α-Phenoxyacrylophenone.[1,6] A mixture of 50 g. (0.186 mole) of β-dimethylamino-α-phenoxypropiophenone[1] and 50 ml. of *N,N*-dimethylaniline was heated under reflux for 1 hr. After cooling to room temperature the reaction mixture was dissolved in 300 ml. of ether and the ethereal solution extracted twice with 400 ml. of 1*N* hydrochloric acid. The ethereal solution was dried over anhydrous magnesium sulfate, the ether removed, and the residue recrystallized from ethanol. There was obtained 35.4 g. (85%) of colorless prisms melting at 100–102°.

α-p-Chlorophenoxyacrylophenone was prepared by heating β-dimethylamino-α-*p*-chlorophenoxypropiophenone under reflux with *N,N*-dimethylaniline, as described above for α-phenoxyacrylophenone. The product after recrystallization from anhydrous ethanol consisted of colorless prisms melting at 102.5–104.5°, yield, 65%.

Anal. Calcd. for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.76; H, 4.17; Cl, 13.32.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies on Naphthalides. III.[1] Action of Substituted Phenylacetic Acids, Quinaldine and Picolines on Naphthalic Anhydride

WILLIAM IBRAHIM AWAD AND OSMAN MOHAMAD ALY

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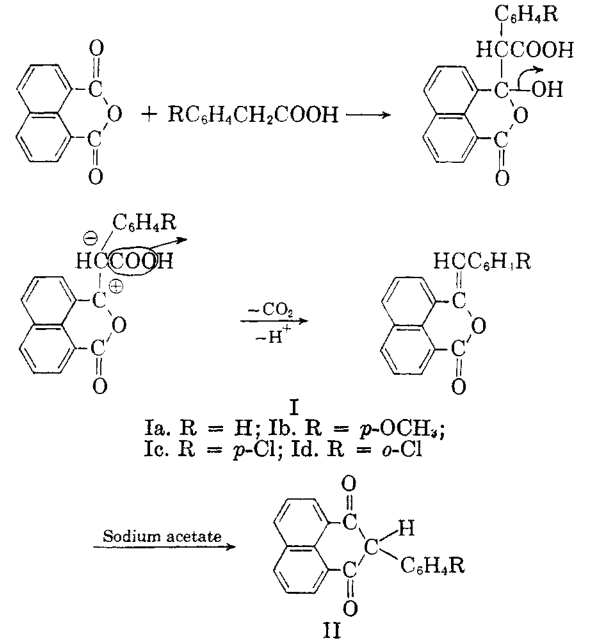
Substituted phenylacetic acids were condensed with naphthalic anhydride, to show the effect of different groups on the products, which are 3-benzalnaphthalides (I) or β-diketones (II). Other active methylene compounds, *e.g.* quinaldine, α-picoline, and γ-picoline were allowed to condense with naphthalic anhydride to produce the corresponding pyronaphthalones.

The authors[1] have already shown that naphthalic anhydride reacts with phenylacetic acid and sodium acetate to give a mixture of 8-phenyl-*peri*-naphthindan-7,9-dione (IIa) and 3-benzalnaphthalide (Ia). This work is now extended to investigate the effect of substitution in the aromatic ring of phenylacetic acid on the above Perkin condensation.

A semiquantitative study on the relative yields of the β-diketones (II) to the benzalnaphthalides (I) has been taken as a criterion for this investigation (*cf.* Table I). The following mechanism is proposed for this condensation:



I
Ia. R = H; Ib. R = *p*-OCH_3;
Ic. R = *p*-Cl; Id. R = *o*-Cl

II
IIa. R = H; IIb. R = OCH_3; IIc. R = *p*-Cl

TABLE I

RELATIVE YIELDS OF β-DIKETONES AND BENZALNAPHTHALIDES

	Benzalnaphthalide, %	β-Diketone, %	Total yield, %
Phenylacetic acid	16	50	66
p-Methoxyphenylacetic acid	22.3	40	62.3
p-Chlorophenylacetic acid	9	13	22
o-Chlorophenylacetic acid	13	—	13
p-Nitrophenylacetic acid	—	—	—

It is likely that II arises from I by the action of sodium acetate by a mechanism analogous to Scheme A (*inter alia*).

In the case of *p*-methoxyphenylacetic acid, the total yield is slightly less than that of phenylacetic acid but the ratio of the diketone is much higher. The total yields in the case of *o*- and *p*-chlorophenylacetic acids are much less when compared with the other two cases. It is also to be noticed that, in the case of the chloro derivatives, the benzal compounds (I) are predominant. No diketone was isolated in the case of *o*-chlorophenylacetic acid, perhaps because the electron attracting groups (*i.e.* Cl, —I>+T) facilitates the partial decarboxylation of such acids prior to condensation which may be responsible for the relatively poor yields in such cases. This is verified by the fact

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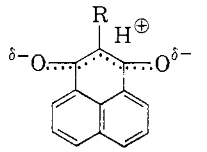
(1) O. M. Aly, W. I. Awad, and A. M. Islam, *J. Org. Chem.*, **23**, 1624 (1958).

that *p*-nitrophenylacetic acid (NO_2, —I, —T effect) does not give any condensation product.

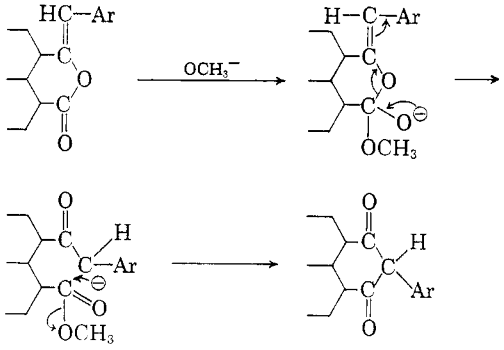
The constitution of the benzalnaphthalide (I) is based on two facts: (i) the ease of their rearrangement into the corresponding β-diketones on treatment with sodium methoxide (*cf.* Nathanson[2] and Eibner[3]), and the presence in the infrared spectra of these naphthalides of a carbonyl stretching frequency in the region of δ-unsaturated lactones[1] (*cf.* Table II). The infrared spectra of the corresponding β-diketones are also shown in the same table.

The β-diketones (II) do not show normal ketonic properties (hydrazones, oximes). They have a pronounced acidic character (soluble in dilute sodium carbonate), and no free —OH stretching frequency appears in the infrared spectra. It is thus not unreasonable that III can be considered as one of the possible unperturbed structures (*cf.* III).



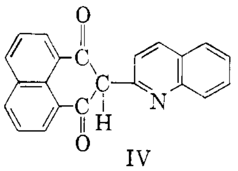
III

When 3-(*o*-chlorobenzal)naphthalide (Id) is treated with sodium methoxide in a trial to get the corresponding diketone, we obtained a yellow crystalline compound which is chlorine free; at the present time we are unable to assign any structure for it and it is still under investigation. Scheme A is proposed for the action of sodium methoxide on benzalnaphthalides to give the corresponding β-diketones:

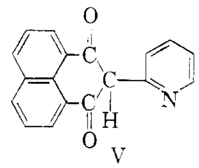


Scheme A

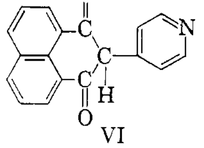
Some other active methylene compounds, namely quinaldine, α-picoline and γ-picoline have been allowed to condense with naphthalic anhydride on the hope of obtaining anticonvulsants and estrogenic antagonists.[4] In the case of quinaldine the reaction was carried out in the presence of sodium acetate or zinc chloride, while in the case of α- and γ-picolines the reaction was successful only by the use of zinc chloride in a sealed tube. In these cases only the diketones are obtained and no benzalnaphthalides. The structure of these nitrogenous diketones (IV), (V), and (VI) is based upon: (i) the stability of these compounds towards sodium methoxide, and (ii) infrared spectra (*cf.* Table II), which indicate a carbonyl stretching frequency in the region of β-diketones.[1]



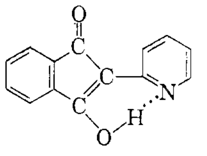
IV



V



VI



VII

TABLE II[a]

INFRARED SPECTRA

Compound	Carbonyl Stretching Frequency cm.$^{-1}$
Ib	1724
Ic	1739
Id	1745
IIb	1626
IIc	1618
IV	1639
V	1639

[a] Infrared measurements were carried out on Perkin-Elmer infracord model 137 using nujol nulls.

Manly, *et al.*[4] stated that structure VII is possible for the pyrophthalones. Such structure could not be detected in the case of the pyronaphthalones IV, V, and VI as no free nor chelated —OH groups could be observed in the infrared spectra. Structure III for the perinaphthalene derivatives seems to play a more important role.

EXPERIMENTAL[5]

Reaction of naphthalic anhydride with p-methoxyphenylacetic acid. A mixture of naphthalic anhydride (5 g.), *p*-methoxyphenylacetic acid (*p*-methoxybenzyl cyanide was prepared according to *Organic Syntheses*,[6] followed by hydrolysis in acid medium in the normal way), and fused sodium acetate (0.3 g.) was heated rapidly to 240–250° and maintained at that temperature for 1 hr. The hot melt was rubbed with 30 ml. of alcohol and allowed to cool. On filtration, a brownish orange product was obtained (6.5 g.). The crude product was extracted with 150 ml. of petroleum ether (b.p. 70–80°) in a Soxhlet extraction apparatus. The extract acquired an orange coloration. On concentration of the petroleum ether solution, an orange yellow product was ob-

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(2) Nathanson, *Ber.*, **26**, 2576 (1893).

(3) Eibner, *Ber.*, **39**, 2203 (1906).

(4) D. G. Manly, A. Richardson, Jr., A. M. Stock, C. H. Tilford, and E. D. Amstutz, *J. Org. Chem.*, **23**, 373 (1958).

(5) Microanalyses were carried out by Alfred Bernhardt, im Max-Planck Institut, Mülheim (Ruhr), Germany. Melting points are not corrected.

(6) *Org. Syntheses*, **36**, 56 (1956).

tained. This product was washed with a hot solution of sodium carbonate. Recrystallization from benzene–petroleum ether (b.p. 40–60°) gave (Ib), 1.7 g., 22.3% as yellow crystals, m.p. 168–169°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 78.94; H, 4.69.

Ib was rearranged quantitatively to the corresponding β-diketone (IIb) on treatment with sodium methoxide solution[1] (melting point and mixture melting point).

The product which was insoluble in petroleum ether (b.p. 70–80°) was recrystallized from benzene (charcoal) to give IIb, 2.9 g., (40%); as orange needles, m.p. 220–222°.

Anal. Calcd. for: $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.85; H, 4.84.

The product was soluble in a cold dilute solution of sodium hydroxide or sodium carbonate.

Reaction of naphthalic anhydride with o-chlorophenylacetic acid. A mixture of naphthalic anhydride (5 g.), *o*-chlorophenylacetic acid (4.3 g.) (prepared in a manner similar to that for *p*-fluorophenyl acetic),[7] and fused sodium acetate (0.5 g.) was treated as described before.

Recrystallization of the product extracted with petroleum ether (b.p. 70–80°) from ethyl alcohol gave Id, 1.1 g. (13%), as yellow needles, m.p. 185–186°.

Anal. Calcd. for $C_{19}H_{11}O_2Cl$: C, 74.39; H, 3.6; Cl, 10.44. Found: C, 74.09; H, 3.49; Cl, 11.21.

When Id was treated with alcoholic sodium methoxide solution a chlorine free yellow product was obtained, m.p. 195–97°.

Anal. Found: C, 83.51; H, 3.85.

The product which was insoluble in petroleum ether (b.p. 70–80°) proved to be naphthalic anhydride (melting point and mixture melting point). No β-diketone was isolated.

Reaction of naphthalic anhydride with p-chlorophenylacetic acid. A mixture of naphthalic anhydride (5 g.), *p*-chlorophenylacetic acid (*cf.* ref. 7) (4.3 g.), and fused sodium acetate (0.3 g.) was treated as described before.

Recrystallization of the product extracted with petroleum ether (b.p. 70–80°) from ethyl alcohol gave Ic, 0.7 g. (9%), as orange yellow needles, m.p. 178–79°.

Anal. Calcd. for $C_{19}H_{11}O_2Cl$: C, 74.39; H, 3.6; Cl, 10.44. Found: C, 74.32; H, 3.52; Cl, 11.16.

The product was rearranged quantitatively to the corresponding β-diketone on treatment with alcoholic sodium methoxide solution (melting point and mixture melting point).

The product which was insoluble in petroleum ether (b.p. 70–80°) was recrystallized from ethyl alcohol to give IIc, 1.0 g. (13%), as orange crystals, m.p. 272–273°.

Anal. Calcd. for $C_{19}H_{11}O_2Cl$: C, 74.39; H, 3.60; Cl, 10.44. Found: C, 73.74; H, 3.59; Cl, 10.99.

The product (IIc) was soluble in a cold dilute solution of sodium hydroxide or sodium carbonate.

Reaction of naphthalic anhydride with quinaldine. A mixture of naphthalic anhydride (1.0 g.), quinaldine (1.5 g.), and a catalytic amount of fused zinc chloride or sodium acetate (0.3 g.) was heated rapidly to 230–240° for 3 hr. The reaction mixture was then poured on cold water, whereby a dark solid mass was obtained. Recrystallization of the product so obtained from ethyl alcohol gave IV, 1 g. (62%), as deep red needles, m.p. 254–255°. The product separated from benzene solution as deep violet rosets and from concentrated benzene solution as olive green crystals.

Anal. Calcd. for $C_{22}H_{13}O_2N$: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.98; H, 3.98; N, 4.50.

Reaction of naphthalic anhydride with α-picoline. A mixture of naphthalic anhydride (2 g.), α-picoline (3 ml.), and a catalytic amount of fused zinc chloride was heated in a sealed tube at 200° for 4 hr. The reaction product was poured on cold water and the solid mass so obtained was washed with a little methyl alcohol, then allowed to dry. The crude product was dissolved in dry benzene and chromatographed over silica gel. On elution with dry benzene, a colorless fraction (0.9 g.) was obtained which proved to be naphthalic anhydride (melting point and mixture melting point). An orange fraction was also obtained, which on concentration gave V, 0.8 g. (30%), as orange needles, m.p. 268–269°. It was soluble in dilute solution of sodium hydroxide or sodium carbonate.

Anal. Calcd. for $C_{18}H_{11}O_2N$: C, 79.11; H, 4.06; N, 5.13. Found: C, 79.17; H, 4.04; N, 5.10.

Reaction of naphthalic anhydride with γ-picoline. Naphthalic anhydride (2 g.), γ-picoline (3 ml.), and catalytic amount of fused zinc chloride was treated as discussed above. Naphthalic anhydride was also isolated here and VI, 0.60 g. (23%), was isolated as orange needles, m.p. 258–59°. It was soluble in a dilute solution of sodium hydroxide or sodium carbonate.

Anal. Calcd. for $C_{18}H_{11}O_2N$: N, 5.13. Found: N, 4.57.

ABBASSIA, CAIRO
EGYPT, U.A.R.

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(7) F. L. M. Patisson and B. C. Saunders, *J. Chem. Soc.*, 2745(1949).

[CONTRIBUTION FROM THE YERKES RESEARCH LABORATORY, E. I. DU PONT DE NEMOURS & CO., INC., FILM DEPARTMENT]

Carbamates. IV. The Reactions of Disubstituted Carbamates with Alcohols

NORMAN G. GAYLORD[1]

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The reaction of ethyl *N,N*-disubstituted carbamates with alcohols in the presence of the sodium alkoxide of the alcohol yields either carbamates or carbonates, apparently as a function of the relative base strengths of the disubstituted amine and the alkoxide. Thus, the reactions of isobutyl alcohol with ethyl *N,N*-diethyl- and *N*-ethyl-*N*-phenylcarbamates, and benzyl alcohol with ethyl *N*-ethyl-*N*-phenylcarbamate and *N*-*N′*-dicarbethoxypiperazine yield the corresponding carbamates. The reaction of isobutyl alcohol with ethyl *N,N*-diphenylcarbamate yields principally diisobutyl carbonate and diphenylamine, while the reaction of benzyl alcohol with ethyl *N,N*-diphenylcarbamate yields dibenzyl ether, by decarboxylation of the carbonate, and diphenylamine.

It has previously been reported[2] that the reactions of ethyl carbamate with low boiling alcohols, *e.g.*, isobutyl alcohol, with acid catalysis, or with high boiling alcohols, *e.g.*, benzyl alcohol,

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(1) Present address: The Western Petrochemical Corporation, Polymer Division, 96 Roanoke Avenue, Newark 5, N. J.

(2) N. G. Gaylord and C. E. Sroog, *J. Org. Chem.*, 18, 1632 (1953).