0–5°. Three grams of chlorohydroxyoctadecanols, m. p. 61–62°, was obtained (55% yield).

Anal. Calcd. for $C_{18}H_{37}O_2Cl$: C, 67.4; H, 11.6; Cl, 11.0; OH, 10.6. Found: C, 67.5; H, 11.8; Cl, 10.5; OH, 10.2.

Preparation of 9,10-Dihydroxyoctadecanol (1,9,10-Octadecanetriol).—Five grams of 9,10-epoxyoctadecanol, m. p. 54–54.5°, was heated for two hours at 100° with 100 ml. of glacial acetic acid. The solution was then poured into 1000 ml. of water, and the upper semi-solid layer was refluxed with 0.2 *N* alcoholic potassium hydroxide for forty-five minutes. The alkaline solution was poured into 1000 ml. of cold water, and the precipitate was filtered off and washed free of alkali. A yield of 4.7 g. of 9,10-dihydroxyoctadecanol, m. p. 84.5–86°, was obtained.

Determination of Epoxy Oxygen.—The method of Nicolet and Poulter[6] was employed, using a 0.2 *N* solution of dry hydrogen chloride in anhydrous ether and a two-hour reaction time.

Determination of Peroxides.—Wheeler's method[7] was employed.

(6) Nicolet and Poulter, THIS JOURNAL, **52**, 1186 (1930).

(7) Wheeler, *Oil and Soap*, **9**, 89 (1932).

Summary

1. A large-scale laboratory procedure for the preparation of perbenzoic acid, based upon the work of Jorissen,[2] has been developed. Benzaldehyde in acetone solution was oxidized with air in the presence of ultraviolet radiation to yield perbenzoic acid in 40–45% yield. This solution was satisfactory for the epoxidation of oleic acid, methyl oleate, and oleyl alcohol.

2. Raymond's method[3] for the coöxidation of oleic acid and benzaldehyde has been improved. The mole ratio of benzaldehyde to oleic acid has been reduced from 27:1 to 10:1, and the isolation of 9,10-epoxystearic acid has been simplified.

3. 9,10-Epoxyoctadecanol, m. p., 54–54.5°, and a mixture of 9,10- and 10,9-chlorhydroxyoctadecanols, m. p 61–62°, were prepared for the first time.

PHILADELPHIA, PA. RECEIVED AUGUST 31, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL CO., INC.]

Catalytic Hydrogenation of Pyridinyl and Quinolinyl Esters of Sulfonic Acids

BY CHESTER J. CAVALLITO AND THEODORE H. HASKELL

The authors have recently[1] described the catalytic hydrogenation of pyridinols, quinolinols and their esters with aromatic carboxylic acids. The aromatic sulfonic acid esters have now been prepared and it has been found that some types behave differently on hydrogenation than the analogous carboxylic acid esters.

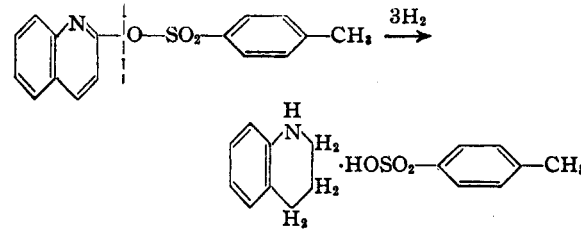
Hydrogenation was carried out in a dioxane solution at 55° with a palladium catalyst as described in the previous publication. The pyridinol and quinolinol esters of *p*-toluenesulfonic acid served as type compounds in this investigation.

Catalytic hydrogenation of the 5-, 6-, 7- and 8-(*p*-toluenesulfonoxy)-quinolines yielded primarily the corresponding 1,2,3,4-tetrahydro derivatives. It will be recalled that the 5-, 6- and 7-benzoxyquinolines behave in a similar manner. Whereas 8-benzoxyquinoline after hydrogenation undergoes rearrangement to N-benzoyl-1,2,3,4-tetrahydro-8-quinolinol, 8-(*p*-toluenesulfonoxy)-1,2,3,4-tetrahydroquinoline was stable and did not undergo rearrangement. This is similar to the behavior of the *ortho* aminophenyl esters.[2]

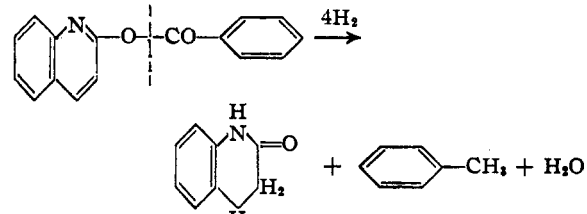
Hydrogenation of the 2- and 3-(*p*-toluenesulfonoxy)-quinolines yielded the same end-product, a water-soluble crystalline compound which was identified as the 1,2,3,4-tetrahydroquinoline salt of *p*-toluenesulfonic acid. Three molar equivalents of hydrogen were absorbed during the hydrogenation.

(1) Cavallito and Haskell, THIS JOURNAL, **66**, 1166 (1944).

(2) Raiford and Shelton, *ibid.*, **65**, 2048 (1943).



This behavior is considerably different from that of 2-benzoxyquinoline which underwent cleavage at a different point[1]



or that of 3-benzoxyquinoline which yielded the corresponding 1,2,3,4-tetrahydro derivative.

The 4-(*p*-toluenesulfonoxy)-quinoline was too unstable to allow isolation in sufficiently pure form for hydrogenation.

With the observation that hydrogenolysis and hydrogenation reactions could proceed to yield the water soluble tetrahydroquinoline salt of *p*-toluenesulfonic acid, closer examination of the reduction products from the 5-, 6-, 7- and 8-esters showed the presence of small amounts of the water soluble salt along with the tetrahydro-

TABLE I

No.	Compound	Appearance	Crystn. solvent*	Yield, %	M. p., °C.	Nitrogen, % Calcd.	Found	Reduction product
1	2-Benzenesulfonoxyquinoline	Granular crystals	*a*	65	90	4.91	4.97	A[i]
2	2-(*p*-Toluenesulfonoxy)-quinoline	Prisms	*a*	58	82	4.68	4.78	19
3	3-(*p*-Toluenesulfonoxy)-quinoline	Prisms	*b*	81	90	4.68	4.86	19
4	5-(*p*-Toluenesulfonoxy)-quinoline	Prisms	*a*	73	85	4.68	4.88	12
5	6-(*p*-Toluenesulfonoxy)-quinoline	Needles	*c*	50	98	4.68	4.70	13
6	7-(*p*-Toluenesulfonoxy)-quinoline	Plates	*a* or *c*	85	116	4.68	4.94	14
7	8-(*p*-Toluenesulfonoxy)-quinoline	Prisms	*a*	62	115	4.68	4.53	15
8	2-(*p*-Toluenesulfonoxy)-pyridine	Prisms	*d*	55	53	5.62	5.60	
9	3-(*p*-Toluenesulfonoxy)-pyridine	Prisms	*b*	75	80	5.62	5.61	17
10	4-(*p*-Toluenesulfonoxy)-pyridine	Prisms	*b*	20	>70 dec.	5.62	5.30	16 & 17
11	2-(*p*-Toluenesulfonamido)-pyridine	Prisms	*a* or *f*	60	212	11.29	11.61	..
12	5-(*p*-Toluenesulfonoxy)-1,2,3,4-tetrahydroquinoline	Prisms	*c*	90±	106	4.62	4.32[h]	..
13	6-(*p*-Toluenesulfonoxy)-1,2,3,4-tetrahydroquinoline	Granular crystals	*d*	90±	109	4.62	4.50[h]	..
14	7-(*p*-Toluenesulfonoxy)-1,2,3,4-tetrahydroquinoline	Prisms	*c*	90±	100	4.62	4.34[h]	..
15	8-(*p*-Toluenesulfonoxy)-1,2,3,4-tetrahydroqunioline	Prisms	*c*	90±	76	4.62	4.51[h]	..
16	Pyridinium *p*-toluenesulfonate	Plates	*e* or *g*	..	116	5.57	5.43	..
17	Piperidinium *p*-toluenesulfonate	Plates	*f* or *g*	..	130	5.45	5.42	..
18	Quinolinium *p*-toluenesulfonate	Prisms	*f*	..	115	4.65	4.46	..
19	1,2,3,4-Tetrahydroquinolinium *p*-toluenesulfonate	Prisms	*e*	..	140	4.59	4.45[i]	..

* Crystallization solvents: [a] 95% ethanol, [b] 60% ethanol, [c] Skellysolve C, [d] Skellysolve B–benzene, [e] water, [f] dioxane, [g] alcohol–ether. [h] Calcd. for $C_{16}H_{17}O_3NS$: C, 63.37; H, 5.61. Found, 5-isomer: C, 63.78; H, 5.65; 6-isomer: C, 63.41; H, 5.51; 7-isomer: C, 63.66; H, 5.30; 8-isomer: C, 63.56; H, 6.01. [i] Reduction product made alkaline, extracted with ether and the 1,2,3,4-tetrahydroquinoline obtained converted to the hydrochloride, m. p. 180°.

quinoline esters. The pure tetrahydro-esters did not undergo hydrogenolysis on further attempted reduction, indicating that any ester cleavage which occurs must take place previous to reduction of the pyridino ring. By using increasing quantities of catalyst, relatively more of the water soluble cleavage products could be formed at the expense of the tetrahydroquinoline esters.

The 4-(*p*-toluenesulfonoxy)-pyridine was stable enough to allow its isolation; however, upon standing for several days, some chemical change took place. This compound on hydrogenation readily absorbed one mole of hydrogen to yield the pyridine salt of *p*-toluenesulfonic acid. Further hydrogenation proceeded more slowly. The 2-(*p*-toluenesulfonoxy)-pyridine was more resistant to reduction than the corresponding quinolinyl ester. Of the pyridinyl esters, the most readily hydrogenated was 3-(*p*-toluenesulfonoxy)-pyridine which gave piperidinium *p*-toluenesulfonate.

It thus appears that sulfonic acid esters of pyridinols and quinolinols are reduced more or less readily to salts of the sulfonic acid with the hydrogenated pyridino ring bases in those instances in which the ester linkage is attached to the pyridino ring. If the ester is attached to the benzo ring as in the 5-, 6-, 7- or 8-positions of quinoline, hydrogenation of the pyridino ring proceeds with relatively little hydrogenolysis of the ester linkage.

The effect of the methyl group in the *p*-toluenesulfonic esters was considered by comparing 2-benzenesulfonoxyquinoline with the *p*-toluenesulfonic ester. Hydrogenation proceeded in the same manner; however, the benzenesulfonic ester was reduced more slowly.

No hydrogen absorption resulted in the attempted reduction of an amide, 2-(*p*-toluenesulfonamido)-pyridine.

Experimental[3]

Pyridinols and Quinolinols.—These were obtained as described in the previous publication.[1]

Pyridinyl and Quinolinyl Esters.—The ester of 4-pyridinol was prepared by the reaction of *p*-toluenesulfonyl chloride with the sodium salt of 4-pyridinol in dry ether.

The attempted preparation of the 4-quinolinol ester was carried out in the same manner. The other esters were prepared by heating the pyridinol or quinolinol with 1.2 to 1.5 molar equivalents of the acid chloride in pyridine on a steam-bath for one hour. After cooling, water was added and the precipitated crude ester was recrystallized from an organic solvent as indicated in Table I.

Isolation and Identification of Reduction Products. After hydrogenation was complete as measured by hydrogen absorption (one to two hours for 0.005 to 0.01 mole of compound), the catalyst was filtered off and the dioxane solvent removed under reduced pressure. The residue was extracted with 10 cc. to 20 cc. of water and filtered. The aqueous solution was treated with charcoal, then concentrated in a desiccator to yield any water-soluble salts. Water-insoluble products were crystallized from solvents as indicated in Table I.

The identity of the salts of *p*-toluenesulfonic acid with

(3) Analyses and properties of the esters and their hydrogenation products are presented in Table I.

organic bases was confirmed by preparing and identifying the hydrochlorides of the bases and by conducting mixed melting points of the salts with authentic samples prepared by treating *p*-toluenesulfonic acid with the appropriate base in ether.

Summary

The 5-, 6-, 7- and 8-(*p*-toluenesulfonoxy)-quinolines yielded primarily the corresponding 1,2,3,4-tetrahydro derivatives on catalytic hydrogenation with a palladium catalyst, whereas the 2- and 3-isomeric esters gave the 1,2,3,4-tetrahydroquinoline salt of *p*-toluenesulfonic acid. The 4-ester is very unstable.

The *p*-toluenesulfonoxypyridines were reduced to pyridinium and piperidinium *p*-toluenesulfonates, the 3-isomer being hydrogenated completely and rapidly, the 4-isomer more slowly, and the 2-isomer most slowly.

The 2-(*p*-toluenesulfonoxy)-quinoline was more rapidly reduced than the corresponding benzenesulfonoxy derivative.

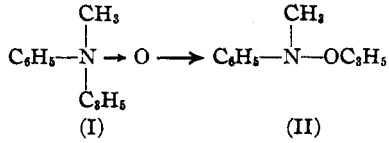
RENSSELAER, N. Y. RECEIVED SEPTEMBER 12, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rearrangement of Allyl Groups in Dyad Systems. Amine Oxides

BY ROGER F. KLEINSCHMIDT AND ARTHUR C. COPE

Meisenheimer has shown that allylmethylaniline oxide (I) rearranges readily on heating with aqueous sodium hydroxide to give O-allyl-N-methyl-N-phenylhydroxylamine (II).[1] The

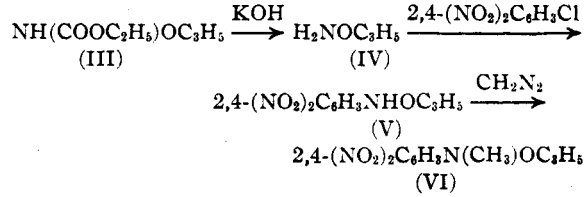


(I) (II)

structure of the isomerization product was established by reduction with zinc dust and acetic acid to methylaniline and allyl alcohol, by hydrogenation to O-propyl-N-methyl-N-phenylhydroxylamine, and by hydrolysis with hydrochloric acid. The hydrolysis products which were isolated were methylaniline, *p*-chloro-methylaniline, and acrolein. Their formation was attributed to cleavage of II in two ways; into allyl alcohol and $C_6H_5N(CH_3)$-Cl (which by rearrangement could give chloromethylaniline), and into methylaniline and acrolein. Allylethylaniline oxide and benzylmethylaniline oxide[2] later were shown to rearrange in the same way, although the structures of the isomerization products were not proved in these cases.

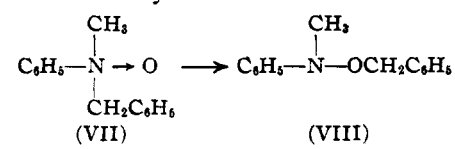
Beyond calling attention to the similar mobility of allyl groups in allyl thiocyanate and in the allyl ethers of phenols and enols,[3] Meisenheimer made no commitment concerning the mechanism of the rearrangement. Considering the analogy of tautomerism in triad and dyad systems, it seemed to us very probable that the isomerization could be explained as a rapid, thermal rearrangement of an allyl group in a dyad system, resembling the Claisen rearrangement. If this interpretation is correct, the only function of the sodium hydroxide present in the reaction mixture is to convert the amine oxide from a salt into the free base. Another possible mechanism is an anionotropic shift, in which the $C_6H_5N(CH_3) \rightarrow O$ fragment separates as an anion and recombines through oxygen rather than nitrogen. We have re-investigated the rearrangement, in order to confirm the structures of the compounds concerned and obtain evidence for the mechanism of the reaction.

Oxidation of allylmethylaniline with perbenzoic acid gave the amine oxide, I, which rearranged rapidly in alkaline solution to the isomer, II. Preliminary attempts to synthesize II by an independent method which would confirm its structure were unsuccessful, but it was possible to synthesize the 2,4-dinitro derivative of II by the sequence of reactions



Nitration of II with fuming nitric acid in glacial acetic acid gave the same dinitro derivative, confirming its structure.

Benzylmethylaniline oxide (VII) also was prepared and rearranged by heating in alkaline solution. The isomerization product proved to be O-benzyl-N-methyl-N-phenylhydroxylamine, VIII. Its structure was established by hydrolysis with dilute hydrochloric acid, which yielded benzaldehyde, methylaniline, and *p*-chloro-methylaniline. Cleavage of VIII by hydrogenation to benzyl alcohol and methylaniline verified this structure.



(VII) (VIII)

The fact that the benzyl group does not undergo inversion during the rearrangement furnishes no

(1) Meisenheimer, *Ber.*, **52**, 1667 (1919).

(2) Meisenheimer, Greeske and Willmersdorf, *ibid.*, **55**, 513 (1922).

(3) As in the Claisen rearrangement and related reactions: see Tarbell *Chem. Rev.*, **27**, 495 (1940).