxy-2-oxo-3-phenylazo-1,2,3,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**336**) and *α*-(*N*-methylphenylhydrazono)-cyanoacetamidrazone (**337**).

The formula scheme **15**→**344** (p. 950) should be:



15 **344**

A. Guzmán, S. Mendoza, E. Diaz, *Synthesis* **1981** (12), 989-991:
The structure of compound **6** (p. 990) should be:



6

Abstract 6269, *Synthesis* **1981** (12), 1015:
The legend under the formula scheme should read: n = 1, 2, 3.