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NEW COMPOUNDS

Reduction of 2-Nitro-*p*-cymene

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Commercial 2-nitro-*p*-cymene has been carefully purified, and the following reduction products have been prepared: *trans*-2,2′-azo-*p*-cymene; 2,2′-hydrazo-*p*-cymene and its hydrochloride; 2-amino-*p*-cymene and its hydrochloride; and 2,2′-diisopropyl-5,5′-dimethyl-4,4′-diaminobiphenyl and its dihydrochloride. Purities have been evaluated by using modern techniques, and the compounds are better characterized than before.

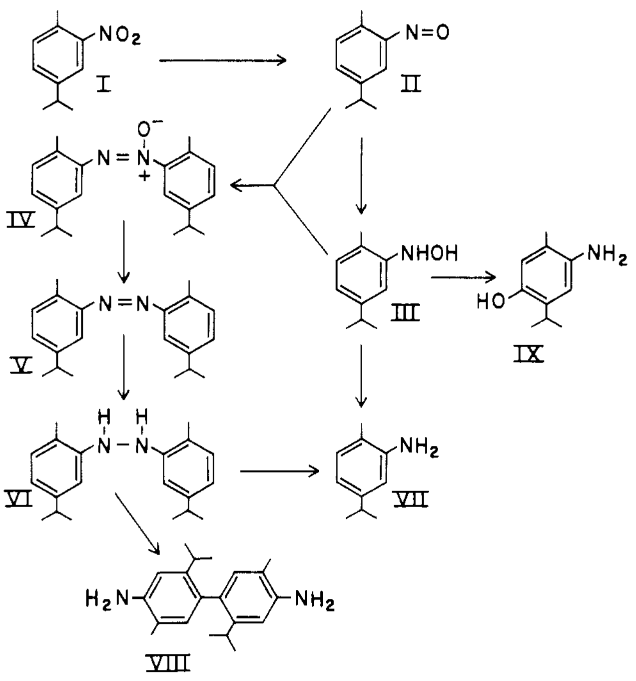
2-Nitro-*p*-cymene (I) and the reduction products shown in Scheme I were of interest for many years as possible dye intermediates. The references which have accumulated since the first attempt to prepare I in 1856 (*1*) are too numerous to cite, but the literature has been reviewed (*2*). Despite considerable attention, the compounds were never adequately characterized by modern standards. In the present work, reduction products obtained from carefully purified I have been examined, and the literature has been clarified regarding their properties.

Experimental Section

Purification of 2-Nitro-p-cymene (I). Commercial samples of I (Eastman Kodak Co. and Aldrich Chemical Co.) were purified by fractional distillation through a Nester-Faust spinning band column at 5–10 mm with pot and head temperatures of 120–138 and 95–110 °C, respectively. Both temperatures gradually increased as impurities were distilled out, remained constant during the collection of pure I, and increased slightly when additional impurities appeared in the distillate in the later stages. The reflux ratio was greater than 100:1, and a typical distillation required about 1 week. The distillate was monitored by programmed temperature GLC using SE-30 or DC-200 as the stationary liquid phase and by HPLC on a Porasil BC-18 column with gradient elution using an ethanol-water mobile phase. Probable impurities identified by chromatographic parameters were 3-nitro-*p*-cymene, *p*-nitrotoluene, 2,4-dinitrotoluene, 2,6-dinitro-*p*-cymene, *p*-tolyl methyl ketone, and *m*-nitro-*p*-tolyl methyl ketone; four additional peaks remained unassigned. A typical distillation of 65 mL of crude I yielded 40 mL of chromatographically pure material: 60-MHz NMR ($CDCl_3$) δ 1.31 (d, 6 H, J = 7 Hz), 2.64 (s, 3 H), 3.08 (septet, 1 H, J = 7 Hz), 7.47 (d, 1 H, J = 8 Hz), 7.67 (d, 1 H, J = 8 Hz), 8.12 (s, 1 H); mass spectrum (70 eV) *m/e* 179, 164, 162, 133, 117, 105, 91, 77; IR (neat) 3070, 2972, 2941, 2880, 1562, 1546, 1527, 1508, 1505, 1460, 1450, 1384, 1364, 1348, 1288, 1277, 1210, 1164, 1078, 895, 870, 833, 805, 763 cm^{-1}; UV (ethanol) 261 nm (ϵ 5050), 305 (shoulder, ϵ 1820).

Preparation of trans-2,2′-Azo-p-cymene (V). Purified I in ether was reduced to V with lithium aluminum hydride by the method of Nystrom and Brown (*3*). Excess reductant was destroyed by aqueous potassium acid tartrate, and ether washings of the insoluble salts were combined with the ether layer. After removal of the ether, the crude product was recrystallized from methanol as red plates. A small amount of 2-amino-*p*-cymene (VII) was detected chromatographically in the reaction mixture: yield 65%; mp 90.4–91.6 °C; 60-MHz NMR ($CDCl_3$) δ 1.30 (d, 6 H, J = 7 Hz), 2.74 (s, 3 H), 3.00 (septet, 1 H, J = 7 Hz), 7.38 (s, 1 H), 7.40 (s, 1 H), 7.64 (s, 1 H); mass spectrum (70 eV) *m/e* 294, 279, 252, 251, 133, 118, 117, 105, 91; IR (Nujol mull) 3038, 3018, 1203, 1172, 1154, 1120, 1055, 1040, 907, 738, 642 cm^{-1}; IR (CCl_4) 2940, 2900, 2860, 1585, 1560, 1515, 1460, 1385, 1365 cm^{-1}; UV-vis (ethanol) 236 nm (ϵ 9200), 338 (12 200), 450 (780). Recrystallization from aqueous methanol gave an orange powder instead of the red plates, mp 88.5–89.0 °C. The melt partially solidified and remelted at the higher temperature reported above.

Scheme I



Preparation of 2,2′-Hydrazo-p-cymene (VI). Azocymene (V) was reduced to the hydrazo compound (VI) by a standard procedure utilizing diimide generated from hydrazine and hydrogen peroxide (*4*). The colorless, platelike crystals which appeared during the reduction were exceedingly labile after separation from the diimide solution even with careful exclusion of air. No 2-amino-*p*-cymene was detected chromatographically in the reduced solution: UV (ethanol) 241, 275 nm.

Preparation of 2,2′-Hydrazo-p-cymene Hydrochloride. The ethanolic solution obtained as above and containing the hydrazo compound was diluted with water and extracted with ether. After the ether was dried with magnesium sulfate, dry hydrogen chloride was passed into the solution. The hydro-

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chloride salt separated as a white powder which was washed with ether and dried in vacuo, mp 258 °C (dec).

Preparation of 2-Amino-p-cymene (VII). A mixture of 40 mL of I, 50 mL of water, and 40 g of iron powder was stirred, and 100 mL of 12 M hydrochloric acid was added dropwise at a rate to maintain an even reflux. The mixture was refluxed for an additional 30 min and cooled. The pH was adjusted to about 14 with potassium hydroxide pellets, and the free amine was removed by steam distillation. The distillate was extracted with ether which was then dried with magnesium sulfate and evaporated. The crude amine residue was distilled at 10 mm to obtain the pure amine: yield 90%; bp 90 °C, 1 mm; bp 235 °C, 756 mm; 100-MHz NMR (neat) δ 1.16 (d, 6 H, $J = 7$ Hz), 1.87 (s, 3 H), 2.69 (septet, 1 H, $J = 7$ Hz), 6.44 (d, 1 H, $J = 16$ Hz), 6.69 (d, 1 H, $J = 16$ Hz), 6.95 (s, 1 H); mass spectrum (70 eV) m/e 149, 134, 119, 106, 91; IR (neat) 3458, 3367, 3215, 3050, 3010, 2960, 2930, 2900, 2868, 1632, 1620, 1609, 1573, 1508, 1453, 1422, 1377, 1358, 1330, 1300, 1275, 1259, 1210, 1180, 1150, 1050, 935, 858, 803 cm^{-1}; UV (ethanol) 234 nm (ϵ 6600), 286 (2130). Substitution of tin for iron led to the same yield. This compound can also be obtained by the same reduction procedure starting with azocymene. No contamination by the 3-amino isomer was found by GLC. VII is a colorless liquid which darkens rapidly upon exposure to air.

Preparation of 2-Amino-p-cymene Hydrochloride. VII was dissolved in petroleum ether and dry hydrogen chloride was bubbled through the solution. The amine hydrochloride precipitated as a white powder. Alternatively, the pH of the steam distillate of the amine was adjusted to about 3 by using concentrated hydrochloric acid, and water was evaporated until precipitation occurred. The salt was filtered and dried in a heated vacuum desiccator: mp 211.4–212.5 °C; 60-MHz NMR ($CDCl_3$) δ 1.70 (d, 6 H, $J = 7$ Hz), 2.67 (s, 1 H), 3.03 (septet, 1 H, $J = 7$ Hz), 7.45 (s, 2 H), 7.78 (s, 1 H); IR (Nujol mull) 3180, 3040, 2980, 2885, 2580, 1595, 1590, 1530, 1505, 1455, 1420, 1380, 1365, 1280, 1040, 930, 880, 830 cm^{-1}; UV (ethanol) 230 nm (ϵ 420), 261 (540), 264 (500), 270 (590), 282 (120). The hydrochloride is much more stable than the free amine and is the recommended storage form.

Preparation of 2,2′-Diisopropyl-5,5′-dimethyl-4,4′-diaminobiphenyl (VIII). This substituted benzidine was prepared from the hydrazo compound (VI) by the classical benzidine rearrangement. Concentrated hydrochloric acid was added dropwise to the stirred, deoxygenated, ethanolic solution of VI until the apparent pH was below 3. The solution was made alkaline with potassium hydroxide pellets, and the free base was precipitated by the addition of water. The yellow material was redissolved in ethanol, the solution was treated with charcoal, and VIII was crystallized by the dropwise addition of water to the warm solution: yield 90%; mp 173.3–174.1 °C; 100-MHz NMR ($CDCl_3$) δ 1.04 (d, 12 H, $J = 7$ Hz), 2.09 (s, 6 H), 2.75 (septet, 2 H, $J = 7$ Hz), 3.62 (br, 4 H), 6.71 (s, 1 H), 6.82 (s, 1 H); mass spectrum (70 eV) m/e 296, 281, 253, 239, 238, 223, 222, 209, 208; IR (CCl_4) 3420, 3350, 3010, 2950, 2920, 2860, 1634, 1615, 1555, 1485, 1393, 1355, 1335, 1284, 1252, 1228, 1174, 1153, 1103, 1029, 1004, 900, 865 cm^{-1}; UV (ethanol) 239 nm (ϵ 16400), 289 (4900). No impurities were detected chromatographically. The dihydrochloride of VIII was crystallized as red needles by slowly cooling an aqueous ethanolic solution of VIII which had been acidified with hydrochloric acid, mp 305 °C (dec).

Satisfactory elemental analyses of the following compounds were included for review in the original manuscript: I, V, VIII, and the hydrochlorides of VI and VII.

Instruments. The following instruments were employed: ultraviolet spectra, Perkin-Elmer Model 202; NMR spectra, Varian Model T-60 or JEOL Model MH-100; mass spectra, Varian Model M-66; infrared spectra, Perkin-Elmer Model 421; GLC, Varian Series 1400 with flame ionization detector; HPLC, Waters Model ALC 202 with ultraviolet (254 nm) and refractive index detectors.

Discussion

The nitration of p-cymene is not clean, and the 2-nitro-p-cymene available even today contains about 10% p-nitrotoluene, 10% 3-nitro-p-cymene, and at least eight other impurities totalling about 10%. It is virtually impossible to monitor the purification except by modern chromatography, and hence the reduction products obtained by earlier workers were in fact mixtures.

Infrared, NMR, and mass spectral data on the compounds reported here are consistent with the structures shown in Scheme I and with high purity. A complete X-ray crystallographic study of V has been published elsewhere (*5*); this clearly shows the substitution pattern as 2,2′ and proves that V as prepared here is the trans isomer. Definite assignment of 2-substitution for the other compounds in Scheme I is then possible.

In general, boiling points are somewhat lower and melting points higher in this study than in the older literature. The boiling point of 235 °C for VII may be compared with 240–241 (*6*), 241–242 (*7*), and 242 °C (*8*). The melting point of 211.4–212.5 °C for the hydrochloride of VII may be compared with 207 °C (*6*, *9*, *10*). The melting point of 90.4–91.6 °C for azo compound V may be compared with 86 (*11*, *12*) and 85–87 °C (*13*), both of which are below that for even the lower melting of the two crystalline forms reported here.

An attempt to prepare III by a procedure recommended for reducing nitrobenzene to N-phenylhydroxylamine with zinc dust (*14*) yielded only the amine, VII.

Electrochemical reductions, although explored only briefly, appear to offer routes to intermediate compounds in Scheme I which we were unable to obtain in good yield using chemical reductants. For example, reduction of I in a 1:4 water–ethanol solution using a mercury pool cathode at −1.4 V vs. SCE gave quantitative conversion into III based upon a coulometric n value of 4. Upon being warmed with hydrochloric acid, III yielded p-aminothymol (IX) by a well-known rearrangement (*15*). The formation of IX along with other products was earlier observed in electrolysis of I without potential control in solutions containing sulfuric acid (*16*, *17*).

Oxygenation of the solution containing electrolytic reduction product III yields II, which upon electrolysis at a cathode potential of −1.4 V vs. SCE is reduced quantitatively to VI as evidenced by a coulometric n value of 3 and a nearly quantitative recovery of VIII after acidification to effect the benzidine rearrangement.

Acknowledgment

The work reported here was begun by K.D.H., Jr., under the direction of J. N. LeConte (deceased 1973) in an undergraduate research program at East Carolina University. Helpful discussions with D. J. Goldsmith and L. Mandell are gratefully acknowledged.

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Synthesis of Novel Energetic Compounds. 4

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Reported here are the synthesis and physical properties of eight novel azido compounds. These include four polyalkylene glycol diazides and four tetraazido polyesters. The compounds have been characterized in terms of freezing point, density, refractive index, thermal stability, and impact sensitivity. The properties of these polyazides indicate that these compounds are thermally stable, are relatively insensitive to impact, and possess a wide liquid range.

The synthesis of novel energetic azido compounds has been reported in previous papers of this series (*1-3*). The synthetic chemistry of energetic polyazides has been extended in the current work to include polyalkylene glycol diazides and tetraazido polyesters, and is described herein.

For the synthesis of the polyalkylene glycol diazides from the corresponding glycols, the classical approach of proceeding through the intermediate ditosylate derivative was first considered. From a practical standpoint, the use of the tosylate moiety as a leaving group has the disadvantages of carrying such a large molecular weight material through the reaction sequence, which results in lower yields and higher costs. To circumvent this problem, an alternate, more practical approach for the synthesis of the azido compounds was developed. This approach was based on converting the polyethylene glycol dinitrates, which are readily obtained in quantitative yield from the glycols and nitric acid, to the corresponding diazides:

$$HO(CH_2CH_2O)_nCH_2CH_2OH \xrightarrow{HNO_3} O_2NO(CH_2CH_2O)_nCH_2CH_2ONO_2 \xrightarrow{NaN_3} N_3(CH_2CH_2O)_nCH_2CH_2N_3$$

On the basis of this work, the series of commercially available polyethylene glycols of molecular weights ranging from 200 to 400 (PEG-200, PEG-300, and PEG-400) have been converted to the corresponding diazides (PEG-200-DA, PEG-300-DA, and PEG-400-DA). Polypropylene glycol 425 diazide (PPG-425-DA) was also prepared and characterized.

The tetraazido polyesters were readily prepared by the esterification of aliphatic and aromatic diacid chlorides with diazidoalkanols. Four examples of this new class of compounds which have been prepared and characterized include bis(2,3-diazidopropyl) adipate (2,3-DAPA), bis(1,3-diazidoisopropyl) adipate (1,3-DAIPA), bis(2,3-diazidopropyl) *o*-phthalate (2,3-DAPP), and bis(1,3-diazidoisopropyl) *o*-phthalate (1,3-DAIPP). The method of preparation is shown in Scheme I.

The identity of these new compounds was confirmed by infrared spectroscopy and elemental analyses. The compounds have been characterized in terms of freezing point, density, refractive index, thermal stability (DSC and weight loss at 74 °C), and impact sensitivity. The properties of these polyazides, as summarized in Tables I and II, indicate that these com-

Scheme I

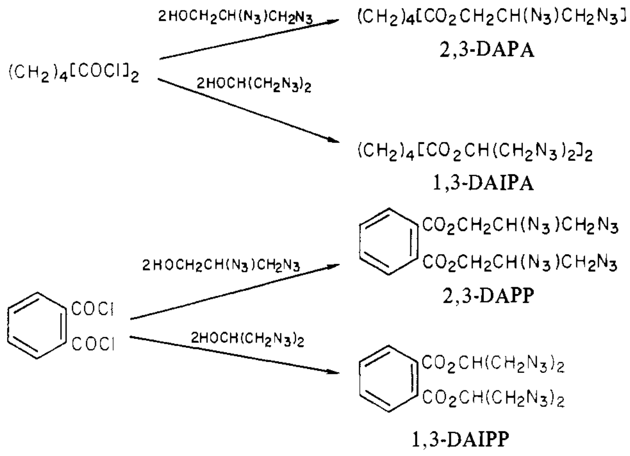

Table I. Properties of Diazide Compounds

	PEG-200-DA	PEG-300-DA	PEG-400-DA	PPG-425-DA
freezing point, °C	<−70	−45	−20	<−80
density, g/cm³	1.12	1.12	1.11	1.03
refractive index at 25 °C	1.4694	1.4685	1.4705	1.4538
DSC (10 °C/min)				
onset of exotherm, °C	175	165	180	160
peak of exotherm, °C	221	218	220	212
weight loss after 24 h at 74 °C, %	6.2	3.1	0	5.8
impact sensitivity,[a] in. lb	>100	>100	>100	ND[b]

[a] By comparison, trimethylolethane trinitrate = 40 in. lb.
[b] ND = not determined.

Table II. Properties of Tetraazido Compounds

	2,3-DAPA	1,3-DAIPA	2,3-DAPP	1,3-DAIPP
freezing point, °C	20	20	−35	−30
density, g/cm³	1.26	1.25	1.31	1.31
refractive index at 25 °C	1.5050	1.5014	1.5516	1.5498
weight loss after 24 h at 74 °C, %	0.5	0.5	ND[b]	ND[b]
impact sensitivity,[a] in. lb	ND[b]	200	95	155

[a] By comparison, trimethylolethane trinitrate = 40 in. lb.
[b] ND = not determined.

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