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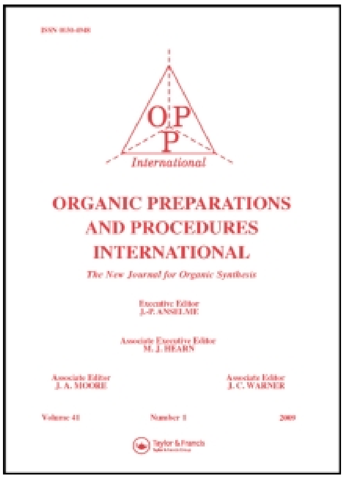

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K. D. Franz[a]; R. C. Haddon[a]
[a] Research School of Chemistry Australian National University, Canberra, A.C.T., AUSTRALIA

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IMPROVED SYNTHESES OF 9-HYDROXY- AND 9-BUTOXY-1-PHENALENONE[†]

Submitted by K. D. Franz* and R. C. Haddon[††]
(11/1/79)

Research School of Chemistry
Australian National University
P. O. Box 4
Canberra A.C.T. 2600
AUSTRALIA

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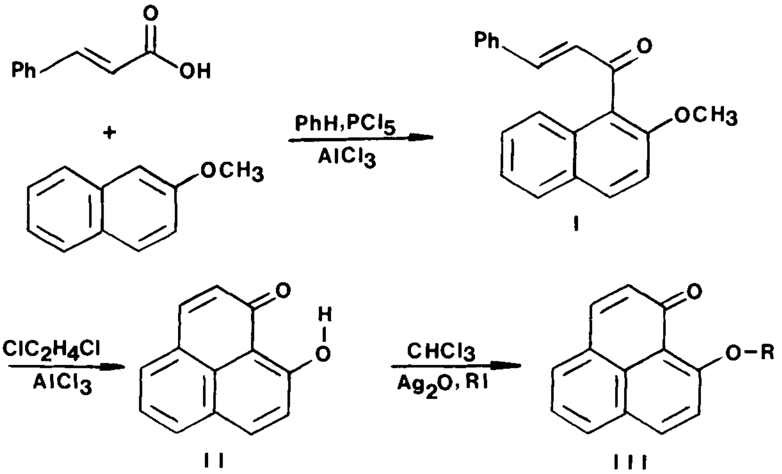
9-Alkoxyphenalenones (III), convenient starting materials for a variety of 1,9-diheterosubstituted phenalenium ions,[1,2] have been obtained from 9-hydroxy-1-phenalenone (II).[3] We have modified the method of Koelsch and Anthes[3a] and report a simplified and improved synthesis.



A crucial step in the chemistry of 1,9-diheterosubstituted phenalenes is the etherification of the strongly hydrogen bonded β-hydroxyketone II. The amounts of expensive silver oxide (Ag_2O) and alkyl halides have been reduced considerably compared with those for the original preparation.[2] Although it seems likely that the reaction proceeds <u>via</u> the corresponding silver salt as an intermediate,[4] Koelsch and Anthes[3a] failed to isolate a product from the direct reaction of the silver salt with methyl iodide. The present procedure works as well for R = CH_3, CH_2CH_3, and $CH(CH_3)_2$[2] and is illustrated with R = $\underline{n}\text{-}C_4H_9$.

EXPERIMENTAL

All the required chemicals are commercially available (Aldrich, Merck) and were used without further purification. The reactions should be performed in a well-ventilated fume hood because of the large quantities of HCl which are liberated. As with other unsaturated polycyclic hydrocarbons, skin contact and inhalation should be avoided.[5]

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1-Cinnamoyl-2-methoxynaphthalene (I).- A mixture of 500 ml of benzene, *trans*-cinnamic acid (70 g, 0.47 mole) and 2-methoxynaphthalene (70 g, 0.44 mole) was placed in a 2 l., three-necked, round-bottom flask fitted with a condenser and mechanical stirrer. Phosphorus pentachloride (100 g, 0.48 mole) was added to the mixture with vigorous stirring at room temperature. When the evolution of HCl had ceased, the solution was heated at reflux for 10 minutes, and then cooled to room temperature. $AlCl_3$ (70 g, 0.525 mole) was then added to the solution. On heating at reflux for a further 30 minutes, more HCl was evolved and the mixture darkened. The deep red solution was cooled in an ice bath and hydrolyzed carefully with a mixture of 300 g of ice and 150 ml of conc. HCl. A bright yellow solid precipitated and two phases separated. The whole mixture was filtered and the residue was recrystallized from 500 ml of boiling benzene giving 70-80 g of I. The benzene layer of the reaction mixture was evaporated to dryness and the residue was removed from the flask with the aid of two 100 ml portions of methanol and collected (10-20 g of I). The combined product was dried under vacuum overnight yielding 80-100 g 1-cinnamoyl-2-methoxynaphthalene (64-82%), mp. 135-140°; lit.[3a] mp. 140°; ^{1}H-NMR ($CDCl_3$): δ 3.8 (3H), δ 7-8(13H). The dried product may be used for the synthesis of II without further purification.

9-Hydroxy-1-phenalenone (II).- To a solution of 90 g (0.31 mole) of I in 1.3 l. of 1,2-dichloroethane in a 2 l., three-necked round-bottom flask fitted with a condenser and mechanical stirrer was added $AlCl_3$ (175 g, 1.31 mole). The reaction mixture was then slowly heated to boiling and kept refluxing for 1 hr. with stirring.[6] During this time HCl was evolved. After the reaction was over, the flask was cooled in an ice bath and the product was carefully hydrolyzed with a mixture of 220 ml of conc. HCl and 220 g ice with vigorous stirring. The dark brown solid was filtered and extracted in a beaker with two 500 ml portions of boiling 1,2-dichloroethane; the extracts were combined with the organic layer of the filtrate. The solvent and traces of water were removed on a rotatory evaporator yielding 75 g of crude product. The final purification was achieved by sublimation at 150-180°C (10^{-1} Torr) giving 40-50 g (66-82%) of pure 9-hydroxy-1-phenalenone, mp. 200-202°; lit.[3a] mp. 200°.

Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58; H, 4.11. Found: C, 79.49; H, 4.11. The ^{1}H-NMR spectrum shows a characteristic multiplet for seven protons at δ 7-8 and a singlet for the bridging proton at δ 14.8 ($CDCl_3$).

9-Butoxy-1-phenalenone (III, R = n-Bu).- 9-Hydroxy-1-phenalenone (II) (40 g, 0.2 mole), Ag_2O (0.26 g, 0.12 mole), and 500 ml $CHCl_3$ were placed in a 1 l., three-necked round-bottom flask with a condenser with drying tube and mechanical stirrer.[7] The mixture was refluxed gently with stirring and slowly changed color from black to brown. After 1 hr., the first of 5 ml of 1-iodobutane was added to the reaction and this procedure was repeated every 2 hrs. until 20 ml of the iodide have been used. After 2 hrs., a final 10 ml were added to the mixture and the reaction was kept boiling until the color of the suspension changed to pale grey (typically after 12-15 hrs.). The dark yellow solution was filtered from the solid through a medium frit and the residue was washed at least three times with 100 ml portions of $CHCl_3$. The combined filtrates were concentrated on a rotary evaporator to give a heavy, nearly black oil. This was diluted with 200 ml of xylene and again evaporated on a boiling water bath until no more

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volatile components could be collected. The crude oily product could be solidified by passing a stream of compressed air into the flask for about three hrs. The dark brown yellow cake is sufficiently pure for further work and there are no impurities detectable in the ^{1}H-NMR spectrum. The compound may be purified to yellow, platelike crystals, either by recrystallization from petroleum ether (100-120°) or by chromatography on Al_2O_3 (0.05-0.2 mm particle size) with $CHCl_3$, yielding 39-45 g (77-89%) 9-butoxy-1-phenalenone, mp. 65°, lit.[2] mp. 65°.

<u>Anal</u>. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.80; H, 6.43.

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* To whom inquiries should be addressed at BASF AG, 6700 Ludwigshafen, West Germany

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†† Present address, Bell Laboratories, 600 Mountain Avenue, Murray Hill, N.J. 07974, USA.

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4. Treatment of the residue of an incomplete reaction with pyridine and evaporation of the red solution gave 1,9-phenalenedionatosilver, $C_{13}H_7O_2Ag$: Calcd.: C, 51.52; H, 2.33, Ag, 35.59. Found: C, 51.59; H, 2.51; Ag, 36.37.
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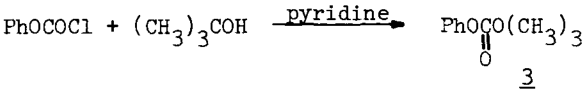
6. After ca. 15 minutes a dark brown solid is formed on the top of the reaction mixture so that more vigorous stirring is required.
7. The yields are improved by using ethanol free chloroform. Although there has been no accident so far, the reaction should be performed behind a safety shield (Ag_2O, R-I, $CHCl_3$!) and in a well-ventilated fume hood (alkyl iodides are suspected to be carcinogenic).

t-BUTYL PHENYL CARBONATE

Submitted by John W. Scott* and David Parker
(9/4/79)

Chemical Research Department
Hoffmann-La Roche Inc.
Nutley, New Jersey 07110

In contrast to a previous report [J. Am. Chem. Soc., 79, 98 (1957)], pyridine has been found to be an excellent base for the preparation of t-butyl phenyl carbonate (93-95%).



$$PhOCOCl + (CH_3)_3COH \xrightarrow{pyridine} PhO\underset{\underset{O}{\|}}{C}O(CH_3)_3$$

3

PROCEDURE

t-Butyl Phenyl Carbonate (3).- A stirred mixture of 1.103 ℓ. (868 g., 11.72 moles) of t-butyl alcohol (Matheson Coleman and Bell), 938 ml. (924 g., 11.65 moles) of pyridine (Fisher Scientific Company) and 1.75 ℓ. of methylene chloride was cooled with a tap water bath as 1.82 kg (11.62 moles) of phenyl chloroformate (PPG Industries, Inc.) was added at a rate such that the temperature remained ⩽28° (5.5 hrs); small amounts of ice were added to the bath to help control the exotherm. The water bath was left in place

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