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Regioselective Substitution in Hindered Aromatics. 4-Nitrophthalic Acid from Nitration and Nitric Acid Oxidation of Indene, 1,2-Dihydronaphthalene, and Their Polymers

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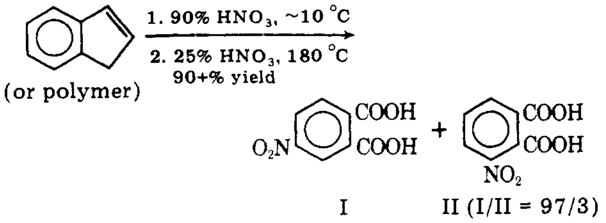
Renewed interest in the chemistry of 4-aminophthalic anhydride[1-4] prompts us to report on an efficient synthesis of 4-nitrophthalic acid, one of its precursors, from indene, 1,2-dihydronaphthalene, and polyindene.

Results and Discussion

Nitrophthalic acids are conventionally prepared by nitration of phthalic anhydride (or acid).[5,6] An approximately 50:50 mixture of 4-nitro and 3-nitro isomers (I and II, respectively) is then separated by fractional crystallization. This procedure is not applicable to large-scale production of a single isomer as availability of one isomer would always depend on an outlet for the other. Selective synthesis of 3-nitrophthalic acid can be accomplished via nitration of naphthalene, followed by subsequent oxidation of 1-nitronaphthalene.[7] To our knowledge, however, there is no procedure available to selectively prepare the more useful 4-nitrophthalic acid (or anhydride) from inexpensive raw materials. Earlier we reported that selective para substitution on an aromatic nucleus can be attained if polymeric or oligomeric substrates are used.[8] Nitration of styrene or polystyrene, followed by oxidation of their nitro intermediates, gave good yields of nitrobenzoic acids, with 90% selectivity to the para isomer. Extending this work, we now report on the selective synthesis of 4-nitrophthalic acid from indene, polyindene, and 1,2-dihydronaphthalene (eq 1).



I

II (I/II = 97/3)

(1)

Table I. Preparation of Nitrophthalic Acids

	expt no.		
	1	2	3
substrate, RH	indene[i]	polyindene[h,j]	1,2-dihydronaphthalene[h,k,o]
nitration[a]			
HNO_3 concn (wt %)	90	90	90
HNO_3,[b] g (mol)	162.5 (2.58)	162.5 (2.58)	162.5 (2.58)
RH, g (mol)[c]	30 (0.26)	30 (0.26)	30 (0.225)
time, h[d]	4.5	3.5	3.5
temp, °C (±2 °C)	−6	10	10
HNO_3 consumed, mol	0.39	0.40	N.D.
HNO_3 consumed, mol/mol of RH	1.51	1.55	N.D.
product, g (%)[e]	44.8 (94.1)	48.0 (100)	N.D.
oxidation			
nitro-RH, g (mol)[e]	30 (0.154)	48 (0.26)	N.D.
HNO_3 concn (wt %)	25	25	25
HNO_3,[b] g (mol)	94.8 (1.5)	137.3 (2.2)	N.D.
HNO_3, mol/mol of nitro-RH	9.7	8.4	N.D.
time, h	1	1	1
temp, °C (±1 °C)	180	175	175
pressure, psig	250	260	265
HNO_3 consumed, mol	0.82	1.17	N.D.
HNO_3 consumed, mol/mol of nitro-RH	5.32	4.53	N.D.
product, g (%)[e,f]	53.1 (101)	50.4 (92.5)	41.7 (86.0)
anal, %[g] (4/3/P/O)	93.0[l]/2.8[m]/0.7[n]/3.5	80.2/1.6/0.5/17.7	68.4/6.0/3.5/22.1
ratio 4-nitro/3-nitrophthalic acids	97.1/2.9	98.0/2.0	91.9/8.1

[a] Atmospheric pressure. [b] As 100% HNO_3. [c] Assume 100%. [d] Include 30 min post-addition stirring period. [e] Calculated, assume HNO_3 forms mono- and dinitro-RH. [f] Weight percent calculated vs. maximum moles of 4-nitrophthalic acid possible using assumed molecular weight of nitro-RH. [g] Mole percent 4-nitrophthalic acid/3-nitrophthalic acid/phthalic acid/others (unknowns, GLC). [h] Single experiments only; not optimized. [i] Registry no. 95-13-6. [j] Registry no. 9003-64-9. [k] Registry no. 447-53-0. [l] Registry no. 610-27-5. [m] Registry no. 603-11-2. [n] Registry no. 88-99-3. [o] N.D. is not determined.

Nitration can be carried out with nitric acid alone or in combination with sulfuric acid. Best results were obtained with 90% nitric acid since polyolefin and the nitrated intermediate were completely soluble in this medium. Use of mixed acid (HNO_3–H_2SO_4) resulted in product precipitation, incomplete nitration, and lower yields of nitrophthalic acids. Use of additional solvent such as acetic acid or chlorinated hydrocarbons could also facilitate the reaction.[9] As nitric acid is used as well for the ensuing oxidation, it was most convenient to use nitric acid alone in the first step. Following nitration with fuming nitric acid, sufficient water was added to dilute the acid down to the level needed for oxidation. The nitration with 90% nitric acid has been studied in the temperature range of −10 to 30 °C, with comparable results. Temperatures of around 170–185 °C, nitric acid concentrations of around 25%, and holding times of 1 h typify our best oxidation conditions.

Experiment 1 (Table I) represents a typical result with indene. Indene, an abundant coproduct of ethylene manufacture via steam cracking of naphtha, is the feedstock of choice for

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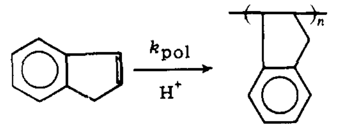
Table II. Isomer Ratios for Nitration/Oxidation of Aromatic Substrates

substrate	para/meta/ortho or α/β ratio	ref
ethylbenzene	48.2/6.5/45.3	*a*
styrene	90.0/7.5/2.5	*b*
indane	50.0/50.0	*c*
indene	97.1/2.9	*d*
tetralin	51.6/48.4	*c*
1,2-dihydronaphthalene	91.9/8.1	*d*
o-xylene	31.0/69.0	*e*

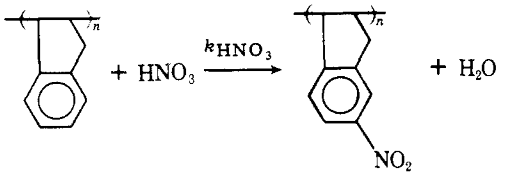
[a] A. V. Topchiev, "Nitration of Hydrocarbons and Other Compounds", Pergamon Press, New York, 1959, p 22.
[b] Reference 8.
[c] H. Tanida and R. Muneyuki, *J. Am. Chem. Soc.*, **87**, 4794 (1965).
[d] Present work.
[e] G. A. Olah, *Am. Chem. Soc. Symp. Ser.*, **No. 22**, 27 (1976).

the preparation of 4-nitrophthalic acid by our procedure.[10] Experiments 2 and 3 (Table I) show that polyindenes and 1,2-dihydronaphthalene afford equally high ratios of 4-nitro- to 3-nitrophthalic acid. Yields were not optimized with these feedstocks as they are less desirable for economic reasons. A French group reported on the nitration of polyindene, but their attempts to determine the position of the entering nitro group were unsuccessful.[11] On thermal depolymerization above 250 °C their products ignited spontaneously.

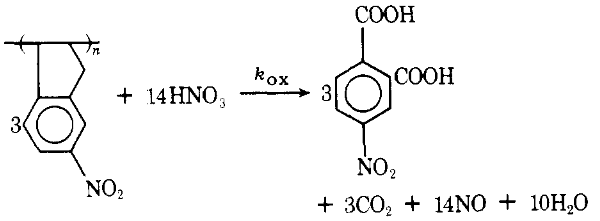
Selectivity data from successive nitrations and oxidations of styrene, indene, and 1,2-dihydronaphthalene are compared to those from their saturated alkylaromatic analogues in Table II. Greater selectivity obtained with the nitrated oligomers derived from olefinic feedstocks than with alkylaromatics can be explained by steric factors.



(2)



(3)



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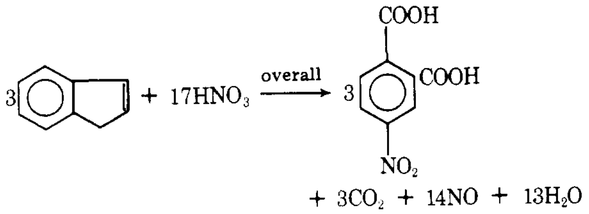
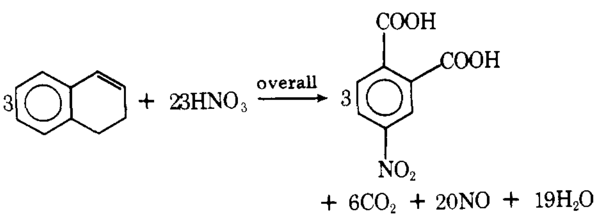


(5)



(6)

The reaction mechanism sequentially involves oligomerization, nitration, and oxidation (eq 2–4). With olefins as starting materials, oligomerization and nitration occur during interaction with nitric acid, while polymeric substrates undergo only nitration. It is well known that reactive olefins are instantaneously and quantitatively converted to polymers on contact with strong acids.[12] With nitrations preceeding or competitive with polymerization, different isomer distributions would be expected for monomer and polymer. That similar selectivities are observed from both feedstocks suggests that oligomers are intermediates in the overall synthesis, i.e., $k_{pol} > k_{HNO_3}$. Nitrated polyindenes (empirical formula $C_9H_6NO_{2.4}\cdot\frac{1}{2}H_2O$) were actually isolated and characterized as the product of indene nitration. Their molecular weight distribution (gel permeation chromatography) ranged from 96 to 9850, with 43% in the n = 2–5 and 53% in the n = 6–40 range. The ratio of aromatic to aliphatic protons (NMR) suggested indane and indanone structures to be present, the latter being further supported by infrared absorption at 1734 cm^{-1} (carbonyl band). The presence of indanone structures implies that partial oxidation occurs during nitration.

The overall nitric acid oxidations of indene and dihydronaphthalene are represented by eq 5 and 6. Detailed mechanistic aspects of the nitric acid oxidation reaction are beyond the intent of this communication.

Pure 4-nitrophthalic anhydride was readily prepared from the crude 4-nitrophthalic acid via azeotropic dehydration with *o*-xylene and crystallization in 85% yield (isolated). The yields of 4-nitrophthalic anhydride isolated, based on indene, are typically of the order of 75–80%.

Experimental Section

Nitration and Oxidation Apparatus. Nitration reactions were carried out in standard laboratory glassware, while oxidations were carried out in a 1 L, 316 stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie. Pa.). The autoclave was equipped with a cooling coil and heaters and was connected to temperature and pressure controllers and recording instruments. Nitrophthalic acids were analyzed by gas–liquid chromatography (GLC) on a 6-ft × $\frac{1}{8}$-in. stainless steel column packed with 10% OV-1 on 80/100 mesh Gas Chromosorb Q (175 °C, FID, 275 °C injector, 250 °C detector). The products appear on the chromatogram as anhydrides, following the sequence: phthalic anhydride (0.5 min), 4-nitrophthalic anhydride (1.5), and 3-nitrophthalic anhydride (2.1). The areas of peaks were measured using a digital integrator connected to a computer. As a check, the peak areas were also compared with those of the standard solutions of comparable composition. The chromatographic analyses were further confirmed by ^{13}C NMR (±3%). Indene (98+%, Eastman) and 1,2-dihydronaphthalene (97%, Aldrich) were commercial samples and were used as received. The latter also contained 0.6% of 1,4-dihydronaphthalene, 0.7% of tetralin, and 1.1% of naphthalene. For polyindene preparation, indene of 91% purity was used (6% indane, 3% unknowns, Aldrich). After polymerization the unreacted indene and indane were washed out with *n*-hexane.

Experimentation. In a typical experiment, 25 g of indene were incrementally added while stirring to 150 g of 90% nitric acid maintained at −5 ± 2 °C. After completion of addition, the reaction mixture was stirred for 1 h at −5 °C and allowed to warm up to room temperature, with stirring, over 1.5 h. The solution was poured onto 200 g of ice, diluted with 50 mL of water, and transferred to the autoclave. After addition of 100 mL of water, the reaction mixture was oxidized at 183 ± 1 °C for 1 h (250 psig, max, 1200 rpm). After evaporation of product to dryness on a rotary evaporator and collecting the distillate, a total of 42.9 g of tan solids was obtained. Analysis (GLC) showed 95.5 mol % of 4-nitrophthalic acid, 0.9% of 3-nitrophthalic acid, 1.8% of phthalic acid, and 2.1% of unknowns. Titration of the distillate showed that 1.24 mol of nitric acid were consumed (5.74 mol/mol of feed).

Preparation of Polyindene. A total of 59 g of indene (91% purity) were incrementally added over 2 h while stirring to 496 g of 85% sulfuric acid maintained at 10 ± 2 °C. After addition was completed, reaction was stirred for 20 min and poured onto 500 g of ice and 500 g of water. Filtration, followed by washing with water and air drying, gave 49.5 g of salmon-colored solid. The product was digested with *n*-hexane in a blender and filtered to afford 42.1 g of polymer (90.09%

C, 7.17% H, and 0.34% S; theoretical $(C_9H_8)_n$ = 93.06% C and 6.94% H). Gel permeation chromatography in tetrahydrofuran vs. polystyrene standards showed the polymer to have molecular weight distributions from about 230 (dimer) to 10 000 (86 indene units); mid range of the distribution was at 1150 (10 units). Therefore, 50% of polymer was oligomeric with degree of polymerization (n) being 2–6, and 50% with 6–86.

Synthesis and Purification of 4-Nitrophthalic Anhydride. Crude 4-nitrophthalic acid (50 g, 84% purity), isolated from nitration/oxidation of indene by evaporation of product mixture to dryness, was heated under reflux in the presence of *o*-xylene (225 mL) and 3.8 g of charcoal (Darco, G-60) until a theoretical amount of water had been collected in a Dean-Stark trap (3–5 h). Dehydration was carried out under nitrogen atmosphere. At the end of the dehydration, the mixture was cooled to about 90 °C and the hot product mixture was vacuum filtered through a 0.6 × 9-cm bed of celite. The filtrate was chilled (0–5 °C) and allowed to crystallize overnight. Filtration, followed by washing with *n*-hexane, produced 28.5 g (74%) of xylene-free 4-nitrophthalic anhydride, mp 107–114 °C, which was 97.5% pure (GLC). Starting with a purer product, 57.3 g (96.2% 4-nitrophthalic acid) from a run comparable to experiment 1, led to recovery of 46.8 g (85%) of 4-nitrophthalic anhydride of 99.4% purity, mp 114–117 °C (lit.[13] mp 117–119 °C). The NMR and IR spectra of product were identical with that of authentic sample.

Acknowledgment. We thank Dr. E. W. Albaugh and Mr. J. C. Suatoni for determining the molecular weight distributions of polyindene and nitrated polyindenes.

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Regiospecific Intramolecular Cyclization in 7-Keto-*endo*-2-*cis*-decalylcarbinyl Methanesulfonate

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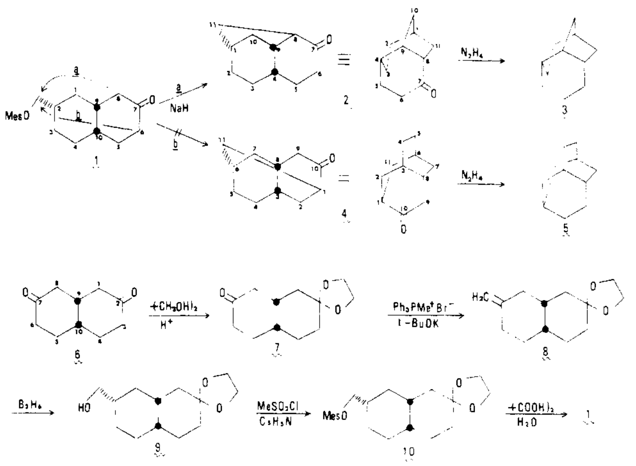
Many tricyclic compounds including natural sesquiterpenes have been synthesized via base-catalyzed intramolecular cyclizations of bicyclic keto tosylates and mesylates, which involves nucleophilic attack of α-ketocarbanion on the sulfonate-substituted, potentially cationic carbon atom.[1] In each of these syntheses, structure around the carbonyl group as well as relative orientation of the carbanion and the sulfonate-bearing carbon atom was so designed that only one product was expected to form on cyclization. Thus, the precursors were constructed under the strategies either that the carbonyl group was situated adjacent to a bridgehead in order to be enolizable only in one direction[1a,c,d,f,g] or that, although both of the α-carbon atoms could ionize, one of them cyclized to a much more stable tricyclic structure than the other did.[1b,e,h,i]

Scheme I



During our attempts to carry out independent syntheses of tricycloundecane isomers, cyclization of 7-keto-*endo*-2-*cis*-decalylcarbinyl mesylate (**1**) was examined. However, this substrate, in contrast to those studied so far,[1] could cyclize via either of the two carbanion centers C-6 and C-8. The former carbanion would afford 2,4-bishomobrendan-7-one (tricyclo[6.2.1.$0^{4,9}$]undecan-7-one, **2**), while the latter would afford tricyclo[4.4.1.$0^{3,8}$]undecan-10-one (**4**). There seems to exist no reason for the preferential formation of one carbanion over the other, and the resulting ketones **2** and **4** should have similar thermodynamic stabilities because[2] the corresponding hydrocarbons were calculated[3] to possess comparable heats of formation ($\Delta H^\circ_f = -25.94$ and -26.10 kcal/mol for **3** and **5**, respectively). Nevertheless, our experimental results were quite contrary to our expectation because 2,4-bishomobrendan-7-one (**2**) was formed selectively.

The keto mesylate **1** was prepared from *cis*-decalin-2,7-dione (**6**)[1b,4] via the route shown in Scheme I. The ethylene ketal **7** was used for the Wittig methylenation since the known diethyl ketal[1b] was partly hydrolyzed under the present reaction conditions. Hydroboration of **8** gave exclusively one hydroxymethyl isomer, which most probably had the endo structure **9** because of the established preferable exo attack of diborane on bridged olefins.[5] This configurational assignment is consistent with the successful cyclization of **1**.

The product of sodium hydride catalyzed cyclization of **1** showed only one major peak (92% of the combined peak areas), together with several unidentified minor constituents, upon preparative VPC. Golay column GC–MS indicated that the isolated major fraction was comprised of only a single component corresponding to a tricycloundecanone. IR and ^{13}C NMR spectra demonstrated an asymmetrical molecular structure with the ketone function in a six-membered ring. Wolff–Kishner reduction of the above product mixture gave 2,4-bishomobrendane (**3**)[6] (93%) and several unknowns, but no tricyclo[4.4.1.$0^{3,8}$]undecane (**5**)[7] at all.

We consider the cause for the observed regioselectivity in the cyclization of **1** to be ascribed mainly to the difference in the entropies of activation for the two transition states **2t** and **4t** leading to **2** and **4**, respectively. If we take the conformer **1g** as the ground state for the cyclization, **2t** has almost the same skeletal conformation as that of **1g**. In contrast to this, the process leading to **4** is required to pass through **4t**, and the conformation of **1g** should be altered greatly in order to reach it. Accordingly, the entropy of activation for **4t** should have a large negative value as compared with that for **2t**, and this

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