Quinolinequinones. VI. Reactions with Aromatic Amines[1]

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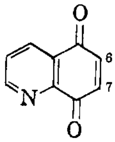
In the reactions of 5,8-quinolinequinone (I) with *p*-toluidine and *p*-chloroaniline in alcohol solution at room temperature the yields of 6-amino derivatives were significantly higher than those of the 7-amino derivatives and with *N*-methylaniline the ratio of 6-amino to 7-amino derivative was about 6:1. In the presence of cerium ion strong activation at the 6-position was observed as the 6-amino derivatives were formed exclusively and total yields were greatly improved. In reactions with 6-chloro- and 7-chloro-5,8-quinolinequinone, *p*-toluidine added at the open 7- or 6-position in the absence of cerium ion but in the presence of this catalyst, the amino group entered the 6-position regardless of whether substitution of halogen or addition at the open position was involved. Although 6-methoxy-5,8-quinolinequinone reacted readily with *p*-toluidine in the presence of cerium ion to form the expected substitution product, 7-methoxy-5,8-quinolinequinone reacted very slowly, and the major product was that formed by addition at the 6-position. Cerium ion also strongly catalyzed the addition of *p*-nitroaniline to 1,4-naphthoquinone and the replacement of the methoxyl group in 2-methoxy-1,4-naphthoquinone by a *p*-toluidino group. Although 2-chloro- and 2-bromo-1,4-naphthoquinone reacted with *p*-toluidine at room temperature to form the halogenated oxidized addition products preferentially, significant yields of 2-*p*-toluidino-1,4-naphthoquinone were also isolated both in the presence and absence of cerium ion.

The reaction of amines with quinones to form aminohydroquinones which undergo disproportionation with unchanged quinone to yield aminoquinones is well known.[2] In 1884 Fischer and Renouf noted that 5,8-quinolinequinone (I) (5,8-quinolinedione) similarly added aniline but did not purify the isomeric products.[3] Long and Schofield more recently carried out a qualitative separation by fractional crystallization of the 6- and 7-anilino-5,8-quinolinequinones resulting from this reaction.[4,5] The objective of the current program is a quantitative determination of each of the two possible products which may be obtained when 5,8-quinolinequinone (I) and certain of its derivatives are treated with amines under various conditions. The present paper is limited to the reactions of aromatic amines.



I

In the general procedure, the reactants in equimolar quantities were stirred in alcohol solution while alcohol-saturated air was passed into the flask to oxidize at least part of the by-product hydroquinone formed in the disproportionation step.[6] In working up the reaction mixtures all orange, red, or purple material that could be dissolved in benzene was chromatographed on silicic acid columns. Although these separations were carried out on a semimicro scale, trace amounts of the aminoquinones were readily detectable by their characteristic highly colored bands and those obtained in yields as low as 2% could be easily isolated and characterized by melting point and mixture melting point determinations. 6-*p*-Toluidino-5,8-quinolinequinone and the 6-*p*-chloroanilino derivative were prepared as reference compounds from 6-methoxy-5,8-quinolinequinone,[7a] which reacts with aromatic amines by replacement of the methoxyl group.

The effects of varying reaction conditions in the addition of *p*-toluidine to 5,8-quinolinequinone (I) are shown in Table I. The predominating isomer in all of these experiments was 6-*p*-toluidino-5,8-quinolinequinone. In alcohol solution in the absence of catalyst the ratio of this compound to the 7-amino derivative was about 1.3:1 (experiments 1 and 2) but in acetic acid solution this ratio rose to about 7:1 (experiment 3).

In preliminary tests with added cupric acetate[8] to oxidize by-product hydroquinone, a dark, partly colloidal complex[9] precipitated from the reaction mixture and yields were poor, but none of the 7-amino isomer was detected. Yields were greatly improved and desired products could be more readily liberated from their metal complexes when

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(1) A grant (G11387) from the National Science Foundation in support of this work is greatly appreciated.

(2) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 853.

(3) O. Fischer and E. Renouf, *Ber.*, **17**, 1644 (1884).

(4) R. Long and K. Schofield, *J. Chem. Soc.*, 3919 (1953).

(5) V. Petrow and B. Sturgeon, *ibid.*, 570 (1954), carried out the same reaction, apparently isolating the less soluble isomer. They also reported the addition of aniline to 7-bromo-5,8-quinolinequinone to form the 6-anilino-7-bromoquinone.

(6) When air was passed into an alcohol solution of 5,8-hydroxyquinoline, oxidation appeared to be slow; the reactions of Table I were, therefore, somewhat prolonged.

(7) Y. T. Pratt with N. L. Drake, (a) *J. Am. Chem. Soc.*, **77**, 37 (1955); (b) *ibid.*, **82**, 1155 (1960); (c) *ibid.*, **79**, 5024 (1957).

(8) R. Baltzly and E. Lorz, *ibid.*, **70**, 861 (1948); A. H. Crosby and R. E. Lutz, *ibid.*, **78**, 1233 (1956).

(9) An 8-quinolinol chelate may be formed from a 6-amino-5,8-quinolinequinone in its tautomeric form, as well as from the hydroquinone of the starting material or the product. The precipitate, on decomposition with acetic acid, yielded only about 22% by weight of the desired product. It might be possible, however, to develop a method for separating isomers by taking advantage of the fact that the 7-aminoquinones should not form chelates.

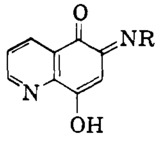

TABLE I

REACTIONS OF 5,8-QUINOLINEQUINONE WITH *p*-TOLUIDINE

Expt. no.	Temp., °C.	Time, hr.	Solvent	Added reagent, moles/mole quinone	Yields,[a] % 6-Amino deriv.	7-Amino deriv.
1	27	48	EtOH	None	30	24
2	80	4	EtOH	None	17	14
3	26	48	HOAc	None	33	5
4	26	48	EtOH	1 Ce $Cl_3 \cdot 7H_2O$	68	Trace?[b]
5	26	48	EtOH	7 H_2O	28	21
6	26	48	EtOH	0.1 $CeCl_3 \cdot 7H_2O$	69	Trace?[b]
7	27	48	EtOH	0.001 $CeCl_3 \cdot 7H_2O$	38	15
8	28	48	HOAc	1 $CeCl_3 \cdot 7H_2O$	35	0

[a] All yields are based on total amount of I taken, although much of it may remain as by-product hydroquinone.[6] [b] Presence of the 7-amino isomer was indicated only by a trace band on the chromatogram at the location and of the color characteristic of this compound.

TABLE II

REACTIONS OF AMINES WITH 5,8-QUINOLINEQUINONE

			$CeCl_3$ absent			1 Mole $CeCl_3$ present		
				Yields,[a] %			Yields,[a] %	
Amine	Temp., °C.	Time, days	Expt. no.	6-Amino deriv.	7-Amino deriv.	Expt. no.	6-Amino deriv.	7-Amino deriv.
p-Toluidine	27	2	1	30	24	4	68	Trace?[b]
p-Chloroaniline	25	4	9	19	13	10	68	Trace?[b]
N-Methylaniline	26	4	11	14	2	12	55	0
N-Methylaniline, 10 moles[c]	25	4	13	28	5[d]	14	62[d]	0

[a,b] See Table I,*a*,*b*. [c] Ten moles of amine per mole of quinone were used. [d] After extraction of the reaction mixture with chloroform and removal of solvent, the residue was triturated with low-boiling petroleum ether (in which neither isomer is significantly soluble) to remove excess amine.

cerous chloride heptahydrate[10] was used as the oxygen carrier. When the amount of catalyst per mole of quinone was 0.1 mole or more, the 6-amino compound was the exclusive product (experiments 4, 6, and 8) and even a trace amount of cerous chloride, insufficient to increase total yield, significantly increased the proportion of this isomer (experiment 7). Since catalysis of certain nucleophilic reactions by water has been reported,[11] the effect of the seven moles of water contained in the catalyst was explored in experiment 5; no catalytic effect by water alone was observed.

The results of reactions of two other types of aromatic amines with 5,8-quinolinequinone (I) in alcohol solution at room temperature are given in Table II. *p*-Chloroaniline, a negatively substituted primary aromatic amine, and *N*-methylaniline, a mixed aliphatic–aromatic secondary amine, added slowly in the absence of cerous chloride and the yields of desired products were low (experiments 9 and 11). The yield of *N*-methylanilino derivative was doubled, however, by the use of ten moles of amine (experiment 13). Both of these amines also attacked the 6-position of I preferentially and with *N*-methylaniline, the least reactive of the three amines studied, the ratio of 6-aminoquinone to 7-aminoquinone was about 6:1 (experiments 11 and 13). In the presence of cerous chloride the 6-amino isomers were formed exclusively and in satisfactory yields (experiments 10, 12, and 14). The results with *N*-methylaniline, in which the total yield was more than tripled by the use of cerium ion, (experiments 11 and 12) indicated that this reagent must function not only as an oxygen carrier (which could at most double the yield) but also as a catalyst for reaction at the 6-position rather than merely an inhibitor of reaction at the 7-position.

A more general catalysis of the addition of aromatic amines to quinones by cerous chloride was demonstrated by the reaction of *p*-nitroaniline with 1,4-naphthoquinone. In the absence of this catalyst only 1% of the expected addition product, 2-*p*-nitroanilino-1,4-naphthoquinone[12] was obtained in five weeks at room temperature while in a simultaneous run under identical conditions except for the presence of 0.1 mole of cerous chloride a 74% yield was obtained in three weeks and an 81% yield in five weeks.

In the experiments of Table III the reactions of *p*-toluidine with certain halogen and methoxyl derivatives of 5,8-quinolinequinone and 1,4-naphthoquinone were investigated. Two moles of *p*-toluidine were used in reactions with haloquinones so that any released halogen acid would be converted to the salt by excess amine. In the absence of cerium ion 6-chloro-5,8-quinolinequinone (experiment 15) and 2-chloro- and 2-bromo-1,4-

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(10) Lucius and Brüning, Ger. Patent 262,180 (1911) [*Chem. Abstr.*, **7**, 3423 (1913)]; J. C. Schurman and E. I. Becker, *J. Org. Chem.*, **18**, 211(1953).

(11) For example, catalysis of the amination of esters was noted by A. R. Day, *et al.*, *J. Am. Chem. Soc.*, **72**, 5635 (1950); **70**, 1946 (1948); **71**, 1245 (1949).

(12) C. Baltzer, *Ber.*, **14**, 1899 (1881), similarly obtained this compound at high temperatures in unspecified yield.

TABLE III

REACTIONS OF SUBSTITUTED QUINONES WITH *p*-TOLUIDINE

			$CeCl_3$ absent			$CeCl_3$ present			
				Yields,[b] %				Yields,[b] %	
Quinone[a]	Temp., °C.	Time, hr.	Expt. no.	Substn. prod.	Addn. prod.	Expt. no.	Moles $CeCl_3$	Substn. prod.	Addn. prod.
6-Chloro-QQ[c]	27	48	15	7	76[d]	16	1.0	94[e]	...
7-Chloro-QQ[c]	26	48	17	0	69	18	1.0	0	87
2-Chloro-NQ[c]	25	48	19	14	75[f]	20	1.0	27	62
2-Bromo-NQ[c]	27	48	21	26	58	22	1.0	33	47
6-Methoxy-QQ	29	2	23	No reaction		24	1.0	93[g,h]	...
6-Methoxy-QQ	27	2				25	0.1	95[g,i]	...
7-Methoxy-QQ[j]	26	500	26	[k]		27	1.0	22	33[l]
7-Methoxy-QQ[j]	60[m]	18				28	1.0	2	46
2-Methoxy-NQ	80	12	29	<10%[n]	...	30	0.1	80	...

[a] QQ = 5,8-quinolinequinone (I); NQ = 1,4-naphthoquinone. [b] Yields based on total amount of quinone taken. See ref. 15. [c] Two moles of amine per mole of quinone used. [d] In a check run at 25° the yields were 9% of substitution product and 76% of addition product. [e] Not chromatographed but total product extracted from reaction mixture and recrystallized from benzene–low boiling petroleum ether. The Beilstein test was negative for both the crystals and the concentrated mother liquor. [f] In a check run at 25° the yields were 12% of substitution product and 77% of addition product. [g] Not chromatographed. [h] Done under nitrogen. [i] The same results were obtained in methanol solution. With 0.01 mole of cerous chloride in methanol the reaction was far from complete in 6 hr., but the yield was 94% after 24 hr. [j] Reactions done in methanol to prevent ester exchange. [k] No color change in 48 hr. and 97% recovery of starting material in contrast to 27 in which a purple color developed immediately. [l] 29% of the starting material remained undissolved when reaction was stopped; total yield on material consumed was 78%. [m] The mixture stood at room temperature an additional 35 hr. [n] 74% of the starting material was recovered and the crude red product obtained in 10% yield contained a considerable amount of starting material.

naphthoquinone[13,14] (experiments 19 and 21) each yielded a mixture of the two possible products with the oxidized halogenated addition compound[15] predominating, but 7-chloro-5,8-quinolinequinone did not form a detectable amount of the substitution product involving reaction at the 7-position[5] (experiment 17). In the presence of cerium ion the amino group entered the 6-position in both 6-chloro- and 7-chloro-5,8-quinolinequinone, the first of these forming the substitution product (experiment 16) and the second, the oxidized addition product with no indication of direct catalytic activation of the halogen (experiment 18). The cerium catalyst did produce a significant effect upon the reaction of 2-chloro-1,4-naphthoquinone, doubling the low yield of replacement product, but 62% of the oxidized addition product was still obtained (experiment 20). This additional evidence of only weak activation of the halogen by cerium ion indicates that the influence of the catalyst on reactions of 6-chloro-5,8-quinolinequinone is exerted primarily through the heterocyclic nitrogen atom. The results with 2-bromo-1,4-naphthoquinone, in which the halogen is much more reactive, were not appreciably affected by the presence of cerium ion (experiments 21 and 22). The 26% yield of replacement product obtained in the uncatalyzed reaction (experiment 21) was somewhat unexpected in view of earlier reports on the addition of aniline to this quinone at higher temperatures.[14]

Previous experiments have shown that although 6-methoxy-5,8-quinolinequinone reacts readily at room temperature with aliphatic amines to form 6-amino derivatives, it is relatively inert toward *p*-toluidine and gives only a 40% yield of the desired products in acetic acid solution under reflux.[7a] In the present work cerous chloride was found to be a powerful catalyst for this reaction (experiments 24 and 25). (Seven moles of water alone did not exert a catalytic effect.) On the other hand, 7-methoxy-5,8-quinolinequinone reacted only very slowly with *p*-toluidine even in the presence of cerium ion and the principal product at 26° and almost the exclusive product at 60° was 6-*p*-toluidine-7-methoxy-5,8-quinolinequinone (experiments 27 and 28).[16,17]

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(13) T. Zincke, *Ber.*, **21**, 1027 (1888) and P. T. Cleve, *ibid.*, **21**, 891 (1888); **23**, 954 (1890), reported that 2-chloro-1,4-naphthoquinone formed 3-anilino-2-chloro-1,4-naphthoquinone in unspecified yield when heated in alcohol with aniline. Cleve's analytical data, particularly in the first paper (in which calculated and found values were apparently reversed), indicate the possibility of contamination by the substitution product. Zincke gave no details.

(14) Previous workers obtained 3-anilino-2-bromo-1,4-naphthoquinone by heating 2-bromo-1,4-naphthoquinone with aniline, but reported no details. T. Zincke and M. Schmidt, *ibid.*, **27**, 2753 (1894); C. Liebermann and S. Schlossberg, *ibid.*, **32**, 2095 (1899).

(15) "Addition" is used here to designate attack by amine at the unsubstituted ethylenic carbon atom; "substitution" refers to attack at the substituted carbon atom with loss of the original functional group. The two types of reactions probably occur through closely related mechanisms.

(16) The state of oxidation of the cerium ion in its role as catalyst is difficult to establish. Although experiment 24 was conducted under nitrogen it was impossible to determine whether very small amounts of the added Ce^{+3} were oxidized by the quinone or by traces of oxygen present. The 93% yield of product obtained, however, indicates that little, if any quinone is reduced by even a mole (0.5 equivalent) of Ce^{+3}. It was further found that in the presence of air and only 0.01 mole of catalyst (Table III*i*) the reaction rate was very much slower than that of experiment 24 so that the amount of Ce^{+4} which might be formed in experiment 24 would be unlikely to produce the rapid rate observed. It is therefore considered probable that Ce^{+3} can function as the catalyst.

(17) In test tube experiments in which alcohol solutions of *p*-toluidine and 6-methoxy-5,8-quinolinequinone were treated with acids or various metal ions, the red color characteristic of the amination product developed rapidly with sulfuric and phosphoric acids, zinc, lead, and magnesium acetates, and with cadmium chloride but not with barium acetate or the more soluble barium citrate.

TABLE IV
PRODUCTS

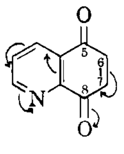
Substitutent	M.p., °C.[a]	Color and Form	Solvent	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found[b]
		5,8-Quinolinequinones					
7-*p*-Toluidino-	191.5–192.5	Purple needles	C_6H_6-Skelly F[c]	72.72	72.54	4.58	4.83
6-*p*-Chloroanilino	237–238	Purple needles	C_6H_6-Skelly F	63.28	63.40	3.19	3.33
7-*p*-Chloroanilino	285.0–286.5	Purple needles	C_6H_5-Skelly C[c]	63.28	63.55	3.19	3.12
6-*N*-Methylanilino-	181–182	Red or orange plates	Skelly C	72.72	72.82	4.58	4.73
7-*N*-Methylanilino-	139–140	Red plates	Cyclohexane	72.72	73.00	4.58	4.85
6-Chloro-7-*p*-toluidino	226–227	Red needles	C_6H_6-Skelly F	64.11	64.28	3.70	3.75
7-Chloro-6-*p*-toluidino-	207.5–208.5	Red needles	$CHCl_3$-Skelly F	64.11	64.40	3.70	4.00
7-Methoxy-6-*p*-toluidino-	171.0–172.5	Purple needles	Skelly C	69.38	69.15	4.79	4.92
		1,4-Naphthoquinones					
2-*p*-Nitroanilino-[d]	338.5–340.0 (dec.)	Red needles	HOAc	65.30	65.35	3.43	3.68
2-Bromo-3-*p*-toluidino-	183–184.5	Red needles	Skelly C[c]	59.66	59.82	3.54	3.72

[a] All melting points are corrected. [b] Microanalyses by Professor Franz Kasler. [c] Skelly F = petroleum ether, b.p. 30–60°; Skelly C = petroleum ether, b.p. 90–100°. [d] Previously characterized only as melting above 270° (ref. 12).

The general catalytic action of cerium ion on the reactions of aromatic amines with methoxyquinones was illustrated by its effect on the reaction of *p*-toluidine with 2-methoxy-1,4-naphthoquinone[18] (experiments 29 and 30).

The properties of the aminoquinones prepared in these studies are given in Table IV.

The results of these experiments, in which the 6-position of 5,8-quinolinequinone (I) is favored for amine addition, are consistent with those observed by Thomson *et al.* in studies with juglone acetate (5-acetoxy-1,4-naphthoquinone) and related compounds.[19] Thomson's theoretical explanation may therefore be adapted to 5,8-quinolinequinone (I) in which the heterocyclic nitrogen withdraws electrons from the quinonoid ring in contrast to the acetoxy group of juglone acetate which releases electrons. The site of negative group attack on a quinone depends upon which of the carbonyl carbon atoms more strongly attracts the electrons of the ethylenic double bond. The 8-carbonyl carbon atom of 5,8-quinolinequinone (I) is located at the α-position with respect to the pyridine ring and is more electron-deficient than the 5-carbonyl carbon atom which occupies the β-position, just as the carbon atom of the methyl group of α-picoline is more electron-deficient than that of β-picoline. This deficiency of C-8 is transferred to C-6 by withdrawal of electrons from the double bond between the 6- and 7-carbon atoms and leads to preferential attack by a negative group at the 6-position.[20] The amino group preferentially entered the 6-position of I and its derivatives in all of the uncatalyzed reactions described here with the exception of the addition of *p*-toluidine to 6-chloro-5,8-quinolinequinone, in which the electron-attracting effect of the halogen directs the entering group to the position adjacent to the substituent. In the presence of a strong proton acid or cerium ion functioning as a Lewis acid[21] the electron-attracting power of the heterocyclic nitrogen atom is greatly increased by coördination with a positive ion. The reactivity of the 6-position is so strongly enhanced that this position is attacked exclusively in the previously reported addition of hydrogen chloride[7b,22] to 5,8-quinolinequinone (I) as well as in all of the cerium-catalyzed amine reactions investigated here except that with 7-methoxy-5,8-quinolinequinone, in which the electron-releasing effect of the substituent to some extent counteracts the influence of the positive charge at the heterocyclic nitrogen. The close relationship of the activated form of 5,8-quinolinequinone (II) to the chelating form of 8-quinolinol (III) is noteworthy.



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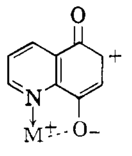

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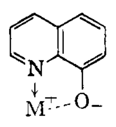

III

The powerful catalytic effect of cerous chloride observed in the addition of *p*-nitroaniline to 1,4-naphthoquinone and the replacement of the methoxyl group in 2-methoxy-1,4-naphthoquinone

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(18) L. F. Fieser, *J. Am. Chem. Soc.*, **48**, 2922 (1926), found that this reaction took place in good yield when the quinone and amine were heated under reflux for 10 min. in acetic acid solution.

(19) R. H. Thomson, *et al.*, *J. Org. Chem.*, **13**, 377 (1948); **16**, 1082 (1951); **25**, 36 (1960); *J. Chem. Soc.*, 2910 (1953).

(20) The remote possibility that the addition of amines to 5,8-quinolinequinone (I) was reversible at room temperature was explored. When 6-*p*-toluidino-5,8-quinolinequinone was treated with 1 mole of I or when 7-*p*-toluidino-5-8-quinolinequinone was treated with 1 mole of I and 1 mole of cerous chloride for 24 hr. under standard conditions, the original aminoquinones were recovered essentially unchanged.

(21) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, p. 142.

(22) L. P. Hammett (ref. 21, p. 336) has postulated that the addition of hydrogen chloride to homocyclic quinones involves initial protonation of oxygen. With quinolinequinone, however, protonation or association with hydrogen of the heterocyclic nitrogen would take precedence over protonation of the carbonyl oxygen.

may be ascribed to coördination of the Lewis acid catalyst with a carbonyl group.

Experimental

General Amination Procedure.—In the general procedure 1 mmole each of pure quinone[7] and amine were mixed in 6 ml. of absolute alcohol and the suspension was stirred magnetically while a slow stream of alcohol-saturated air was passed into the flask. Precipitates were scraped from the sides with a microspatula from time to time. When cerous chloride heptahydrate was used, it was powdered and combined with the amine before the quinone was added. In all reactions of halogenated quinones 2 mmoles of amine were used. In reactions at reflux temperatures air saturated with the solvent at the temperature of the condenser water was slowly admitted through a tube reaching to the bottom of the solution.

At the end of the reaction period the mixture was treated with ice, water, and 0.5 to 1.0 ml. of acetic acid. Crystalline precipitates were usually filtered off and washed well with water and the mother liquors were extracted with chloroform after the addition of a little sodium chloride solution to prevent emulsification. Alternatively the whole mixture could be extracted with chloroform after the addition of water and acetic acid. In either case all red, orange, or violet color was removed from the aqueous layer and the extract was washed three times with saturated sodium chloride solution. The extract was then partially dried by passing through a fluted filter and evaporated to dryness in an air stream under reduced pressure. Drying agents and decolorizing agents were avoided to prevent any preferential adsorption of a minor constituent. Aliquots of both precipitate and extract were recombined for the chromatograms described below.

Isolation of Products from Quinolinequinone and Derivatives.—Fisher certified reagent silicic acid[23] was shaken in a large container with a horizontal motion to allow the larger particles to settle to the bottom and the top 20% was skimmed off and discarded. Before the adsorbent was placed in the chromatograph tube, it was slurried with dry benzene (care being taken to break up aggregates) and the suspension was allowed to stand about 0.5 hr. Columns were not more than 12 cm. high so that satisfactory flow rates were achieved under moderate nitrogen pressure and development could be completed within 1 to 3 hr. A layer of dry sodium chloride protected the top of the column.

One hundred grams of silicic acid formed a column 10 cm. high and 4.3 cm. in diameter and was generally more than sufficient for separating the products from one-third mmole of quinone.[24] The material from the reactions of quinolinequinones was adsorbed on the column from benzene solution and developed with dry benzene containing amounts of absolute alcohol varying from 0.2% to 1.0%. Dark byproducts remained at the top of the column and the desired components usually produced broad orange or red bands; only that of the 6-*p*-toluidino-7-methoxy derivative was purple. The lower band could be allowed to pass through the tube or both bands could be removed from the top after the column was allowed to drain completely.[25] The adsorbates were eluted with acetone and, if necessary, a little 95% ethanol, and the solutions were evaporated to dryness under reduced pressure. The last traces of silicic acid were removed by filtering a chloroform solution of the residue through a small fluted filter. The products were generally crystallized by dissolving in hot benzene, boiling down to a low volume and precipitating completely with a large volume of low-boiling petroleum ether. It was necessary to crystallize 7-*N*-methylanilino-5,8-quinolinequinone from cyclohexane. The products were weighed to the nearest 0.5 mg.

The crude product from the reaction between *p*-chloroaniline and 5,8-quinolinequinoline in experiment 10 contained cerium as shown by an ashing test. To determine whether this ion formed a complex not completely broken up by adsorption on silicic acid, the material was directly chromatographed as above. The major band gave a 57% yield of 6-*p*-chloroanilino-5,8-quinolinequinone. All material above this band was eluted with acetone and 95% alcohol and after removal of the solvent, the residue was dissolved in acetic acid and the solution was treated with water and extracted with chloroform. The extract was evaporated to dryness and rechromatographed on silicic acid to give an additional 11% of product. It therefore appears that this compound formed a cerium chelate[9] more stabilized by resonance than that of 6-*p*-toluidino-5,8-quinolinequinone so that it was not completely decomposed at the concentration of acetic acid used in working up these reactions by the standard procedure. Treatment with 25–35% acetic acid prior to chromatography would eliminate this problem (see amination of 6-methoxy-5,8-quinolinequinone below).

Isolation of Products from Halonaphthoquinones.—Naphthoquinone derivatives were much less strongly absorbed on silicic acid than were quinolinequinone derivatives. The products from the reaction of 0.25 mmole of 2-chloro- and 2-bromonaphthoquinone and *p*-toluidine (experiments 19–22) were dissolved in benzene and treated with 2 volumes of petroleum ether (b.p. 30–60°) for adsorption on a column of 120 g. of silicic acid made up with the same solvent mixture. In experiments 21 and 22 this mixture was also used for development, and in experiments 19 and 20 the developing agent was a 1:1 mixture of the two solvents. The purest sample of 2-*p*-toluidino-1,4-naphthoquinone obtained melted at 206–207°,[26] and that of its 3-chloro derivative melted at 204.5–206.0°.[27]

Purity of 2-Chloro- and 2-Bromo-1,4-naphthoquinone.—Since both these halogenated naphthoquinones were prepared from 1,4-naphthoquinone, it was necessary to determine whether these starting materials for experiments 19–22 contained any of the parent quinone which could form the unhalogenated amino derivatives by addition.

Known mixtures of 1,4-naphthoquinone with each of the halogenated quinones could be separated on silicic acid columns with a mixture of 5 parts benzene and 1 part 30–60° petroleum ether as solvent and developing agent. As little as 1% of the parent quinone (the more strongly adsorbed compound) could be detected with the aid of ultraviolet light because of the fluorescence of silicic acid when free of adsorbate. Similar chromatograms of samples of the 2-chloro- and 2-bromo-1,4-naphthoquinones used in the amine experiments showed no evidence of the presence of the parent quinone. Slight decomposition of these quinones was observed in the form of a very narrow orange band at the top of the columns. When a sample of the chloroquinone was freed of this top band and rechromatographed, a similar band reappeared. Its color deepened rapidly upon exposure to ultraviolet light. This band contained less than 1% of material, however, and did not interfere with the detection of small amounts of added naphthoquinone.

Further evidence that the bromoquinone was free of unhalogenated quinone was the absence of the bands at 828 and 928 cm.$^{-1}$ characteristic of the infrared spectrum of the parent quinone.

Amination of 6-Methoxy-5,8-quinolinequinone and 2-Methoxy-1,4-naphthoquinone.—In reactions of these two

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(23) Fisher Scientific Co., New York, N. Y.

(24) In experiments 11 and 13 the products from 1 mmole of quinone were chromatographed on 120 g. of adsorbent.

(25) All of the 7-amino derivations from the reactions of Table II were less strongly adsorbed than the 6-amino derivatives. Of the reactions of Table III the oxidized halogenated addition products were less strongly adsorbed than the substitution products but 6-*p*-toluidino-7-methoxy-5,8-quinolinequinone was more strongly adsorbed than the substitution product (experiments 27 and 28).

(26) L. Elsbach, *Ber.*, **15**, 687 (1882), reported 202–203°.

(27) A. Plagemann, *ibid.*, **15**, 487 (1882), reported 196°.

quinones with *p*-toluidine the general amination procedure was followed except that air was not supplied, since oxidation of hydroquinone was not involved and it was found unnecessary to provide air for oxidation of the cerous chloride. When the alcoholic solution of 6-methoxy-5,8-quinolinequinone and *p*-toluidine was first boiled a short time, cooled under nitrogen, and then treated with 1 mole of catalyst, the reaction proceeded rapidly to completion in a nitrogen atmosphere (experiment 24).[16] In the other reactions of 6-methoxy-5,8-quinolinequinone and 2-methoxy-1,4-naphthoquinone with *p*-toluidine only 0.1 mmole of catalyst was used. The products obtained on the addition of water and acetic acid to the reaction mixture were fairly pure, contained no inorganic material and were not chromatographed.

6-*p*-Chloroaniline reacted much more slowly with 6-methoxy-5,8-quinolinequinone than did *p*-toluidine, giving only a 67% yield of desired product after 4 hr. at room temperature in the presence of 0.1 mole of ceroute chloride. When 2 moles of amine were used under the same conditions a high yield of crude aminoquinone was obtained. This material, like that obtained by adding *p*-chloroaniline to 5,8-quinolinequinone (I) (see above), contained cerium as shown by an ashing test. The inorganic material was removed by dissolving the crude product in acetic acid and precipitating with 2 or 3 volumes of water. The product thus obtained in 92% yield melted at 237.5–238.5°.

Addition of *p*-Nitroaniline to 1,4-Naphthoquinone.—A suspension of 1 mmole of 1,4-naphthoquinone in 6 ml. of absolute alcohol containing 1 mmole of *p*-nitroaniline and 0.1 mmole of cerous chloride heptahydrate was warmed slightly to dissolve the quinone. The clear solution was allowed to stand at room temperature in a stoppered flask and air was blown into the flask on alternate days. At intervals (given below) the reddish-orange precipitate was filtered off and washed well with absolute alcohol and then with a little hot alcohol. The combined filtrate and washings was evaporated in an air stream at room temperature under reduced pressure to the original volume of the reaction mixture and the reaction was allowed to continue. The solution was saturated with air twice a week. The following crops of crystals were obtained: after 6 days, 0.16 g. (55%); after 3 weeks, 0.055 g. (19%); after 5 weeks, 0.02 g. (7%); total yield, 81%. The melting point was 336.0–337.5°.

The experiment without cerous chloride was done simultaneously and under identical conditions except that the solution was saturated with air less frequently.

The Acetolysis of 4-Methyl-3-penten-1-yl *p*-Toluenesulfonate[1]

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4-Methyl-3-penten-1-yl tosylate was prepared and its acetolysis studied. The rate of acetolysis at 45° is approximately 1200 times that of ethyl tosylate. The products are 2-cyclopropylpropene and the acetate of 4-methyl-3-penten-1-ol. Both the rate and the products of solvolysis provide evidence that the reaction proceeds with participation of the olefinic bond.

Following the study of cholesteryl tosylate by Winstein and Adams,[3] participation of the carbon–carbon double bond during solvolysis reactions has become well established.[4] By far, the majority of authenticated cases of homoallylic participation has involved compounds in which the olefinic bond is strategically located in a ring system so as to favor interaction with the carbon undergoing solvolysis. An attempt to detect such interaction in the simplest homoallylic compound, allylcarbinyl chloride, yielded negative results[5] although nitrous acid deamination of allylcarbinylamine does lead to products resulting from homoallylic participation.[6] This report presents evidence that the acyclic compound, 4-methyl-3-penten-1-yl tosylate, undergoes acetolysis with participation of the olefinic bond.[7]

Synthesis.—Preparation of the required alcohol (I) by selective dehydration of 4-methyl-1,4-pentanediol has been reported.[8] The yield of the desired product is poor and on repeating this preparation the alcohol was found to exhibit weak absorption at 11.2 μ indicating contamination by the isomer, 4-methyl-4-penten-1-ol. The following synthesis was found to yield I in a high state of purity. Equilibration of 4-methyl-2-pentenoic acid (II) with the β,γ-unsaturated isomer (III) was carried out according to the published method.[9] Separation of the mixture of acids (20 α,β:80 β,γ) was not possible by careful fractional distillation nor was the mixture of alcohols resulting from hydride reduction separable in this way. Finally, it was found that methylation of the acid mixture under controlled conditions led to methyl 4-methyl-3-pentenoate of 99% purity. The separation takes advantage of the differing esterification rates

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[3] S. Winstein and Rowland Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).

[4] For reviews and references, see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," J. Wiley & Sons, Inc., New York, N. Y., 1961, pp. 385–389 and A. Streitwieser, Jr., *Chem. Rev.*, **56**, 725 (1956).

[5] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

[6] E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961).

[7] Early reports which pointed to the possibility of participation during solvolysis of derivatives of this compound have been noted by Roberts and Mazur. See footnote 4 of ref. 5.

[8] L. Williams and H. Schinz, *Helv. Chim. Acta*, **35**, 2401 (1952).

[9] S. E. Boxer and R. P. Linstead, *J. Chem. Soc.*, 740 (1931); A. A. Goldberg and R. P. Linstead, *ibid.*, 2343 (1928).