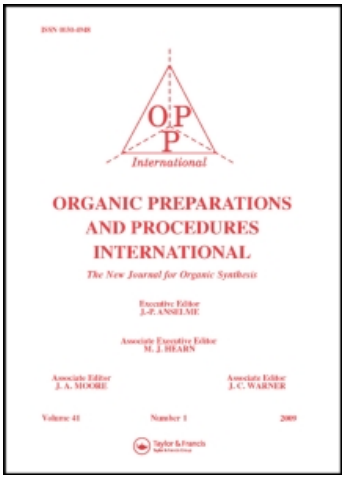

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SYNTHESIS OF OXY AND THIOARYLENE BISNAPHTHALIC ANHYDRIDES

G. A. Loughran[a]; F. E. Arnold[a]
[a] Air Force Materials Laboratory Wright-Patterson, Air Force Base, Ohio

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Table III. N-(4-Acetamidobenzenesulfonyl)-3-methyl-4-aryl-hydrazono-2-pyrazolin-5-ones (IIc)[a]

Ar	Yield (%)	mp. (°C)	Color
Ph	58	257	Yellow plates
2-NO_2Ph	65	250	Yellow plates
3-NO_2Ph	65	248	Yellow plates
2-MePh	60	241	Orange needles
2-MeOPh	65	251	Orange needles

a) See footnote of Table II.

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*To whom all correspondence should be addressed: Laboratory for Carbohydrate Research, Massachusetts General Hospital, Boston, MA 02114.

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5. Melting points were taken on a Kofler-hot stage apparatus and are uncorrected.

SYNTHESIS OF OXY AND THIOARYLENE BISNAPHTHALIC ANHYDRIDES

Submitted by (3/9/76) G. A. Loughran and F. E. Arnold*

Air Force Materials Laboratory
Wright-Patterson Air Force Base
Ohio 45433

Bis-1,8-naphthalic anhydride monomers are made by the

nucleophilic displacement reaction of the salts of aromatic diols or dithiols with 4-bromonaphthalic-1,8-naphthalic anhydride [(L. Graube, Ber., 36, 3768 (1903)].

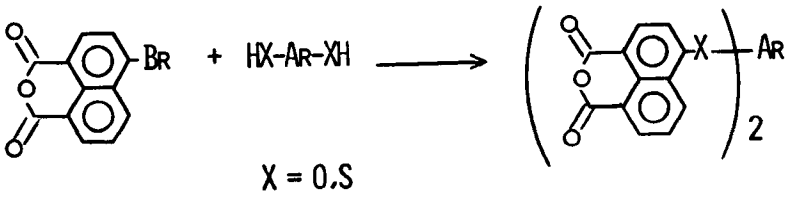

TABLE. Bis-1,8-naphthalic Anhydrides

Compound Number	Ar	X	Yield (%)	Recrystallization Solvent
I	2,2'-Biphenylene	O	95	dioxane
II	1,3-Phenyl	O	82	acetone
III	1,3-Phenyl	S	75	dioxane
IV	4,4'-Diphenyl Sulfide	O	97	chlorobenzene
V	4,4'-Diphenyl Sulfone	O	99	DMAC

EXPERIMENTAL

2,2'-Bis(4-oxy-1,8-naphthalic anhydride)biphenyl (I). - To a solution containing 2.32 g (0.0125 mole) of o,o'-dihydroxybiphenyl in 150 ml of N,N-dimethylacetamide (DMAC) was added, under a nitrogen atmosphere, 10 ml of a 10% aqueous solution of 6.93 g (0.025 mole) of 4-bromo-1,8-naphthalic anhydride in 150 ml of benzene was added dropwise over a one-hour period as the temperature rose to 100° and water was removed as an azeotrope. The benzene was removed after 8 hrs. and the reaction mixture was precipitated into water to give an orange solid which was collected and dried at room temperature. The product was recrystallized from p-dioxane to give 6.9 g (95%), mp. 286-287°.

Ir (KBr) 1730, 1770 (C=O); mass. spec.: (M^+ 578).

Anal. Calcd. for $C_{36}H_{18}O_8$: C, 74.73; H, 3.14
Found: C, 74.67; H, 3.21

1,3-Bis(4-oxy-1,8-naphthalic anhydride)phenylene (II). - To a solution of 1.10 g (0.01 mole) of resorcinol in 50 ml of anhydrous benzene was added 1.04 g (0.02 mole) of sodium methoxide. The solution was stirred at room temperature for 1 hr. and 5.52 g (0.02 mole) of 4-bromonaphthalic acid anhydride in 100 ml of DMAC was added. The reaction mixture was heated to 80° to remove the benzene and then slowly heated to 150° and maintained at that temperature for 6 hrs. The cooled solution was poured over ice to precipitate a light yellow solid. The bis-anhydride was collected, washed with water, dried under reduced pressure and recrystallized from acetone to afford 4.10 g (81.6%) mp. 271-272°.
Ir (KBr) 1730, 1770 (C=O); mass. spec.: (M^+ 502).

Anal. Calcd. for $C_{30}H_{14}O_8$: C, 71.71; H, 2.80
Found: C, 71.63; H, 2.69

1,3-Bis(4-thio-1,8-naphthalic anhydride)phenylene (III). - To a solution of 1.92 g (0.02 mole) of potassium-t-butoxide in 100 ml of tetrahydrofuran was added, under a nitrogen atmosphere, 1.42 g (0.01 mole) of m-benzenedithiol. To this solution was then added dropwise a solution of 5.54 g (0.02 mole) of 4-bromonaphthalic acid anhydride in 200 ml of DMAC to give a brown liquid which changed to clear amber upon complete addition of the anhydride. The reaction mixture was heated to 150° and maintained at that temperature for 6 hrs. After cooling to room temperature, the inorganic salts were removed

by filtration and the solvent was removed under reduced pressure. The gummy tan residue was recrystallized from dioxane with charcoal treatment and dried under reduced pressure to give 4 g (75%) mp. 223-224°.

Ir (KBr) 1730, 1770 (C=O); mass. spec.: (M^+ 534).

Anal. Calcd. for $C_{30}H_{14}O_6S_2$: C, 67.41; H, 2.64; S, 12.00
Found: C, 67.15; H, 2.62; S, 11.98

4,4'-Bis(4-oxy-1,8-naphthalic anhydride)diphenylsulfide (IV).- To a solution containing 1.92 g (0.02 mole) of potassium-t-butoxide in 200 ml of tetrahydrofuran was added, under a nitrogen atmosphere, 2.18 g (0.01 mole) of 4,4'-dihydroxydiphenyl sulfide to give the dipotassium salt of the diol as a white precipitate. A solution containing 5.54 g (0.02 mole) of 4-bromonaphthalic acid anhydride in 200 ml of DMAC was added and the tetrahydrofuran was removed by distillation. The reaction mixture was heated to reflux for 6 hrs. and the solvent removed under reduced pressure. The residual solid was recrystallized from 200 ml of chlorobenzene to give 5.9 g (97%), mp. 275-276°.

Ir (KBr) 1730, 1770 (C=O); mass. spec.: (M^+ 610)

Anal. Calcd. for $C_{36}H_{18}O_8S$: C, 70.81; H, 2.97; S, 5.25
Found: C, 70.69; H, 2.85; S, 5.36

4,4'-Bis(4-oxy-1,8-naphthalic anhydride)diphenylsulfone (V). - To a solution containing 3.13 g (0.0125) mole of 4,4'-dihydroxydiphenyl sulfone in 150 ml of DMAC was added, under a nitrogen atmosphere, 10 ml of 10% aqueous sodium hydroxide solution. The mixture was heated to 80°, and a solution of

6.93 g (0.025 mole) of 4-bromo-1,8-naphthalic anhydride in 200 ml of toluene was added dropwise over a one-hour period as the temperature rose to 100° and water was removed as an azeotrope. The toluene was removed after 8 hrs. and the reaction mixture was precipitated into water to give a yellow solid which was collected and dried at 160°/40 mm. The product was recrystallized from DMAC to give 7.5 g (93%), mp. > 400° (dec.).

Ir (KBr) 1730, 1770 (C=O); mass. spec.: (M^+ 642)

Anal. Calcd. for $C_{36}H_{18}O_{10}S$: C, 67.28; H, 2.82; S, 4.94
Found: C, 67.03; H, 2.70; S, 5.15