Formation of Cyclohexane *vs.* Tetrahydropyran Derivatives on Reaction of Glutaraldehyde with Nitroalkanes[1,2]

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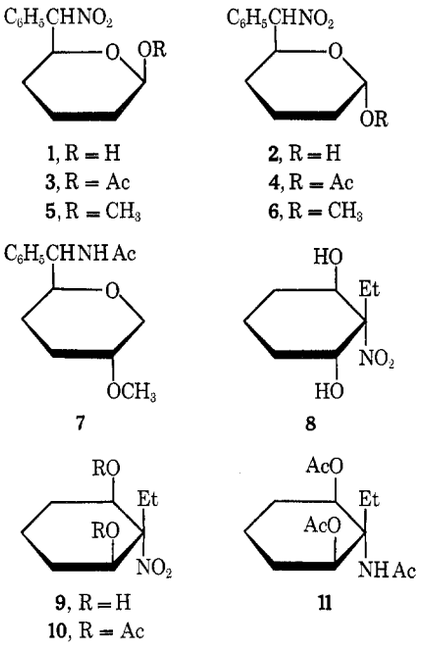
Considerable evidence has accumulated that the base-catalyzed addition of nitroalkanes to dialdehydes proceeds *via* cyclization to yield carbocyclic nitrodiols,[3] although these educts may give rise to a variety of other reactions. Examples are the Cannizzaro reaction which takes place in the case of glyoxyl[4] and naphthalene-1,8-dicarboxaldehyde,[5] and the addition of one nitroalkane per aldehyde group in glyoxal[6,7] and succinic dialdehyde.[7] Monoaddition of a nitromethylene compound to only one of the carbonyl functions has been observed in the reaction of *o*-phthalaldehyde with nitromethane which yields carbocyclic products under the common conditions,[8,9] yet can give a 1-hydroxy-3-nitromethylphthalane when performed in anhydrous nitromethane.[9] Inasmuch as three products differing in melting points have been described for the reaction of glutaraldehyde with phenylnitromethane[10-12] and, since structural assignments were only tentative, we re-examined this reaction in order to determine whether, and if so under which conditions, acyclic diaddition products or products resulting from usual dialdehyde–nitroalkane cyclization or monoaddition products may be formed.

Surprisingly, under a variety of conditions which ranged in pH from 7 to 13, the only products detectable by tlc from the reaction of phenylnitromethane with glutaraldehyde turned out to be the C-2-epimeric 2-hydroxy-6-(α-nitrobenzyl)tetrahydropyrans **1** and **2**, from stabilization of the initial monoadduct by internal hemiacetalization. The cis (**1**) and trans isomers (**2**) could be isolated as crystalline mixtures in yields of up to 50%. The cis/trans ratio varied from 2:1 to 1:3, depending on the mode of isolation and the number of



recrystallizations. As a consequence, melting points vary between 120 and 140°, hence easily explaining the discrepancies observed previously. By chromatography on silica gel, the cis isomer **1**, mp 143–145°, was separated in 24% yield. It is stable in neutral solutions of ethanol or dimethyl sulfoxide, but becomes spontaneously equilibrated with **2** on addition of traces of acid (*i.e.*, trifluoroacetic acid) or base (sodium methoxide). Treatment of the epimeric mixture of **1** and **2** or the cis isomer **1** with 2,4-dinitrophenylhydrazine afforded a crystalline product in low yield (20%), which analyzed correctly for a 2,4-dinitrophenylhydrazone of 5-hydroxy-6-nitro-6-phenylhexanal, of which the structure is as yet tentative, since cyclic phenylhydrazino forms cannot be excluded unequivocally by ir or nmr. Acid-catalyzed reactions of the epimers **1** and **2** with acetic anhydride and methanol yielded the corresponding *O*-acetyl **3** and **4** and *O*-methyl derivatives (**5** and **6**) in the form of cis–trans mixtures, in which, as expected from the anomeric effect,[13] the trans isomers predominated. Of these, compounds **4**, **5**, and **6** were obtained in a form free of their anomers. Whereas **1** and **2** are resistant toward hydrogenation with the usual catalysts under normal pressure, more forcing conditions (Raney nickel in water at 100 atm H_2 and 50°) yielded benzylamine isolable in low yield and characterized as its hydrochloride. The methoxy derivative, however, could readily be hydrogenated over Raney nickel to give after acetylation *trans*-2-methoxy-6-(α-acetamidobenzyltetrahydropyran (**7**) in 57% yield.

Structures of compounds **1–7** and their configurations at the anomeric center clearly followed from the nmr data. In DMSO-d_6 the cis isomer **1** showed, aside from an OH doublet at τ 3.36, only one distinct doublet for the benzylic proton (H-7) at τ 4.26 with $J_{6,7}$ = 10 Hz, whereas two are observed in the anomeric mixtures of **1** and **2**, the signal for the trans compound expectedly[14] appearing at higher field (τ 4.40). Similar results with respect to the chemical shift of H-7 are ob-

(1) Last communication of the series "Nitromethane Condensation with Dialdehydes." Paper XIX: F. W. Lichtenthaler and G. Bambach, *J. Org. Chem.*, **37**, 1621 (1972).

(2) This research was supported in part by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(3) For detailed reviews, see F. W. Lichtenthaler, *Angew. Chem., Int. Ed. Engl.*, **3**, 211 (1964); H. H. Baer, *Advan. Carbohyd. Chem.*, **24**, 67 (1969); F. W. Lichtenthaler, *Fortschr. Chem. Forsch.*, **14**, 556 (1970); *Methods Carbohyd. Chem.*, **6**, 250 (1972).

(4) L. W. Kissinger, W. E. McQuistion, M. Schwartz, and L. Goodman, *J. Org. Chem.*, **22**, 1658 (1957).

(5) F. W. Lichtenthaler and A. El-Scherbiney, *Chem. Ber.*, **101**, 1799 (1968).

(6) S. S. Novikov, I. S. Korsakova, and K. K. Babievskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 944 (1960); *Chem. Abstr.*, **54**, 24329 (1960); F. I. Carrol, *J. Org. Chem.*, **31**, 366 (1966).

(7) H. Plaut, U. S. Patent 2,544,103 (1951); *Chem. Abstr.*, **45**, 7587 (1951); U. S. Patent 2,616,923 (1952); *Chem. Abstr.*, **49**, 11701 (1955).

(8) F. W. Lichtenthaler, *Tetrahedron Lett.*, 775 (1963).

(9) H. H. Baer and B. Achmatowicz, *Angew. Chem., Int. Ed. Engl.*, **3**, 224 (1964).

(10) F. W. Lichtenthaler, H. Leinert, and U. Scheidegger, *Chem. Ber.*, **101**, 1819 (1968).

(11) F. W. Lichtenthaler, H. Leinert, and H. K. Yahya, *Z. Naturforsch. B*, **21**, 1004 (1966).

(12) S. Zen, A. Yasuda, H. Hashimoto, and Y. Takeda, *Nippon Kagaku Zasshi*, **90**, 110 (1969); *Chem. Abstr.*, **70**, 97153 (1969).

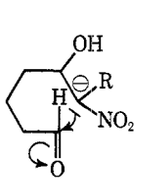
(13) E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970).

(14) H. B. Sinclair and R. T. Sleeter, *Tetrahedron Lett.*, 833 (1970).

tained for the epimeric mixtures **3** and **4** and **5** and **6**. The anomeric proton in the trans series (*i.e.*, **2**, **4**, and **7**) appears as a narrow multiplet with a half-width of 6 Hz, as anticipated for ee and ea couplings. In the cis isomers, H-2 appears at higher field, the expected quartet overlapping with the broad multiplet obtained for H-6 in each case. Additional configurational evidence can be derived from the chemical shifts of the acetoxy resonances at τ 7.91 for equatorial (**3**) and 7.84 for axial orientation (**4**), which is in accord with the acetyl resonance rule.[15]

Two main components in an approximate 2:1 ratio, together with traces of other substances, can be detected by tlc in the reaction mixture of glutaraldehyde with 1-nitropropane. The major product (36% yield) has been characterized and shown to be 1-nitro-1*r*-ethylcyclohexane-2*c*,6*t*-diol (**8**) by nmr and derivatization.[10] The other component (**9**) has now been isolated in low yield due to high-loss fractional crystallizations. Acetylation of **9** gave the di-*O*-acetate **10**, whereas hydrogenation of **9** followed by acetylation yielded the triacetate **11**. The nmr data of these compounds clearly established them to be configurational isomers of **8** and its corresponding derivatives rather than products of other conceivable structures, *i.e.*, those of the lactol type (**1**, Et instead of C_6H_5). The identical steric arrangement of H-2 and H-6 in **10** and **11** readily evolved from their identical chemical shifts and splitting patterns, thus proving a meso configuration for **9** and its ensuing products. The configuration at the ethyl branch pictured in the formula was derived from steric reasoning on the basis of molecular models and hence is tentative. In contrast to **8**, compound **9** is rather unstable, showing a distinct tendency to epimerize to **8** on melting or on short heating in aqueous solution to afford mixtures of **8** and **9** ranging in their ratios from 2:1 to 1:1.

Thus, the base-catalyzed reaction of 1-nitropropane with glutaraldehyde, yields carbocyclic products exclusively by a normal type dialdehyde–nitroalkane cyclization, while phenylnitromethane, also exclusively, gives heterocyclic products by monoaddition to one of the aldehyde functions and subsequent internal hemiacetalization. These differences may be rationalized by the concept that when R is hydrogen or alkyl the carbanion nucleophilicity in the *aci*-nitro anion **12**,



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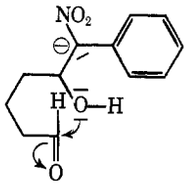

13

R = H, alkyl, CH_2OH, COOR

formed initially, is high enough to exclusively effect attack on the second aldehyde function. With hydroxymethyl or even alkoxycarbonyl residues at the nitromethyl carbon, the course of the reaction is still the same, though probably not as exclusive, as evidenced by a number of dialdehyde cyclizations with nitroethanol[16,17] and alkyl nitroacetate.[17,18] With R = C_6H_5, however, the nucleophilicity of carbanion **13**, whose electron pair is delocalized by the nitro group and the aromatic ring, is sufficiently reduced so as to allow exclusive internal hemiacetalization to tetrahydropyran derivatives.[19] From this it may be concluded that other nitromethylene compounds, whose reactions, with didaldehydes have not yet been studied, *i.e.*, nitroacetone or ω-nitroacetophenone, conceivably will yield both carbocyclic products *via* **12** and heterocyclic products *via* **13**.

Experimental Section[20]

2-Hydroxy-6-(α-nitrobenzyl)tetrahydropyran. 1:1 Mixture of Cis and Trans Isomers 1 and 2.—Phenylnitromethane (27.4 g, 0.2 mol), 25% aqueous glutaraldehyde (80 ml, 0.2 mol), methanol (100 ml), and 1 *N* sodium methoxide (5 ml) were mixed to give a solution of pH 7.0–7.5. After 3 hr at ambient temperature, the felted needles, which had separated, were filtered off and recrystallized from ethanol to give 20.2 g (50%) of **1** and **2** as an approximate 1:1 mixture (nmr): mp 123–125°; ir ($CHCl_3$) 3590 and 3410 (OH), 1555 and 1350 cm^{-1} (NO_2); nmr (DMSO-d_6), τ 2.51 (m, 5, C_6H_5), 4.26 (cis isomer **1**), and 4.40 (trans isomer **2**) (d, 0.5, $J_{6,7}$ = 10 Hz, H-7), 4.82 (narrow m, 0.5, H-2 of **1**), ~5.5 (broad m, 1.5, H-2 of **2** and H-6), ~8.5 [m, 6, $(CH_2)_3$].

Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N 5.90. Found: C, 60.90; H, 6.36; N, 5.94.

Further recrystallizations from ethanol or ethyl acetate gave higher melting mixtures of **1** and **2** (*i.e.*, mp 129–130°, 133–135°[21]) with ratios ranging between 3:1 and 1:2.

Isolation of Cis Isomer 1.—A solution of 25% aqueous glutaraldehyde (20 ml, 0.05 mol) and phenylnitromethane (6.9 g, 0.05 mol) in 100 ml of methanol–water (1:1) was brought to pH 11–11.5 by the dropwise addition of 1 *N* sodium hydroxide with stirring. A precipitate, separating after 1 hr at ambient temperature, redissolved on further stirring. After another 3 hr, the solution was freed from methanol by evaporation, subsequently acidified with 2 *N* HCl to about pH 4, and extracted with three 100-ml portions of chloroform. Evaporation of the combined extracts left a yellow oil, containing **1** and **2** in an approximate 2:1 ratio (nmr), which was purified by chromatography on silica gel with chloroform. The main fraction afforded a yellowish sirup on evaporation, which crystallized on trituration with ethanol. Recrystallization from the same solvent gave 2.9 g (24%) of **1** as colorless needles: mp 142–144°; ir ($CHCl_3$), 3590 (OH), 1545, and 1350 cm^{-1} (NO_2); nmr (DMSO-d_6) τ 3.36 (d, 1, $J_{2,OH}$ = 6 Hz, OH), 4.26 (d, 1, $J_{6,7}$ = 10 Hz, H-7), 5.40 (broad m, 2, H-2 and H-6).

Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.79; H, 6.30; N, 5.84.

On addition of trifluoroacetic acid (2 drops) to the above solution of **4** in DMSO-d_6, not only the OH doublet at τ 3.36 disappeared, but the nmr signals of the trans isomer **2** (τ 4.40 and 4.82) emerged, their intensity indicating a 1:1 mixture of **1** and **2**.

Treatment of cis isomer **1** or the epimeric mixture of **1** and **2** with dinitrophenylhydrazine under usual conditions,[22] followed by two recrystallizations of the product that had separated from ethanol, afforded yellow crystals, mp 126° in low yield (20%), that analyzed correctly for a 2,4-dinitrophenylhydrazone of 5-hydroxy-6-nitro-6-phenylhexanal.

2-Acetoxy-6-(α-nitrobenzyl)tetrahydropyran (3 and 4).—To a

(15) F. W. Lichtenthaler and P. Emig, *Carbohyd. Res.*, **7**, 121 (1968); F. W. Lichtenthaler, G. Bambach, and P. Emig, *Chem. Ber.*, **102**, 994 (1969).

(16) F. W. Lichtenthaler and H. Leinert, *Chem. Ber.*, **101**, 1815 (1968).

(17) S. Zen and A. Nishikai, *Bull. Chem. Soc. Jap.*, **42**, 1761 (1969).

(18) S. Zen, Y. Takeda, A. Yasuda, and S. Umezawa, *ibid.*, **40**, 431 (1967); H. Yanagisawa, M. Kinoshita, and S. Umezawa, *ibid.*, **42**, 1719 (1969).

(19) Although it cannot be excluded that steric factors are codetermining in the reaction leading to **13**, inspection of molecular models indicates that they are not of primary importance.

(20) Melting points were determined in a Bock Monoskop apparatus and are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as a internal standard, the chemical shifts being given in τ parts per million.

(21) Attempts to again isolate a product of mp 99°, as described previously,[11] were unsuccessful; presumably a free *aci*-nitro form of **1** had been obtained.

(22) L. F. Fieser in "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 330.

cooled solution of 62.0 g of the anomeric mixture of **1** and **2** (as obtained above) in acetic anhydride (10 ml) was added 2 drops of concentrated H_2SO_4. After 1 hr at room temperature the solution was stirred into ice–water and the precipitate formed was recrystallized from ethanol to afford 1.0 g (42%) of trans isomer **4**: mp 143–145°; nmr ($CDCl_3$) τ 2.67 (s, 5, C_6H_5), 3.78 (m, 1, H-2), 4.66 (d, 1, $J_{6,7}$ = 10 Hz, H-7), 5.15 (broad m, 1, H-6), 7.84 (s, 3, OAc), 8.22 (m, 4, CH_2 at C-3 and C-5), 8.70 (m, 2, CH_2 at C-3); nmr (DMSO-d_6) τ 4.00 (m, 1, H-2) and 4.40 (d, 1, $J_{6,7}$ = 10 Hz).

Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.20; H, 6.14; N, 5.02. Found: C, 60.36; H, 6.37; N, 4.93.

The ethanolic mother liquors, remaining after the isolation of **4**, yielded on evaporation and five recrystallizations a product, melting at 235°, which, on the basis of the intensities of the acetoxy resonances in $CDCl_3$ (7.84 for **4** and 7.91 for **3**) contained approximately 80% of the cis isomer **3**.

2-Methoxy-6-(α-nitrobenzyl)tetrahydropyran (5 and 6).—To 1.0 g of an anomeric mixture of **1** and **2** (*cf.* above) in 10 ml of methanol was added 0.5 g of a strongly acidic ion exchange resin, and the solution was refluxed for 12 hr. Removal of the resin, evaporation to dryness, and filtration of the crystalline residue with a little cold methanol afforded 750 mg (68%) of a product, composed of **5** and **6** in a 1:4 mixture (nmr). Separation was achieved by elution of the mixture from a silica gel column (2.5 × 60 cm) with chloroform. Examination of the 10-ml samples collected, by tlc [R_f values 0.73 (**6**) and 0.50 (**5**) in chloroform], evaporation of the appropriate fractions, and recrystallization, in both cases, from isopropyl alcohol afforded 520 mg (70%) of the trans isomer **6** as felted needles, mp 105°, and 140 mg (19%) of the cis compound **5** as needles: mp 125–127°; nmr ($CDCl_3$) for **6**, τ 2.55 (m, 5, C_6H_5), 4.63 (d, 1, $J_{6,7}$ = 10 Hz, H-7), 5.25 (broad m, 2, H-2 and H-6), 6.59 (s, 3, OCH_3), 8.32 (m, 4, CH_2 at C-3 and C-5), 8.80 (m, 2, CH_2 at C-4). The cis isomer **5** had analogous nmr features except for the chemical shifts for H-7 (τ 4.40) and the methoxy group (6.47).

Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.08; H, 6.77; N, 5.58. Found: C, 62.20; H, 6.74; N, 5.51 (cis isomer). Found: C, 62.12; H, 6.82; N, 5.66 (trans isomer).

***trans*-2-Methoxy-6-(α-acetamidobenzyl)tetrahydropyran (7).**—To a suspension of Raney nickel T4 catalyst[23] (2 ml) in 50 ml of methanol was added 750 mg of the epimeric mixture of methoxy compounds **5** and **6**, as obtained above, followed by hydrogenation under pressure (100 atm H_2) at room temperature for 1 day. After removal of the catalyst the solution was concentrated to about 10 ml, and, upon addition of 2 ml of acetic anhydride, kept overnight at ambient temperature. Evaporation to dryness *in vacuo* (finally 0.2 mm) and trituration of the residue with a small amount of methanol induced crystallization, to afford, after recrystallization from ethanol–water, 530 mg (57%) of **7** as colorless crystals: mp 84–85°; nmr (DMSO-d_6) τ 1.80 (d, 1, $J_{7,NH}$ = 9 Hz, NH), 2.66 (m, 5, C_6H_5), 5.08 (q, 1, $J_{2,7}$ = 4 and $J_{7,NH}$ = 9 Hz, H-7), 5.36 (narrow m, 1, H-2), 6.16 (broad m, 1, H-6), 7.08 (s, 3, OCH_3), 8.07 (s, 3, NHAc), 8.5 (m, 6, ring CH_2).

Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. Found: C, 68.35; H, 7.96; N, 5.26.

Cyclization of Glutaraldehyde with 1-Nitropropane.—To a mixture of 120 g (0.3 mol) of 25% aqueous glutaraldehyde and 40 ml (0.425 mol) of 1-nitropropane was added, with cooling, 1 *N* NaOH (20 ml). The solution was kept at ambient temperature for 3 days and subsequently deionized with a strongly acidic ion exchange resin (Merck I, H^+ form). After removal of the resin and thorough washing with methanol (200 ml) the combined filtrate and washings were evaporated to about 100 ml and, after treatment with activated carbon, taken to dryness, followed by repeated reevaporations from ethanol. Trituration of the residue with chloroform caused crystallization to give on filtration 21.7 g of crude product. Recrystallization from chloroform–petroleum ether (bp 60–80°) (1:2) afforded 20.2 g (36%) of **8** as colorless crystals, mp 90–91°, nmr in ref 10. The mother liquor, remaining after isolation of crude **8**, was evaporated to dryness and the sirupy residue was dissolved in a little ethanol followed by gradual addition of petroleum ether. The crystals that had separated after standing for 2 days consisted of an approximate 1:1 mixture of **8** and **9** (tlc in 20:1 chloroform–methanol, R_f 0.45 (**8**) and 0.62 (**9**), and were subjected to another three recrystallizations from the same solvent mixture, the separation being followed by tlc. Thus, 1.6 g (3%) of **9** was obtained as colorless rhombs. Since partial epimerization of **9** into **8** occurs on melting, as evidenced by tlc, the observed melting point on fast heating of 102–109° does not represent the melting point of pure **9**: nmr ($CDCl_3$) τ 5.60 (m, 2, $W_{1/2}$ = 18 Hz, H-2 and H-6), 6.15 (d, 2, J = 8 Hz, C-2 and C-6 OH), 8.1 (m, 8, 4 CH_2), 9.11 (t, 3, J = 7 Hz, $EtCH_3$); addition of trifluoroacetic acid eliminates the OH doublet, and reduces the half-width of the τ 5.60 multiplet to 10 Hz.

Anal. Calcd for $C_8H_{15}NO_4$: C, 50.78; H, 7.99; N, 7.40. Found (**9**): C, 50.80; H, 7.91; N, 7.24.

2,6-Diacetoxy-1-nitro-1-ethylcyclohexane (10).—A solution of 500 mg of **9** in acetic anhydride (2 ml) containing a trace of concentrated H_2SO_4 was kept at room temperature for 1 hr, and subsequently stirred into ice–water. Recrystallization of the resulting precipitate from petroleum ether–ethyl acetate (10:1) afforded 310 mg (54%) of **10** as colorless spears: mp 88–89°; nmr ($CDCl_3$) τ 4.64 (q, 2, J = 6 and 3 Hz, H-2 and H-6), 7.95 (s, 6, OAc), ~8.1 (m, 8, CH_2), 9.02 (t, 3, $EtCH_3$).

Anal. Calcd for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.80; H, 7.04; N, 4.98.

1-Acetamido-2,6-diacetoxy-1-ethylcyclohexane (11).—To a prehydrogenated suspension of 500 mg of PtO_2 in 10 ml of glacial acetic acid was added a solution of 1.0 g of nitrodiol **9** in acetic acid (30 ml) and the hydrogenation was continued. After uptake of the theoretical amount of H_2 (380 ml, 2 days) the catalyst was filtered off and washed with acetic acid (25 ml) and the combined filtrate and washings were taken to dryness with repeated reevaporations from ethanol. The remaining sirup was acetylated in a mixture of acetic anhydride (10 ml) and pyridine (25 ml) by standing overnight at ambient temperature. Removal of the solvents *in vacuo* (0.1 mm) and trituration of the residue with ice–water (50 ml) afforded a first crop of crystals, concentration of the mother liquor similarly a second, to give 890 mg of crude **11**. Two recrystallizations from water–methanol (10:1) gave 310 mg (24%) of **11** as rhombs: mp 149–151°; nmr ($CDCl_3$) τ 4.31 (s, 1, NH), 4.79 (m, 2, $W_{1/2}$ = 10 Hz, H-2 and H-6), 7.91 (s, 6, OAc), 8.07 (s, 3, NHAc), ~8.15 (broad m, 8, CH_2), 9.21 (t, 3, J = 8 Hz, $EtCH_3$); DMSO-d_6 shifts the NH signal to τ 3.09 and the acetyl resonances to 7.99 (OAc) and 8.16 (NHAc), respectively.

Anal. Calcd for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.13; N, 4.91. Found: C, 58.82; H, 8.16; N, 4.85.

Registry No.—**1** and **2**, 21891-46-3; **3** and **4**, 21891-47-4; **5** and **6**, 34288-57-8; **7**, 34288-58-9; **8**, 34289-82-2; **9**, 34289-83-3; **10**, 34289-84-4; **11**, 34289-85-5.

(23) S. Nishimura, *Bull. Chem. Soc. Jap.*, **32**, 61 (1959).

Oxidation of 4-Alkyl-2,6-di-*tert*-butylphenols with β-Manganese Dioxide

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The preparation of 2,6-di-*tert*-butyl-*p*-benzoquinone (**1**) by the salcomine-catalyzed air oxidation of 2,6-di-*tert*-butylphenol (**2**) was recently reported.[1,2] The oxidation of **2** or 4-alkyl-2,6-di-*tert*-butylphenols (**3a**) with most oxidizing agents gives only a low yield of **1**.[3–5]

(1) H. M. van Dort and H. J. Geursen, *Recl. Trav. Chim. Pays-Bas*, **86**, 520 (1967).

(2) L. H. Vogt, Jr., J. G. Wirth, and H. L. Finkbeiner, *J. Org. Chem.*, **34**, 273 (1969).

(3) M. S. Kharasch and B. S. Joshi, *ibid.*, **22**, 1439 (1957), and references cited therein.

(4) G. R. Yohe, J. E. Dunbar, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, *ibid.*, **21**, 1289 (1956), and references cited therein.

(5) T. Matsura, K. Omura, and R. Nakashima, *Bull. Chem. Soc. Jap.*, **38**, 1359 (1965).