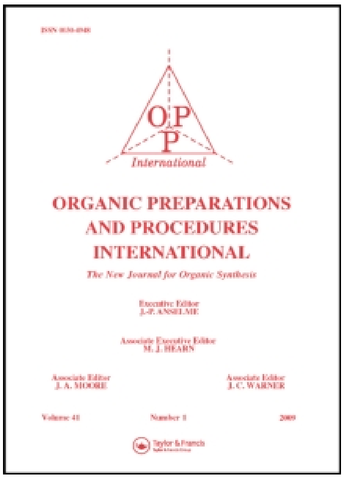

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STUDIES OF ACENAPHTHENE DERIVATIVES. XXV.[1]
PREPARATION OF ACENAPHTHENEQUINONE

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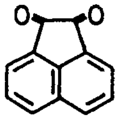
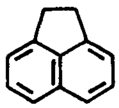
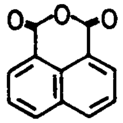
Acenaphthenequinone (I) is a very useful starting material for the preparation of polycarbocyclic and polyheterocyclic compounds. It has been obtained by many procedures[3] such as the oxidation of acenaphthene (II),[4] the Friedel-Crafts reaction of naphthalene with oxalyl chloride[5] and the hydrolysis of acenaphthenequinone dioxime.[6] The oxidation reaction of II with sodium bichromate[4] or calcium permanganate[7] gives I under rather mild conditions. However, all the oxidation methods invariably give 1,8-naphthalic anhydride (III) as a side-product which results from the further oxidation of I, thus rendering the isolation of I in pure form very difficult. The paucity of information prompted us to seek a satisfactory method for the isolation of pure I.


I


II


III

[I-III complex]
IV

Mixture of
I and III
V

It has been reported[8] that the IR spectrum of I had two carbonyl absorptions at 1776 and 1727 cm^{-1} (see Fig. 1a). However, it has now been found that the IR spectrum of pure I obtained from the $CuSO_4$ oxidation reaction of 2-hydroxyacenaphthenone[9] or from the hydrolysis of acenaphthenequinone monoanil[1] did not exhibit the carbonyl band at 1776 cm^{-1} which is ascribable to III. Indeed, the IR spectrum of III displayed two carbonyl absorptions at 1776 and 1735 cm^{-1} (Fig. 1b), while that of pure I shows carbonyl absorptions at 1735 (shoulder) and 1720 cm^{-1} (Fig. 1c).

It has also been reported that the crude product obtained by the oxidation reaction of II, is an isomorphic mixture[10] of I and III, and that the purification of I is very difficult using the usual procedures such as extraction with sodium bisulfite solution. Therefore, we wanted to devise a satisfactory method for the separation of I from crude oxidation mixtures. The composition of I and III in a mixture was estimated by means of the ratio method, using the absorption bands of I and III at 890 and 1310 cm^{-1} respectively.

The oxidation of II[4a] with sodium bichromate dihydrate in glacial acetic acid at 90-95° yielded a crude red oxidation product, which on several recrystallizations from acetic acid or *o*-dichlorobenzene gave IV (containing 50% of I), as yellow needles, whose mp 259-260°[11] was identical with that of pure I. The crude oxidation product was extracted with 40% sodium bisulfite solution and then recrystallized from *o*-dichlorobenzene to afford V, mp 259-260°, as yellow needles (containing 80% of I). While V reacted easily with aniline at 140° to yield acenaphthenequinone monoanil, mp 196-198° (lit[1] mp 194-196°), no

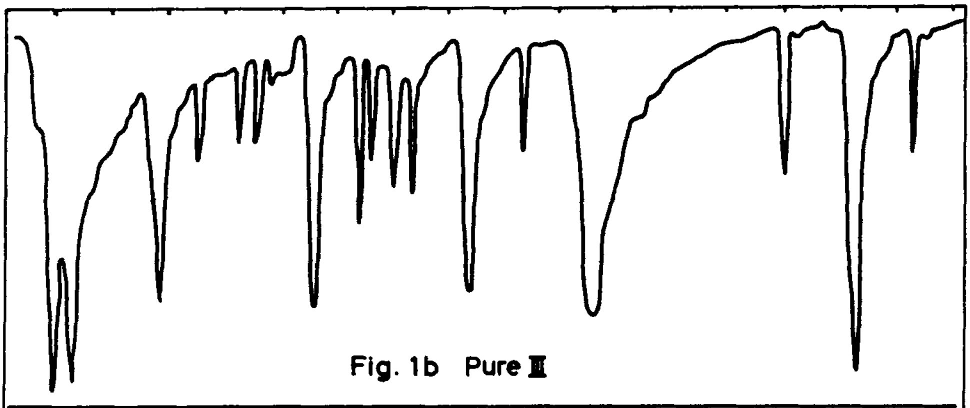


Fig. 1b Pure III

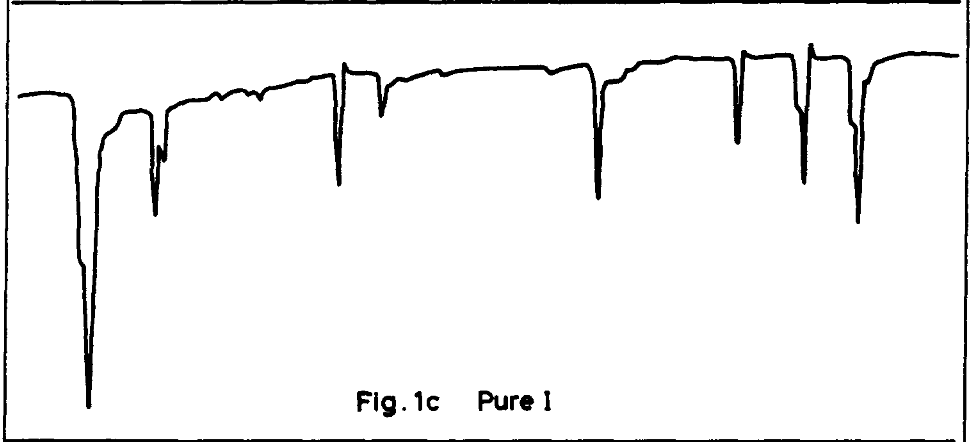


Fig. 1c Pure I

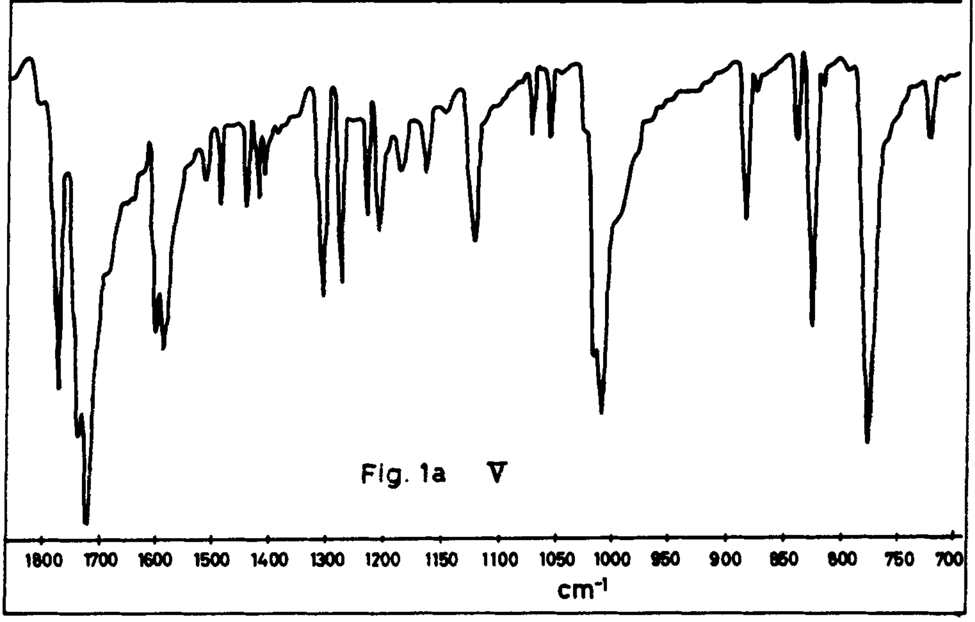


Fig. 1a V

reaction of IV with aniline occurred under the same conditions.

On the basis of the above observations, we deduced that V is a mixture of I and III and that IV is probably a 1:1 complex of I and III. Although the IR spectra of IV and V were very similar, confirmatory evidence for these considerations was provided by the UV spectra as illustrated in Fig. 2 and by the independent preparation of IV from pure I and III.

As is shown in Table 1, it is clear that the 1:1 mixture was easily extracted with 4-10% sodium bisulfite solution but in contrast IV was unaffected.

Table 1. Extraction of IV and of a 1:1 mixture of I and III[a]

Extraction Medium[b]	Temp. (°C)	Time (min)	Percentage of I in IV residue	extract	in 1:1 mixture[c] residue	extract
10% Na_2CO_3	90	20	50	-[d]	76	0[e]
4% $NaHSO_3$	95	10	50	-[d]	0[e]	93
10% $NaHSO_3$	95	3	50	-[d]	0[e]	90
40% $NaHSO_3$	100	20	0[e]	70	0[e]	75

a. Extractions were performed by refluxing for the indicated time. The listed temperatures were those of the respective extractions.

b. One hundred ml of solution was used per gram.

c. Prepared by through mixing of equimolar amounts of I and III.

d. No extraction was achieved.

e. Pure III.

A solution of I and III (1:1) in glacial acetic acid, upon being refluxed for 20 min afforded IV, but similar reactions of

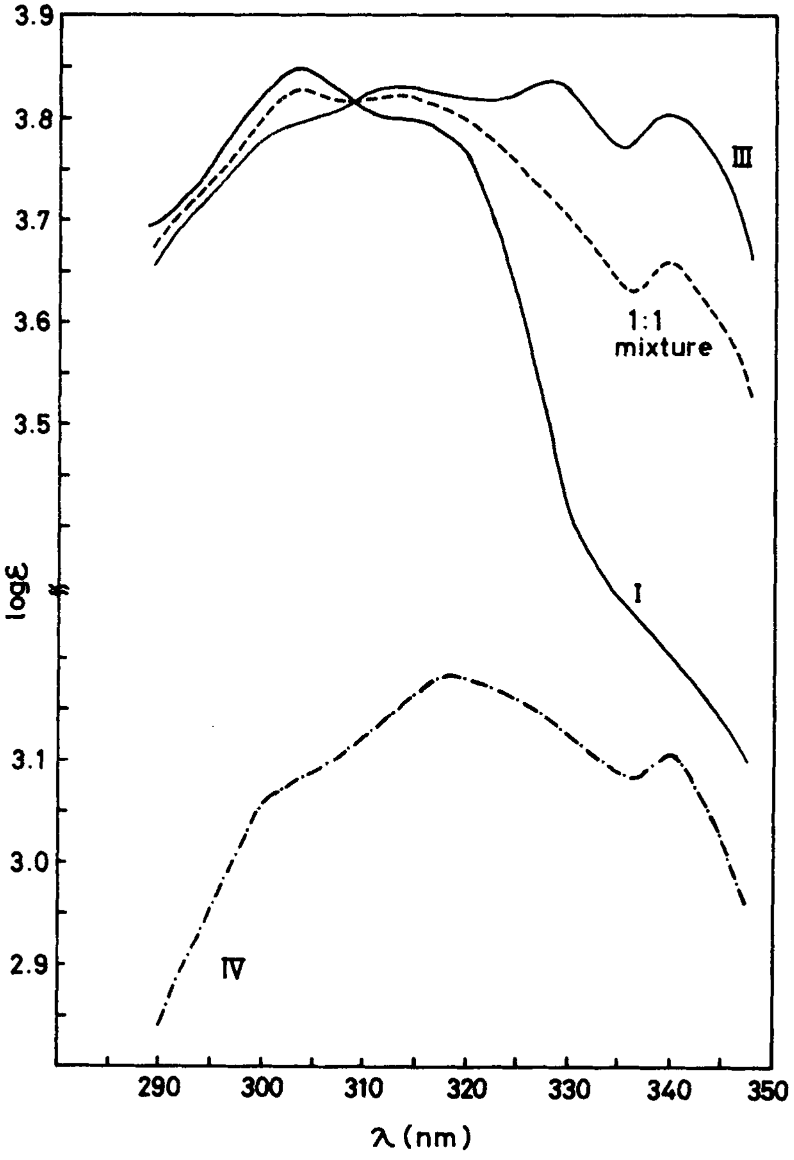
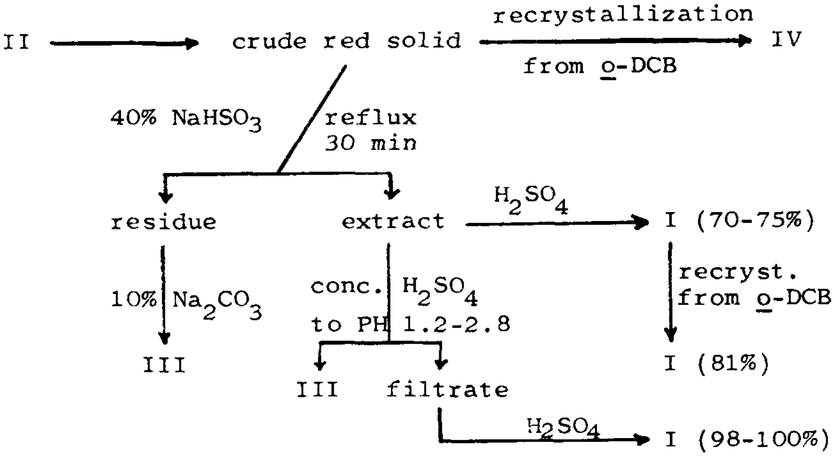


Fig. 2.
UV spectra of I, III and IV in EtOH

I with maleic anhydride or phthalic anhydride did not occur. The 1:1 complex was decomposed by refluxing in 40% sodium bisulfite solution (or with conc. H_2SO_4) and then I was extracted.

The most useful diagram for the separation of pure I is illustrated in Chart 1.

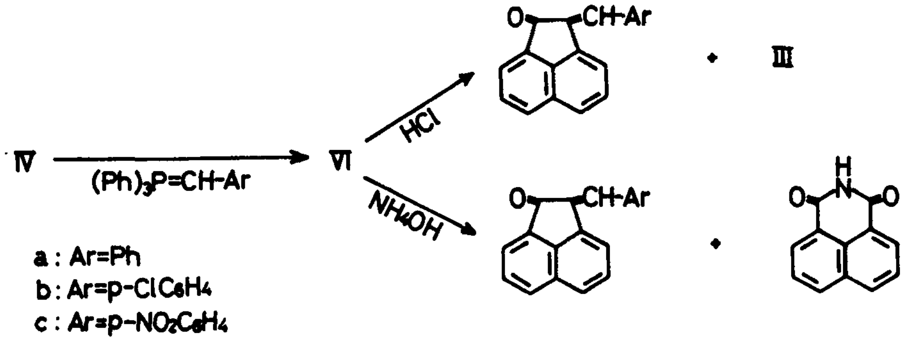


o-DCB: o-dichlorobenzene.
Values in parentheses refer to percentage of I.

Chart 1

It is important to note that while the purity of I was unaffected by recrystallization from o-DCB, HOAc or DMSO, an unusual - and so far unexplained - "oxidation" of I to III occurred in DMF upon attempted recrystallization at reflux.

In the context of this work, it is also interesting that, while IV is unaffected by aniline, it reacted easily with p-substituted benzylidenetriphenylphosphorane in ethanol, to give what appear to be 1:1 complexes (VI) of p-substituted benzylidenacenaphthenones-1,8-naphthalic anhydride. Upon hydrolysis of these complexes with either HCl or NH_4OH, the 2-benzylidenacenaphthenones and either the 1,8-naphthalic anhydride or the corresponding imide respectively, were obtained. This provides an easy preparation of p-substituted 2-benzylidenacenaphthenones from IV.



EXPERIMENTAL

Isolation of pure acenaphthenequinone (I).-- The red solid[12] obtained by the oxidation of 30.0 g of II by the reported method[4a] is heated under reflux with 300 ml of a 40% sodium bisulfite solution for 30 min with stirring. Then 600 ml of hot water is added and refluxing is continued for an additional 5 min. The hot solution is filtered to remove residue (crude III), and the solution is acidified at 80° with 50-60 ml of conc. H_2SO_4 to pH 1.2-2.8. The precipitated pale yellow III is filtered by suction, and the filtrate is then heated to boiling and acidified by the slow addition of 90-100 ml of conc. H_2SO_4. The yellow precipitate is collected, and washed with water until free from acid. The yield of pure I is 30-60%, mp 259-260°. The variation in the yield of pure I is due to variation of yields in oxidation of II to crude products.

General method for the Wittig reaction of IV.-- A solution of 5.0 mmol of p-substituted benzyltriphenylphosphonium halide in 20 ml of absolute ethanol was treated with 5.5 mmol of a 1.0 mmol solution of sodium ethoxide in ethanol with continuous stirring under an atmosphere of nitrogen; the orange yellow color of the phosphorane appeared immediately. After the solution had been stirred for 10 min, 5.0 mmol of a finely powdered IV was added. The mixture was stirred for 20 min at room temperature, and then refluxed for an additional 5 min. After cooling, the product (VI) was filtered and recrystallized.

VIa (Ar=Ph): Yield, 90%. Mp 262-263°. Yellow needles (EtOH).

Anal. Calcd. for $C_{31}H_{18}O_4$: C, 81.94; H, 3.99.

Found: C, 82.03; H, 3.71.

VIb (Ar=p-ClC_6H_4): Yield, 82%. Mp 219-220.5°. Yellow needles (DMF).

Anal. Calcd. for $C_{31}H_{17}O_4Cl$: C, 76.36; H, 3.50.

Found: C, 76.43; H, 3.13.

VIc (Ar=p-$NO_2C_6H_4$): Yield, 91%. Mp 234-234.5°. Golden yellow needles (acetone).

Anal. Calcd. for $C_{31}H_{17}NO_6$: C, 74.54; H, 3.43; N, 2.80.

Found: C, 74.61; H, 3.52; N, 3.12.

A solution of VI (500 mg) in ethanol (15 ml) was treated with 1.0 ml of conc. HCl or conc. NH_4OH solution with stirring at room temperature for 20 min and then heated on steam-bath at 60° for an additional 10 min. Filtration gave quantitative yields of the 2-benzylidenacenaphthenones and of III or of 1,8-naphthalimide, mp 309-310°, as colorless needles from ethanol respectively. These compounds were identical with authentic samples which were obtained previously.[13,14]

REFERENCES

1. Part XXIV of this series: O. Tsuge, M. Tashiro, and K. Oe, The Reports of Research Institute of Industrial Science, Kyushu University, No. 51, 7 (1971).
2. To whom inquiries should be addressed.
3. For a review, O. Tsuge, Kagakukojyo, 7, 65 (1963).
4. a) C. S. Maxwell and C. F. H. Allen, Org. Syn., 24, 1 (1944). b) C. F. H. Allen and J. A. VanAllan, ibid., Coll. Vol., 3, 1 (1955).
5. R. Lesser and G. Gad, Ber., 60, 243 (1927).
6. L. Plakidin and A. E. Kretov, Zhur. Priklad. Khim., 33, 968 (1960); C. A., 54, 17346 (1960).
7. G. T. Morgan and H. A. Harrison, J. Soc. Chem. Ind., 49, 413 (1930); C. A., 25, 3988 (1931).
8. M. L. Tosien and N. Fuson, J. Amer. Chem. Soc., 73, 478 (1951).
9. W. Jugelt and D. Schmidt, Tetrahedron Lett., 1967, 985.
10. A. I. Kiprianov and M. M. Dashevskii, J. Applied Chem., 7, 944 (1934); C. A., 29, 2530 (1935).
11. Wide variations in the melting point of I have been reported: 262° by J. von Braun and O. Bayer (Ber., 59, 921 (1927)); 273-274° by T. C. W. Mak and J. Trotter (Acta Cryst., 16, 324 (1963)); 259-260°,[4b] 243-245°, 256-258°.
12. It has been suggested[4b] that the red color of crude I is

due to the presence of biacenedione. However, when crude red solid was chromatographed on neutral alumina, biacenedione could not be obtained.

13. For the physical properties of 2-benzylidenacenaphthenones, see O. Tsuge, M. Tashiro, and I. Shinkai, Bull. Chem. Soc. Japan, 42, 181 (1969).

14. O. Tsuge and M. Tashiro, ibid., 36, 970 (1963).

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