Photolysis of 3,5-Di-*t*-butylbenzene 1,4-Diazooxide in Olefins.—Two slightly different procedures were followed depending upon whether or not the olefin boiled above 25°. One example of each procedure will be given.

A. **Procedure for Liquid Olefins.**—A cylindrical (29-mm od) Pyrex vessel fitted with a Dry Ice condenser, nitrogen inlet, and drying tube was charged with a solution of 0.419 g (1.80 mmoles) of freshly purified 3,5-di-*t*-butylbenzene 1,4-diazooxide in 42 ml of freshly purified 2,3-dimethylbutene-2. This vessel was immersed in a 49-mm o.d. Pyrex cylinder containing a filter solution (0.002 M potassium chromate–0.006 M potassium dichromate in water) which absorbs wavelengths below 480 mμ. An external cylindrical Pyrex vessel filled with ice and water served to maintain the temperature of the reaction mixture and filter solution between 0 and 10°. While the olefin solution was continuously purged with nitrogen, this concentric array was irradiated with a 275-w, G.E. sun lamp (*ca.* 15 cm from the sample) until the 2070-cm^{-1} diazo band had disappeared (*ca.* 4 hr). When the photolysis was complete, reduced pressure evaporation of the olefin left 0.496 g of crude 1,1,2,2-tetramethyl-5,7-di-*t*-butyl-spiro[2.5]octa-4,7-dien-6-one as a yellow solid which was recrystallized from pentane (−78°) until colorless.

B. **Procedure for Gaseous Olefins.**—A small Teflon-coated stirring bar and 0.500 g (2.15 mmoles) of the purified diazooxide were placed in a 19 × 25 × 615 mm Pyrex combustion tube which was fitted with a Dry Ice condenser, nitrogen inlet, drying tube, and olefin inlet. The combustion tube was partially immersed in a Dry Ice–acetone bath while 50 ml of *cis*- (or *trans*-) 2-butene (99 +% purity) was slowly condensed into the tube. The cold olefinic solution was frozen in liquid nitrogen and degassed by several freeze–pump–thaw cycles, and the tube was sealed while evacuated. The actual irradiation and work-up were carried out as described in part A.

Registry No.—II, 955-02-2; IIIa, 10472-75-0; IIIb, 10472-76-1; IIIc, 10472-77-2; IIId, 10472-78-3; IV, 10472-79-4; stannous chloride adduct of 2,6-di-*t*-butyl-4-aminophenol hydrochloride, 13052-54-5.

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Conformational Analysis. LV. On the Enol Contents of the Cyclanones and the Alternation of Enol Content with Chain Length in the Alkanones[1,2]

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In a series of papers,[3] Gero has reported measurements of the enol contents of a number of cyclic and acyclic ketones, and the results, if correct, present quite a challenge in interpretation to the available methods of conformational analysis.[4] Specifically, there are two dramatic features that may be noted. The first of these is the alternation in enol content with chain length well beyond the distance to which such an alternation might be expected. Thus for example, the members of the series of methyl alkyl ketones, as the alkyl group goes from ethyl to *n*-hexyl, are reported to contain enol contents in the following percentages: 0.12, 0.01, 0.11, 0.10, 0.92. The other unusual point is the large enol contents reported for the cycloalkanones, for instance 9.3% in cyclooctanone, and 4.0% in cyclononanone.

Gero's work was done before the availability of some of the modern physical methods, and was based on a modification of the Kurt Meyer titration. Because of the most unexpected nature of the results obtained by Gero, and because of the potential importance of such results in conformational analysis, we considered it desirable to check some of these numbers by a physical method which did not depend upon a chemical reaction, and the attendant uncertainties. We chose nmr spectroscopy as the method and decided to check specifically the enol contents of cyclohexanone, cycloheptanone, and cyclooctanone, which were reported to be 1.18, 0.56, and 9.3%, respectively.[5] Other studies of enol contents of cyclohexanone under various conditions have found only very small amounts of enol (10^{-2}–10^{-6}%).[6]

A similar determination of the (large) enol content of acetylacetone was reported some years ago by Reeves.[7] We repeated the measurements reported by Reeves on acetyl acetone, and obtained substantially the same results. We next determined the nmr spectra of cyclohexanone, cycloheptanone, and cyclooctanone in methanol under conditions reasonably similar to those used for the chemical determination by Gero.[8] We then repeated the measurements in carbon tetrachloride solvent for cycloheptanone. In no case were we able to detect any presence of a vinyl hydrogen. Even allowing for considerable splitting, it is quite impossible that cyclooctanone could contain such a large proportion of enol, and have the latter remain undetected. For cycloheptanone, it was not immediately obvious that the sample contained less than the stated amount of enol, although none was detected. A sample was therefore prepared which contained 0.00923 g of benzene (for use as an internal concentration standard), and 1.41746 g of cycloheptanone, in a solvent mixture made from 0.192 g of methanol and 0.116 g of water. The stated percentage of enol in cycloheptanone should have yielded a vinyl proton resonance with one-seventh of the area of that given by the benzene in our sample, or a peak height of about 1.5 cm under the condition used, if no allowance is made for splitting. No peak was detectable in the region where vinyl absorbtion was expected, even when this region was scanned very slowly while integrating (the vinyl H of cycloheptanone enol acetate is at τ 5.0 and that of cycloheptanone enol ether is at 5.36), and it was concluded that no more than 0.2% enol could be present and remain undetected. Similarly, it was estimated that no more than 0.4% enol could be present in chloroform.[9]

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[1] Paper LIV: N. L. Allinger, J. Allinger, L. W. Chow, and G. L. Wang, *J. Org. Chem.*, **32**, 522 (1967).

[2] This research was supported by Grant GP 1174 from the National Science Foundation.

[3] A. Gero, *J. Org. Chem.*, **26**, 3156 (1961); **19**, 1960 (1954); **19**, 469 (1954).

[4] E. L. Eliel, N. L. Allinger, G. A. Morrison, and S. J. Angyal, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965.

[5] A Varian Associates A-60A nmr spectrometer (signal/noise = 16) was used.

[6] G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 669 (1947); R. P. Bell and P. W. Smith, *J. Chem. Soc.*, 241 (1966); J. E. Dubois and G. Barbier, *Bull. Soc. Chim. France*, 682 (1965).

[7] L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

[8] Gero used 75% methanol as solvent, while 61–78% methanol was used in the present work.

[9] A 0.25% solution of cycloheptanone enol acetate easily showed the expected triplet at τ 5.0.

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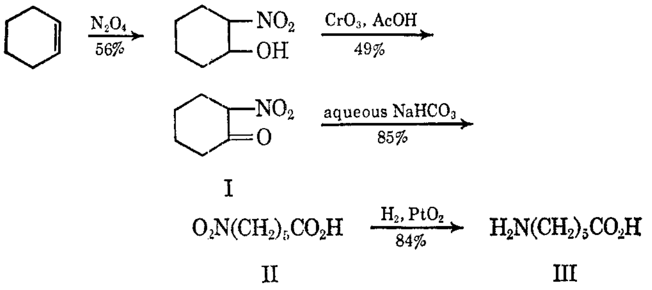
Although there are scattered references in the literature to the basic cleavage of α-nitro ketones,[1] there appears to be little realization of the ease with which this reverse Claisen condensation takes place and of its potential utility.

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 according 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°; $\nu_{\max}^{\text{film}}$ 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.

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[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).