solved in $H_2{}^{18}O$ (150 ml) and the solution was made alkaline and extracted with pentane to remove the cyclohexylamine. The pH of the solution was then adjusted and the hydrolysis was carried to completion. For reactions at pH 6 the dinitrophenol was extracted with chloroform; this step was omitted for reaction in alkali. Barium phosphate was then precipitated, redissolved in acid and reprecipitated, following procedures already described, and then converted into potassium dihydrogen phosphate using Dowex 50W-X8 resin in its acid form followed by neutralization with KOH. Potassium dihydrogen phosphate was then isolated following procedures already described,[9] and its ^{18}O abundance was determined by heating it *in vacuo* with phenylenediamine hydrochloride and guanidine hydrochloride and analyzing the evolved CO_2 mass spectrometrically.[10]

Registry No.—2,4-Dinitrophenyl phosphate, 2566-26-9.

(9) C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, 3574 (1958).
(10) C. A. Bunton and B. N. Hendy, *ibid.*, 627 (1963).

Base-Catalyzed Formation and Reactions of *o*-Nitrophenylacetamides[1a,b]

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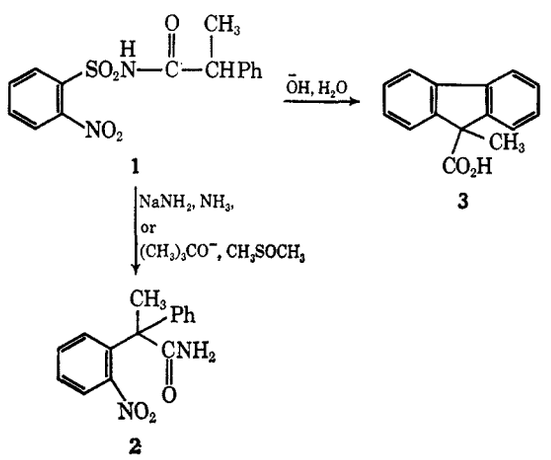
Naito and coworkers[2] have shown that Smiles rearrangement of N-(nitrophenylsulfonyl)acetamides can be a useful synthetic route to nitrophenylacetamides. We subjected N-(*o*-nitrophenylsulfonyl)-2-phenylpropionamide (**1**) to prolonged heating (26 hr) with 10% aqueous sodium hydroxide in an attempt to synthesize 2-(*o*-nitrophenyl)-2-phenylpropionamide (**2**) (Scheme I). The principal product of the reaction was found to

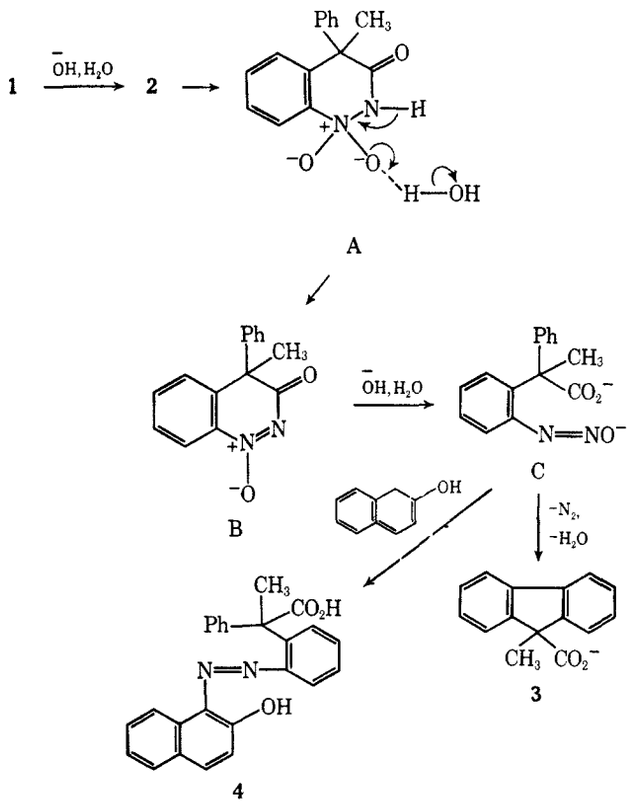
SCHEME I



be a nitrogen-free acid (30% yield). Spectral evidence and comparison with an authentic sample showed the acid to be 9-methylfluorene-9-carboxylic acid (**3**). It proved to be possible to synthesize **2** from **1** by using alternative basic catalysts. Sodium amide in liquid ammonia effects the transformation in 43% yield, whereas use of potassium *t*-butoxide in dimethyl sulfoxide gave **2** in 67% yield.

We propose that the formation of **3** results from base-catalyzed intramolecular condensation of the amide and nitro groups in **2** and that the reaction follows the course outlined in Scheme II.

SCHEME II

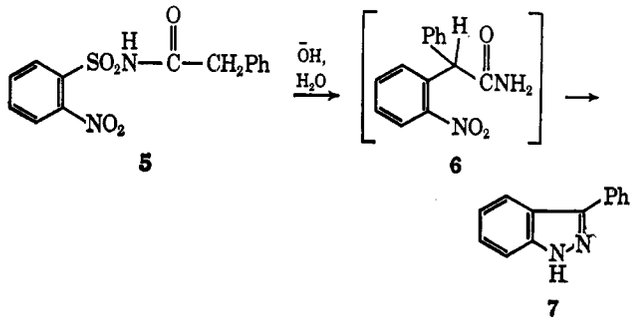


The following observations can be cited in support of this proposal. When **2** is subjected to reaction with aqueous base, **3** is formed in 59% yield after 4.5 hr. Reaction of **1** with aqueous sodium hydroxide in the presence of β-naphthol leads to an azo compound believed to be **4** on the basis of analytical and spectral data. The formation of **4** suggests the intermediacy of a diazonium hydroxide (C) in the reaction. If C is formed by intramolecular condensation from **2**, the final step in the formation of 9-methylfluorene-9-carboxylic acid can readily be explained as a Pschorr cyclization.[3]

The intramolecular condensation between an amide group and nitro group which is proposed to account for the formation of intermediate B is an example of a relatively rare class of reactions, although condensations with many other types of carbon and nitrogen nucleophiles and nitro groups are quite common.[4] The formation of 3-phenylindazole when N-(*o*-nitrophenylsulfonyl)-2-phenylacetamide (**5**) is heated with aqueous base is believed to involve a similar condensation[2,4] proceeding *via* the Smiles rearrangement product **6** (Scheme III). An attempt was made to trap a di-

(1) (a) Supported in part by NIH Grant GM-14344. (b) Abstracted from the Ph.D. Thesis of D. E. Blackburn, University of Virginia, 1969. (c) NASA Trainee, 1964–1967.
(2) T. Naito, R. Dohmori, and O. Nagase, *J. Pharm. Soc. Japan*, **74**, 593 (1954); T. Naito, R. Dohmori, and M. Sano, *ibid.*, **74**, 596 (1954); T. Naito, R. Dohmori, and M. Shimoda, *Pharm. Bull.* (Tokyo), **3**, 34 (1955).
(3) D. F. DeTar, *Org. Reactions*, **9**, 409 (1957).
(4) J. D. Loudon and G. Tennant, *Quart. Rev.* (London), **18**, 389 (1964).

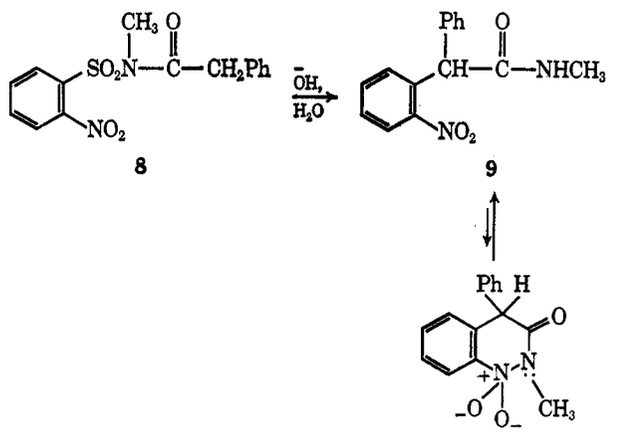
SCHEME III



azonium intermediate by treating **5** with aqueous base in the presence of β-naphthol. No azo compound was formed and the formation of 3-phenylindazole was not inhibited. The diazonium intermediate from **6** may cyclize to **7** faster than it can be trapped by β-naphthol. It is interesting to note that, in contrast to **2** and **6**, the parent compound *o*-nitrophenylacetamide undergoes hydrolysis in preference to intramolecular condensation.[5] The presence of the substituents α to the carbonyl group in **2** and **6** may be important in retarding the rate of hydrolysis sufficiently to permit intramolecular condensation to compete successfully.

Further evidence that condensation reactions involving the amido and nitro functions of **2** lead to the formation of **3** can be inferred from the results obtained with N-methyl-N-(*o*-nitrophenylsulfonyl)-2-phenylacetamide (**8**). Unlike **5**, the N-methyl homolog **8** gives the normal Smiles rearrangement product **9** on reaction with aqueous base (Scheme IV). The N-

SCHEME IV



methyl group can interfere with the intramolecular condensation by preventing loss of water and the formation of a nitrogen–nitrogen double bond.

A convenient synthesis of 2-phenylpropionic acid (hydratropic acid) based on alkylation of the disodio salt[6] of phenylacetic acid was developed during the course of this work and is described in the Experimental Section.

Experimental Section

2-Phenylpropionic Acid.—A solution of sodium amide was prepared by addition of small pieces of sodium (10.4 g, 0.45 g-atom) to liquid ammonia (750 ml) containing a small amount of ferric nitrate. Phenylacetic acid (28.2 g, 0.208 mol) was added and the mixture was stirred for 0.5 hr. Methyl iodide (29.6 g, 0.208 mol) in ether (40 ml) was added. After the reaction mixture had been stirred for 1.5 hr, the ammonia was allowed to evaporate. Ether (250 ml) was added to the residue and the mixture was evaporated to dryness on the steam bath. This procedure was repeated and the residue was then dissolved in water (600 ml) and washed with ether. The aqueous solution was filtered and acidified with hydrochloric acid. The organic layer was separated and distilled to yield pure 2-phenylpropionic acid (24.4 g, 0.162 mol, 78%), bp 92–97° (0.3 mm).

N-(*o*-Nitrophenylsulfonyl)-2-phenylpropionamide (**1**).—2-Phenylpropionyl chloride was prepared from the acid by reaction with thionyl chloride and then distilled. The acid chloride (33.7 g, 0.200 mol) and *o*-nitrobenzenesulfonamide (40.4 g, 0.200 mol) were mixed and heated in an oil bath at 170–180° for 1.5 hr. Crushed ice was added with stirring until the viscous reaction mixture solidified. The water was decanted and the residue was crystallized from ethanol–water giving 74.3 g of crude product, mp 144–155°. Treatment with charcoal and several recrystallizations gave pure **1** (34.3 g, 0.103 mol, 51%): mp 152.5–155°; ν_{NH} 3210, ν_{CO} 1720, ν_{NO_2} 1525, 1350 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.88; H, 4.22; N, 8.38. Found: C, 54.10; H, 4.45; N, 8.67.

Reaction of 1 with Aqueous Sodium Hydroxide.—A solution of **1** (1.7 g, 0.0050 mol) and 10% sodium hydroxide (20 ml, ~0.05 mol OH) was heated on a steam bath for 26 hr. The reaction mixture was acidified causing the separation of an oil which solidified on standing. The mixture was extracted with chloroform and, after concentration, the product was chromatographed on silicic acid. Chloroform eluted 9-methylfluorene-9-carboxylic acid (**3**) which was recrystallized from ethanol–water giving pure **3** (0.33 g, 0.0015 mol, 29%): mp 172–173° (lit.[7] mp 170–171°); λ_{max} (in absolute methanol) 256 mμ s (log ε 4.24), 265 (4.30), 277 s (4.08), 288 (3.75), and 299 (3.73); nmr peaks in $CDCl_3$ at δ 1.75 (3 H, s), 7.2–7.8 (8 H, m) and 10.5 (1 H, s).

The sample was identical (mixture melting point and superimposable infrared spectra) with an authentic sample of **3** prepared by the method of Anet and Bavin.[7]

2-(*o*-Nitrophenyl)-2-phenylpropionamide (**2**).—A solution of **1** (3.34 g, 0.0100 mol) in dimethyl sulfoxide (10 ml) was added to a solution of potassium *t*-butoxide (3.36 g, 0.0300 mol) in dimethyl sulfoxide (50 ml). The solution was heated at 80–85° for 24 hr. The reaction mixture was diluted with saturated aqueous sodium chloride (500 ml) and extracted thoroughly with ether. The ether solution was washed with water and dried over magnesium sulfate. The solution was filtered and evaporated. Crystallization of the residue from benzene–petroleum ether gave **2** (1.10 g, 0.0041 mol, 67% based on unrecovered **1**): mp 129–131°; ν_{NH_2} 3470 and 3360, ν_{CO} 1670, ν_{NO_2} 1535 and 1365 cm^{-1}; nmr peaks in $CDCl_3$ at δ 2.15 (3 H, s), 5.87 (2 H, broad singlet), and 6.9–7.9 (8 H, m).

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.64; H, 5.40; N, 10.35.

Unreacted **1** (1.30 g, 0.0039 mol, 39%) was recovered by acidification of the alkaline aqueous layer remaining from the extraction of **2**.

Reaction of **1** with sodamide (2 mol) in liquid ammonia for 2.5 hr led to formation of a 43% yield of **2** (based on unrecovered **1**) and recovery of 65% of the starting material.

Reaction of 2 with Aqueous Sodium Hydroxide.—2-(*o*-Nitrophenyl)-2-phenylpropionamide (0.63 g, 0.0023 mol) was heated with 10% aqueous sodium hydroxide (7.5 ml, ~0.018 mol OH^-) for 4.5 hr on a steam bath. The reaction mixture was cooled, acidified, and extracted with ether. The ether extract was washed with water, dried, and concentrated using a rotary evaporator. The residue was chromatographed on silicic acid. Chloroform eluted 9-methylfluorene-9-carboxylic acid (0.30 g, 0.0013 mol, 59%), mp 170–172° after recrystallization from ethanol–water.

Reaction of 1 with Aqueous Sodium Hydroxide in the Presence of β-Naphthol.—A mixture of **1** (1.67 g, 0.0050 mol) and β-naphthol (0.72 g, 0.0050 mol) in 10% aqueous sodium hydroxide (30 ml) was heated on a steam bath for 26 hr. The reaction mixture was acidified giving a partially crystalline precipitate. Recrystallization from ethanol–water gave pure 2-phenyl-2-[2-(2-hydroxy-1-naphthylazo)phenyl]propionic acid (**4**, 0.8 g, 0.002 mol, 40%): mp 214–216° dec; ν_{OH} 3450 and 2200–3200,

(5) C. W. Muth, N. Abraham, M. L. Linfield, R. B. Wotring, and E. A. Pacofsky, *J. Org. Chem.*, **25**, 736 (1960).

(6) C. R. Hauser and W. R. Dunnavent, *Org. Syn.*, **40**, 38 (1960).

(7) F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **34**, 991 (1956).

ν_{CO} 1730 cm^{-1}; λ_{max} (in 95% ethanol) 228 mμ (log ϵ 4.59), 315 (3.98), 485 (4.08); nmr peaks in DMSO-d_6 at δ 2.0 (3 H, s), 7.2 (15 H, m), and 13.8 (1 H, s).

Anal. Calcd for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.09; N, 7.07. Found: C, 75.78; H, 5.00; N, 6.83.

Reaction of 5 with Aqueous Sodium Hydroxide in the Presence of β-Naphthol.—N-(*o*-Nitrophenylsulfonyl)-2-phenylacetamide (1.6 g, 0.005 mol) and β-naphthol (0.72 g, 0.005 mol) were mixed with 10% aqueous sodium hydroxide (30 ml) and heated on a steam bath for 14 hr. A gummy precipitate was present. After crystallization from ethanol and elution through a short column of alumina, 3-phenylindazole (0.66 g, 0.0034 mol, 68%), mp 116–118°, was obtained.

Acidification of the aqueous reaction solution precipitated β-naphthol (0.70 g, 0.0049 mol, 97%), mp 121–122° after purification by chromatography.

Reaction of *o*-Nitrophenylacetamide with Aqueous Sodium Hydroxide.—A mixture of *o*-nitrophenylacetamide (1.8 g, 0.010 mol) and 10% aqueous sodium hydroxide was heated on a steam bath for 7 hr. Acidification of the reaction mixture followed by recrystallization of the precipitate from ethanol–water gave *o*-nitrophenylacetic acid (1.0 g, 0.05 mol, 55%), mp 138–141°.

N-Methyl-N-(*o*-nitrophenylsulfonyl)-2-phenylacetamide (8).—N-Methyl-*o*-nitrobenzenesulfonamide (10.8 g, 0.050 mol) and phenylacetyl chloride (12.4 g, 0.080 mol) were heated together at 150–160° in an oil bath for 2 hr. Crushed ice was added to the reaction mixture with stirring and the precipitate was collected by filtration. Several recrystallizations from ethanol gave pure **8** (12.1 g, 0.036 mol, 72%): mp 126.5–128°; ν_{CO} 1700, ν_{NO_2} 1540 and 1355, ν_{SO_2} 1175 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.88; H, 4.22, N, 8.38. Found: C, 53.80; H, 4.17; N, 8.21.

Reaction of 8 with Aqueous Sodium Hydroxide.—A solution of **8** (1.67 g, 0.050 mol) in 10% aqueous sodium hydroxide (12.5 ml) was heated on a steam bath for 4.5 hr. The reaction mixture contained an oil which was dissolved in ether. The aqueous solution was extracted with ether. The combined ether solutions were washed with water, dried, and evaporated. The residue was chromatographed on silicic acid. N-Methyl-(*o*-nitrophenyl)phenylacetamide (**9**) was eluted with chloroform and recrystallized from ethanol (0.37 g, 1.4 mol, 88% based on unrecovered **8**): mp 142–144°; ν_{NH} 3250, ν_{CO} 1645, ν_{NO_2} 1525 and 1345 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.43, H, 5.39; N, 10.32.

Acidification of the aqueous reaction mixture gave unreacted **8** (1.15 g, 0.034 mol, 68% recovery).

Registry No.—**1**, 20512-89-4; **2**, 20512-90-7; **4**, 20512-91-8; **8**, 20512-92-9; **9**, 20512-93-0.

The Synthesis of (+)-, (−)-, and (±)-Dimethyl 3-Methyl-1-cyclopentene-1,2-dicarboxylates and the Corresponding Acids

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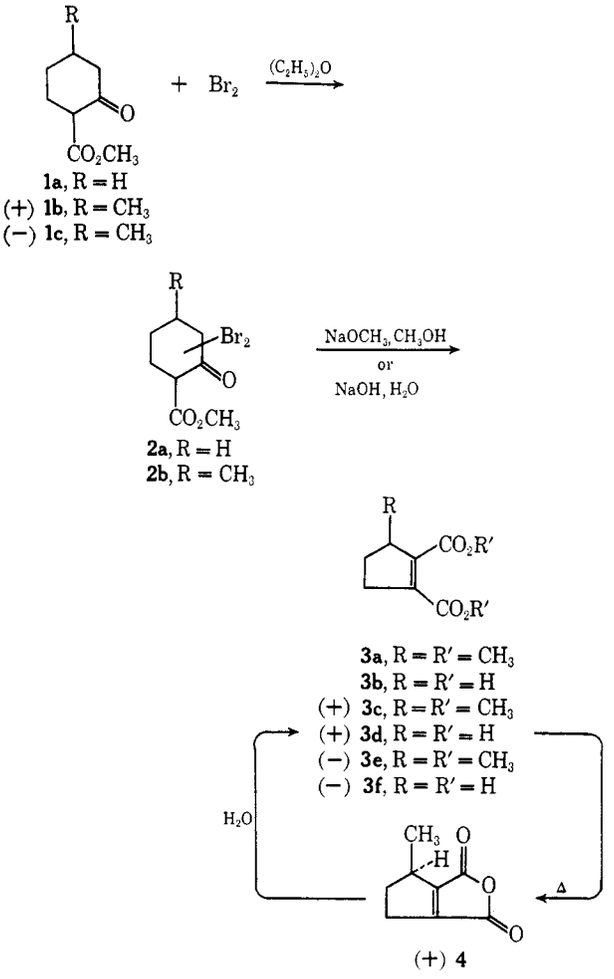
Received March 14, 1969

The synthesis of 1-cyclopentene-1,2-dicarboxylic acid and its dimethyl ester has been reported.[3] However, the reported synthesis of comparable esters with alkyl substitution at positions C-3 and C-4 are time consuming and multistep, and the over-all yields are low.[3c] We describe a convenient two-step general synthesis for esters or acids of these types. This reaction sequence, a Favorskii-type rearrangement of dibromo derivatives of β-keto esters, was first applied to 4,4-dibromo-2-methylacetoacetic acid.[4]

As shown in Scheme I, methyl 2-oxocyclohexanecarboxylate (**1a**), (+)-methyl 4-methyl-2-oxocyclohexanecarboxylate (**1b**), and (−)-methyl 4-methyl-2-oxocyclohexanecarboxylate (**1c**) on treatment with 2.2 molar equiv of bromine afforded the dibromides **2a** and **2b**.[5] These crude unidentified dibromides were then separately treated with a methanolic solution of sodium methoxide. Subsequent work-up provided the new esters (+)-dimethyl (3*R*)-methyl-1-cyclopentene-1,2-dicarboxylate (**3c**) and (−)-dimethyl (3*S*)-methyl-1-cyclopentene-1,2-dicarboxylate (**3e**). Hydrolysis of **2b**[5] yielded the new acids (+)-(3*R*)-methyl-1-cyclopentene-1,2-dicarboxylic acid (**3d**) and (−)-(3*S*)-methyl-1-cyclopentene-1,2-dicarboxylic acid (**3f**).

Dimethyl 1-cyclopentene-1,2-dicarboxylate (**3a**) and the acid **3b** were prepared and identified as described in the Experimental Section. The racemic forms of **3c**

SCHEME I



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(2) Address correspondence and reprint requests to this author.

(3) (a) E. Haworth and W. H. Perkin, *J. Chem. Soc.*, **65**, 978 (1894); (b) L. L. McCoy, *J. Amer. Chem. Soc.*, **89**, 1673 (1967); (c) R. B. Bates, E. J. Eisenbraun, and S. M. McElvain, *ibid.*, **80**, 3413 (1958).

(4) (a) M. Demarcay, *Ann. Chim. Phys.*, **20**, 433 (1880); (b) P. Walden, *Ber.*, **24**, 2025 (1891).

(5) Structure **2b** is used to represent the dibromide from both (+) **1b** and (−) **1c**.