Unfortunately, the reported enol contents for most of the compounds studied by Gero are not within the range of accessibility with the instrumentation available to us. Those which we were able to study, however, showed no detectable enol, in cases where the numbers reported by Gero would have given sizeable and easily detectable amounts of enol. We therefore conclude that the chemical method of analysis used by Gero is inadequate for the type of determination made, probably due in part to the fact that the ketones show tendencies to enolize under the reaction conditions. The interesting variation of enol content with chain length reported by Gero is therefore based on erroneous experimental data, and must be regarded as unproven.

Cleavage of 2-Nitrocyclohexanone by Base

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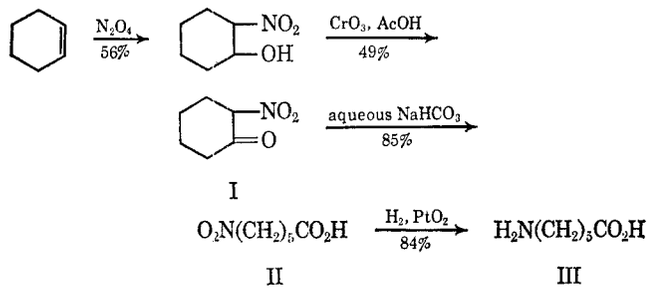
Although there are scattered references in the literature to the basic cleavage of α-nitro ketones,[1] there appears to be little realization of the ease with which this reverse Claisen condensation takes place and of its potential utility.

We have used the reaction in a new synthesis of 6-aminohexanoic acid, which can be readily polymerized to nylon-6. 2-Nitrocyclohexanol was prepared ac-



cording to the procedure of Baldock, Levy, and Scaife.[2] Oxidation with chromium trioxide in acetic acid yielded the nitro ketone (I) in 49% yield[3] plus 11% adipic acid. When I was added to dilute aqueous sodium bicarbonate, carbon dioxide was evolved, and acidification precipitated 6-nitrohexanoic acid (II) in almost quantitative yield. Catalytic reduction to 6-aminohexanoic acid (III) completed the synthesis and confirmed the identity of II, a new compound.

In view of the ready availability of a number of cyclic olefins, the above procedure could be used to prepare a variety of ω-nitro and ω-amino acids.

The extremely facile cleavage reported here is probably responsible for the opinion that nitro compounds derived from active methylene compounds are intrinsically unstable.[5] It explains, for example, the difficulties reported[1a,b] in converting the potassium salts of certain nitro ketones into the free nitro ketones, as well as the often unexpected ring-opened products obtained under alkaline conditions.[1a-c,i]

Experimental Section[6]

2-Nitrocyclohexanone (I).—2-Nitrocyclohexanol (470 mg) was added to a solution of 220 mg of chromium trioxide in 5 ml of acetic acid. After the mixture was stirred overnight at room temperature, most of the acetic acid was removed by distillation *in vacuo* at 40–50°. The residue was washed with a mixture of 10% sulfuric acid and ether, the ether layer being separated and dried over magnesium sulfate.

Evaporation of the ether left a 460-mg crystalline residue. Recrystallization from ether–hexane gave 50 mg (11%) of adipic acid, mp 128–131°; the melting point was raised to 148.5–149.0° (lit.[7] mp 149–150°) by recrystallization from ethylene dichloride. The second crop of crystals (150 mg, 32%) proved to be I, mp 35–36°.[1b] It depressed the melting point of 2-nitrocyclohexanol and gave a positive 2,4-dinitrophenylhydrazone test.[8] Recrystallization from ether gave colorless columns, mp 37.5–38.5°.

Anal. Calcd for $C_6H_9NO_3$: C, 50.34; H, 6.34. Found: C, 50.69; H, 6.51.

A 2,4-dinitrophenylhydrazone[9] prepared from the mother liquor showed the presence of another 80 mg (17%) of I. After two crystallizations from 95% ethanol the orange plates melted at 152.0–153.0°.

Anal. Calcd for $C_{12}H_{13}N_5O_6$: C, 44.58; H, 4.05; N, 21.67. Found: C, 44.78; H, 4.34; N, 21.56.

6-Nitrocaproic Acid (II).—After a solution of 200 mg of I and 120 mg of sodium bicarbonate in 2 ml of water (carbon dioxide was evolved when the solution was prepared) stood overnight at room temperature, it was acidified with dilute hydrochloric acid and extracted with ether. The extract was dried over magnesium sulfate and evaporated to leave 190 mg (85%) of II as a yellow liquid. Distillation gave 150 mg (67%) of a pale straw-colored liquid: bp 136° (0.3 mm); mp 21–22°; ν_{max}^{film} 3020 (sh, broad), 2940, 2860 (sh), 2670 (sh, broad), 1715 (C=O), 1555 (CNO_2), 1440, 1390, 1285, 1230, 1160, 1100, 935, 875, 740 cm^{-1}; nmr (CCl_4), τ −1.71 (singlet, COOH), 5.56 (triplet, J = 6.8 cps, two protons, CH_2NO_2), 7.58 (triplet, J = 6.8 cps, two protons, CH_2COO), 7.7–8.6 (complex overlapped multiplet, six protons, CH_2).

Anal. Calcd for $C_6H_{11}NO_4$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.75; H, 7.17; N, 8.72.

α,*p*-Dibromoacetophenone (220 mg) and 3 ml of 95% ethanol were added to a solution (prepared the previous day) of 100 mg of I and 28 mg of sodium hydroxide in 1 ml of water. The mixture was heated at reflux for 1 hr, then allowed to stand overnight. The ester was removed by filtration (80 mg, mp 58–60°, second crop 70 mg, mp 56–58°). Recrystallization of the first crop from 95% ethanol gave colorless plates, mp 64.0–65.0°.

Anal. Calcd for $C_{14}H_{16}BrNO_5$: C, 46.94; H, 4.50. Found: C, 47.01; H, 4.81.

(1) (a) F. Straux and W. Ekhard, *Ann.*, **444**, 146 (1925); (b) H. Wieland, P. Garbsch, and J. J. Chavan, *ibid.*, **461**, 295 (1928); (c) K. Klager, *J. Org. Chem.*, **20**, 646 (1955); (d) L. Zalukaev and E. Vanag, *J. Gen. Chem. USSR*, **26**, 657 (1956); (e) H. Feuer, J. W. Shepherd, and C. Savides, *J. Am. Chem. Soc.*, **78**, 4364 (1956); (f) T. E. Stevens, *Chem. Ind.* (London), 1546 (1957); (g) H. Feuer and R. S. Anderson, *J. Am. Chem. Soc.*, **83**, 2960 (1961); (h) T. J. de Boer and J. C. van Velzen, *Rec. Trav. Chim.*, **83**, 477 (1964); (i) H. Feuer and P. M. Pivawer, *J. Org. Chem.*, **31**, 3152 (1966).

(2) H. Baldock, N. Levy, and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949).

(3) Griswold and Starcher[4] recently reported a 30% yield by this procedure. Compound I has also been prepared by alkaline nitration of cyclohexanone[1b] and by nitration of 1-acetoxycyclohexene with acetyl nitrate.[4]

(4) A. A. Griswold and P. S. Starcher, *J. Org. Chem.*, **31**, 357 (1966).

(5) N. Kornblum, *Org. Reactions*, **12**, 121 (1962).

(6) Melting points were determined on an electrically heated aluminum block calibrated with known standards and are corrected. The infrared spectrum was determined on a Perkin-Elmer Infracord. The nuclear magnetic resonance (nmr) spectrum was taken on a Varian A-60A instrument.

(7) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. 1, 4th ed, Oxford University Press, New York, N. Y., 1965, p 45.

(8) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 219.

(9) The osazone of Wieland, *et al.*,[1b] probably was derived from the by-product α-diketone which sometimes accompanies the nitration of ketones or their derivatives.[10]

(10) G. B. Bachman and T. Hokama, *J. Org. Chem.*, **25**, 178 (1960).

6-Aminocaproic Acid (III).—A 42-ml, heavy-walled glass vessel equipped with a crown cap and butyl rubber liner was charged with 190 mg of II, 100 mg of platinum oxide catalyst, and 10 ml of 95% ethanol. The vessel was capped, evacuated, filled with hydrogen (58 psig), and tumbled end over end overnight. The vessel was vented and uncapped; the catalyst was removed by filtration. After removal of the solvent by distillation, the residue was crystallized from methanol–ether to give 130 mg (84%) of III, mp 200.5–201.0°. Recrystallization gave 120 mg of pure product, mp 204.0–204.5° (lit.[11] mp 202–203°). A mixture melting point with authentic material[12] showed no depression.

Registry No.—I, 4883-67-4; 2,4-dinitrophenylhydrazone of I, 10269-95-1; II, 10269-96-2; ester of II, 10269-97-3.

(11) Reference 7, p 136.
(12) J. C. Eck in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 28.

Mono- and Diepoxy-1,4-benzoquinones

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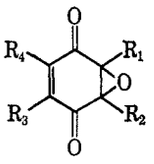
This communication describes the synthesis of a series of mono- and diepoxy-1,4-benzoquinones (I and II) by the direct, base-catalyzed peroxide oxidation of the corresponding quinones. Several monoepoxy-1,4-benzoquinones have previously been synthesized by Alder[1] in a rather complicated manner involving the epoxidation of the cyclopentadienequinone Diels–Alder adducts followed by a high-temperature-induced reverse Diels–Alder cleavage to give the epoxyquinones. No previous reports have appeared describing the unusual diepoxy-1,4-benzoquinone nucleus. These two classes of compounds may be of biological significance as antibiotics[2] as well as possible biosynthetic intermediates to the ubiquitous naturally occurring hydroxyquinones.[3]

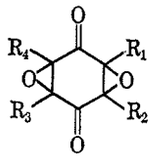
The results reported here are an integral part of an over-all program directed toward the synthesis of several recently reported natural products possessing the epoxy-1,4-benzoquinone nucleus. Sheehan[2] has described the isolation and identification of terreic acid (III), an antibiotic found in culture broths of *Aspergillus terreus*. Yamamoto, *et al.*,[3] have recently reported the characterization of IV, a possible biosynthetic intermediate in the conversion of fumigatin to spinulosin. Finally, Closse, Mauli, and Sigg[4] have identified a partially reduced epoxy-1,4-benzoquinone (V) as a natural product from the culture filtrates of Phoma species. (See Chart I.)

The lack of reports on the epoxides of 1,4-benzoquinones is somewhat surprising in view of the fact that the naphthoquinone series has been extensively studied—at least in regards to their synthesis and

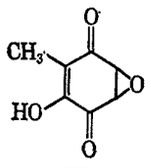
CHART I



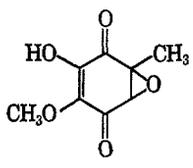
Ia, $R_1=CH_3$; $R_2=R_4=H$; $R_3=CH(CH_3)_2$
b, $R_1=R_3=C(CH_3)_3$; $R_2=R_4=H$
c, $R_1=R_2=R_3=R_4=CH_3$
d, $R_1=R_2=R_3=H$; $R_4=C(CH_3)_3$
e, $R_1=R_2=R_3=H$; $R_4=C_6H_5$



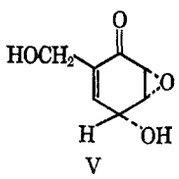
IIa, *cis*- and *trans*-$R_1=CH_3$; $R_2=R_4=H$; $R_3=CH(CH_3)_2$
b, *cis*- and *trans*-$R_1=R_3=C(CH_3)_3$; $R_2=R_4=H$
c, *cis*-$R_1=R_2=R_3=R_4=CH_3$



III



IV



V

natural occurrence.[5–17] The epoxides of several alkyl-substituted naphthoquinones are reported to be readily prepared by the direct oxidation of the quinone with 30% hydrogen peroxide in aqueous ethanol. Although we found this method to be applicable to the benzoquinone series, the yields of the resulting epoxides were generally poor owing to the facile base hydrolysis of the epoxide ring under these aqueous conditions. A modification, described below, employs nonaqueous conditions uilizing *t*-butyl hydroperoxide as the oxidizing agent, Triton B as the base, and absolute ethanol–1,4-dioxane as the solvent.

The monoepoxy-1,4-benzoquinones, Ia–e, were readily obtained in yields of 30–80% by the direct oxidation of the quinone with a stoichiometric amount of *t*-butyl hydroperoxide in 1:1 absolute ethanol–1,4-dioxane utilizing Triton B (30% methanolic benzyltrimethyl ammonium hydroxide) as the base catalyst. The epoxidations were complete within 1–3 hr as detected by gas chromatography on silicon gum rubber $^1/_8$-in. columns run isothermally between 150 and 200°. The products were isolated by pouring the reaction mixtures into water and recrystallization of the resulting precipitate from ethanol.

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