

Product distributions are sharply altered by going to a more acidic catalyst, as shown by experiment 2 with added BF_3 . About 73% instead of 38% of the xylene reacted and about 55 instead of 75% of the ethylene formed polyethylxylene. The 1,3,5-isomer comprised about 70% of the ethylxylene, as opposed to about 5% in experiment 1. These differences are interpreted by postulating that, in the presence of the stronger catalyst, the 1,3,4-structure first formed partly isomerizes to the 1,3,5-structure. The 1,3,5-ethylxylene, which is more basic than its isomers by a factor of 150,⁶ preferentially forms the positively charged σ -complex



This cation does not react with the incoming positively charged ethyl group. The ethyl group must then attack either the uncomplexed *m*-xylene or 1,3,4-ethylxylene.

According to this hypothesis, polyethylxylenes are formed by the addition of ethylene to 1,3,4-ethylxylene and not to 1,3,5-ethylxylene. If, therefore, the rate of isomerizing 1,3,4-ethylxylene were speeded up relative to the rate of ethylene introduction, the yield of polyethylated xylene should drop. The hypothesis was tested in two ways: by increasing the isomerization rate through the use of higher temperatures (experiment 3) and by slowing down the rate of ethylene addition (experiment 4). The resulting product distributions support the hypothesis in that *m*-xylene is alkylated preferentially to 1,3,5-ethylxylene. The *m*-xylene was more than 95% alkylated, as compared with only 38% with hydrogen fluoride alone.

The bottom line of the table gives the relative rates of ethylation of ethylxylene and *m*-xylene.

These were calculated from the product distributions by means of the same equation employed by Condon²

$$\log \left(C_1 + C_2 - \left(\frac{k_2}{k_1} \right) C_2 \right) = \frac{k_2}{k_1} \log C_1$$

where k_1 and k_2 are the rates of ethylation, and C_1 and C_2 are the final concentrations, of *m*-xylene and ethylxylene, respectively. Experiment 1 shows that ethylxylene alkylates 2.8 times faster than *m*-xylene. In experiments 3 and 4, where boron trifluoride was used, the order is reversed; *m*-xylene reacts about 25 times faster than ethylxylene. The relative rate constants are changed about 70-fold.

The explanation used here can also be applied to the results of Norris and Rubinstein.⁷ They found that, when benzene is alkylated with ethyl chloride, the concentration of the aluminum chloride catalyst markedly affects the product distribution. A mole ratio of Al_2Cl_6 to aromatic greater than 1.0 gives mainly 1,3,5-triethylbenzene; less aluminum chloride produces a mixture of polyethylbenzenes. Evidently, HCl-AlCl_3 as well as HF-BF_3 selectively forms a σ -complex with the 1,3,5-trialkylbenzenes and thereby prevents further alkylation.

By using conditions that favor formation of σ -complexes, alkylation of the substituted benzene ring can thus be directed toward a single isomer. Alkylation with such super-acids as HF-BF_3 or HCl-AlCl_3 promises to become a general way to produce high yields of single isomers. Application to other arenes and other olefins will be the subject of future publications.

(7) J. F. Norris and D. Rubinstein, *THIS JOURNAL*, **61**, 1163 (1939).
WHITING, INDIANA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Many-membered Carbon Rings. X. Reduction of Diametric Diketones to Monoketones¹

BY A. T. BLOMQUIST, JULIANNE PRAGER² AND JOSEPH WOLINSKY

RECEIVED AUGUST 31, 1954

Reduction of the readily available diametric diketones 1,9-cyclohexadecanedione and 1,10-cyclooctadecanedione to the muscone-like cyclohexadecanone and cyclooctadecanone has been achieved in good yield *via* catalytic hydrogenolysis of their mono-ethylenedithioketals.

Simple carbocyclic ketones having 14–18 ring members possess a characteristic musk-like odor very similar to that of the naturally occurring *dl*-muscone and civetone. Because of this they are of interest in perfumery as perfume bases and fixatives.

All practical syntheses of such ketones require as intermediates higher α,ω -dicarboxylic acids or their derivatives which are not readily available except through laborious syntheses from lower α,ω -

bifunctional compounds.³ The availability in fair yield of the diametric diketones 1,9-cyclohexadecanedione (I) and 1,10-cyclooctadecanedione (II) from azelaic and sebacic acids *via* cyclization of the bifunctional ketenes derived therefrom⁴ prompted a study of the reduction of such diketones to monoketones.

Of the possible reduction methods which might be applicable here the elegant reductive desulfurization procedure of Wolfrom and Karabinos,⁵

(1) For the preceding paper in this series see A. T. Blomquist and A. Goldstein, *THIS JOURNAL*, **77**, 1001 (1955).

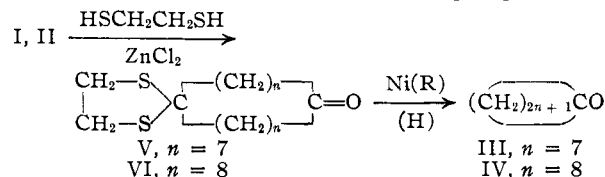
(2) Some of the work reported here was abstracted from part of the dissertation submitted by Julianne Prager in February, 1953, to the Graduate Faculty of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Co., 1953, Vol. III, Part A, pp. 270–273.

(4) A. T. Blomquist and R. D. Spencer, *THIS JOURNAL*, **69**, 472 (1947); **70**, 30 (1948).

(5) M. L. Wolfrom and J. V. Karabinos, *ibid.*, **66**, 909 (1944).

based on the earlier work of Bougault, *et al.*,⁶ and of Mzingo and co-workers,⁷ offered the most promise of success. Its useful application in realizing the transformation under consideration would require (a) satisfactory conversion of a diametric diketone such as I or II to a monodithioketal (V or VI) and (b) reductive desulfurization of such a derivative without reduction of its free carbonyl group.



I and II were obtained in 34 and 24% yield, respectively, by cyclization of the bifunctional ketenes derived from azelalyl and sebacyl chlorides. Modification of the originally described diketene cyclization method⁴ made it possible to effect cyclization of one mole of acid chloride (225–240 g.) in three hours.⁸ Under these conditions isolable quantities of monomeric products of cyclization, cyclooctanone and cyclononanone, were never obtained.

Treatment of the diketones I and II with one molar equivalent of ethanedithiol afforded the expected mixture of products: unreacted I and II, the monodithioketals V and VI, and the corresponding bis-ethylenedithioketals VII and VIII. The latter (VII and VIII) were easily separable from the mixture because of their insolubility in hexane. The monodithioketals V and VI could not be separated easily from unreacted I and II and were used in this impure state in the subsequent reductive desulfurization step.

Ethanol solutions of the impure V and VI were treated with Raney nickel which had been deactivated by refluxing in acetone. Addition of semicarbazide reagent to the resulting ethanolic solutions gave mixtures of semicarbazones, comprising the desired monoketone semicarbazone and the disemicarbazone of original diketone, which could be separated by crystallization. The conversion of I to III semicarbazone was 47%, corresponding to a 90% yield when adjusted for recovery of I from its bis-dithioketal and its disemicarbazone. The conversion of II to IV semicarbazone (21%) was less satisfactory. Its yield, based on recoverable derivatives of II, was 80%.

The monoketones III, m.p. 59.5–60.2°, and IV, m.p. 68–70°, were obtained finally by aqueous oxalic acid hydrolysis of their semicarbazones followed by crystallization and/or sublimation of the regenerated ketones.

Catalytic hydrogenolysis of the two bis-ethylenedithioketals VII and VIII proceeded smoothly to give cyclohexadecane (IX), m.p. 61°, and cyclooctadecane (X), m.p. 70–71°, in good yield.

Experimental Part⁹

Materials.—Azelaalyl chloride, prepared by treating azelaic acid, m.p. 104.5–106.5°, with purified thionyl chloride, was

(6) J. Bougault, E. Cattelain and P. Chabrier, *Bull. soc. chim.*, [5] **5**, 1699 (1938); [5] **7**, 780, 781 (1940).

(7) R. Mzingo, D. E. Wolf, S. A. Harris and K. Folkers, *This Journal*, **65**, 1013 (1943).

(8) R. P. Conger, Ph.D. Dissertation, Cornell University, 1950.

(9) All m.p.'s and b.p.'s are uncorrected unless otherwise noted.

distilled *in vacuo* and the fraction having b.p. 153–157° (6.5 mm.), n_D^{20} 1.4680, was used for cyclization. Sebacyl chloride, Eastman Kodak White Label, was used without further purification.

Reagent grade benzene was distilled through a Vigreux column and stored over sodium wire. Triethylamine, the Matheson Co., was purified by drying over sodium hydroxide pellets, refluxing over successive portions of sodium wire until a fresh piece was not tarnished, and distilling. The fraction boiling over 85° was used.

Cyclization of Azelalyl Chloride.⁸—The apparatus comprised a 5-l. flask fitted with a mechanical stirrer and Y-tube adapter which was attached (1) at the upper vertical end to a Hershberg–Hinman dropping funnel⁴ and (2) at the end of the slanting sidearm to a reflux condenser. The funnel was arranged so that drops fell directly into the reaction vessel. Depending mid-way up the side-arm of the adapter was a take-off tube, closed with a stopcock, for removal of refluxing solvent. The entire apparatus was protected from atmospheric moisture by calcium chloride tubes.

Three liters of benzene were placed in the flask, brought to gentle reflux, and 500 ml. of benzene gradually removed from the take-off trap. Triethylamine, 200 ml., was added at once to the hot benzene and a solution of 31.2 g. (0.1386 mole) of azelalyl chloride in 300 ml. of dry benzene added dropwise from the oven-dried funnel to the stirred refluxing benzene–amine solution over a three-hour period. After completion of the addition, heating was discontinued and the mixture stirred for another hour while cooling. After standing overnight the mixture was filtered to remove precipitated triethylamine hydrochloride. The filtrate was freed of excess triethylamine by washing and then concentrated by removing benzene as rapidly as possible on the steam-bath. A solution of 25 g. of potassium hydroxide in 100 ml. of reagent methanol was added carefully to the concentrated reddish residue and the mixture heated on the steam-bath one hour. The mixture, diluted with 100 ml. of water, was heated (steam-bath) for another two hours and then kept at room temperature overnight. Ether extraction of the alkaline mixture gave 5.85 g. (34.0%) of crude solid I. Sublimation of this material to incipient collection of oily material gave 5.5 g. (31.4%) of diketone (I) having m.p. 80.5–82° (Ruzicka, *et al.*, give m.p. 83–84°¹⁰).

Alternatively, the crude diketone from 30.7 g. (0.132 mole) of azelalyl chloride was converted to its disemicarbazone, m.p. 225–227° (Ruzicka, *et al.*, reported m.p. ca. 240°).¹⁰ The disemicarbazone, 9.0 g. (35% based on azelalyl chloride), was insoluble in boiling methanol.

Anal. Calcd. for $\text{C}_{18}\text{H}_{34}\text{N}_6\text{O}_2$: N, 22.93. Found: N, 23.19.

Refluxing 9.0 g. of the disemicarbazone with a large excess of aqueous oxalic acid gave, after final sublimation, 4.2 g. (24% over-all) of white crystalline I, m.p. 80–82°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{28}\text{O}_2$: C, 76.14; H, 11.18. Found: C, 75.96; H, 10.95.

During the isolation of the disemicarbazone no material was obtained corresponding to cyclooctanone semicarbazone.

Conversion of 1,9-Cyclohexadecanedione (I) to its Ethylenedithioketals.—After removing 50 ml. of benzene by distillation from a solution of 5.44 g. (0.0216 mole) of I in 200 ml. of reagent grade benzene, there was added rapidly 2.03 g. (0.0216 mole) of ethanedithiol (Aldrich Chem. Co.), 20 g. of anhydrous sodium sulfate and 1.5 g. of freshly fused and powdered zinc chloride. The mixture, in a stoppered flask, was placed in the refrigerator overnight and allowed to stand 5 days at room temperature. The insoluble material was separated and thoroughly washed with benzene.

The combined benzene filtrate and washings were evaporated to dryness, redissolved in hexane, leaving 1.0 g. of insoluble material having m.p. 204–210°. This comprised the crude bis-ethylenedithioketal (VII). (An additional 1.1 g. of this material showing m.p. 206–210° was obtained by extracting the benzene-insoluble substances with water and chloroform and subsequently adding hexane to the chloroform extract.) Evaporation of the original hexane solution gave 4.66 g. of crude mono-ethylenedithioketal (V) which solidified in about 3 days. This crude product, containing unreacted diketone, was used for sub-

(10) L. Ruzicka, N. Brugger, C. F. Seidel and H. Schinz, *Helv. Chim. Acta*, **11**, 496 (1928).

sequent transformations without further purification. Its m.p. was not determined.

Pure 1,9-cyclohexadecanedione bis-ethylenedithioketal (VII) was obtained after two recrystallizations from chloroform-hexane of the fraction melting at 204–210°, m.p. 210.5–212°.

Anal. Calcd. for $C_{20}H_{36}S_4$: C, 59.35; H, 8.96; S, 31.69. Found: C, 59.69; H, 8.97; S, 32.06.

Reductive Desulfurization of the 1,9-Cyclohexadecanedione Dithioketals.—The 4.66 g. of crude V described above was added to a suspension of 15 g. of Raney nickel in 200 ml. of ethanol which had been refluxed previously for an hour with 5 ml. of acetone. The mixture was refluxed for 3 hr., cooled and filtered. The filtered Raney nickel was allowed to stand under methanol.

To the ethanolic filtrate was added a solution of 5 g. of semicarbazide hydrochloride and 10 g. of sodium acetate in 10 ml. of water. Although a white precipitate formed immediately, the mixture was allowed to stand 24 hr. before filtering. The methanolic solution obtained after removal of the Raney nickel was treated similarly and the resulting solid semicarbazone combined with that obtained above. The total semicarbazone precipitates were digested with 300-ml. and 250-ml. portions of boiling methanol. The insoluble material weighed 1.59 g. and showed m.p. 221–227° corresponding to that of I disemicarbazone. An additional quantity (0.29 g.) of impure disemicarbazone, m.p. 186–191°, separated when the methanolic filtrates stood at room temperature for one day. Concentration of the methanol solution gave three crystalline fractions of III semicarbazone: (1) 1.0 g. having m.p. 172–173°, (2) 0.77 g. having m.p. 168–172° and (3) 1.25 g. having m.p. 170–175°.

The 3.02 g. of III semicarbazone corresponds to a 47% conversion from I. The yield, adjusted for recoverable diketone derivatives, was 90%.

Similar reductive desulfurization of 730 mg. of VII using 6 g. of Raney nickel in 75 ml. of ethanol gave 170 mg. of IX, m.p. 60–60.2° (Ruzicka, *et al.*, give m.p. 61°¹⁰).

Hydrolysis of 1 g. of III semicarbazone with aqueous oxalic acid gave 0.62 g. (72%) of once sublimed III having an intense musk odor and repeated sublimation raised the melting point to 59.5–60.2° (Ruzicka, *et al.*, reported m.p.'s 63–64°,¹¹ 56°¹²). The infrared spectrum of the ke-

tone in a Halocarbon mull showed carbonyl absorption at 5.87 μ and C–H absorption at 3.4, 6.9 and 7.2 μ .

Cyclization of Sebacyl Chloride.—Following the procedure outlined for cyclization of azelalyl chloride, 245 g. (1.03 moles) of sebacyl chloride in 600 ml. of dry benzene was added over a 3-hr. period to a refluxing solution of 7 l. of benzene and 1 l. of triethylamine. Hydrolysis of the reaction mixture gave 33.4 g. (23.8%) of II which after crystallization from hexane showed m.p. 93–95° (Ruzicka, *et al.*, reported m.p. 96–97°¹⁰).

Conversion of (II) to its Ethylenedithioketals.—Following the procedure described earlier 2.26 g. (0.0094 mole) of II in 200 ml. of reagent grade benzene was treated with 0.758 g. (0.0094 mole) of ethanedithiol, 15 g. of anhydrous sodium acetate, and 5 g. of freshly fused and powdered zinc chloride. After working up the reaction mixture as previously described there was obtained 1.23 g. of crude bis-dithioketal VIII, m.p. 185–188°, and 1.43 g. of impure mono-dithioketal VI, m.p. 73–92°, contaminated with unreacted diketone.

After five recrystallizations from chloroform-hexane the bis-ethylenedithioketal of II showed m.p. 191.2–193.5°.

Anal. Calcd. for $C_{22}H_{40}S_4$: C, 61.05; H, 9.31. Found: C, 61.04, 61.34; H, 9.29, 9.47.

The crude mono-dithioketal VI was not purified prior to reductive desulfurization.

Reductive Desulfurization of 1,10-Cyclooctadecanedione Ethylenedithioketals.—The procedure used was identical with that given earlier for desulfurization of the I dithioketals. From 140 mg. of VIII there was obtained 40 mg. (66.6%) of X, m.p. 70–71° (Ruzicka, *et al.*, reported m.p. 72°¹⁰).

From 0.94 g. of the crude VI after desulfurization and treatment with semicarbazide reagent in the usual way there was obtained 0.78 g. of II disemicarbazone, m.p. 205–220°, and 0.56 g. of IV semicarbazone, m.p. 168–170°. Recrystallization of the latter from methanol raised the m.p. to 180–181° (Ruzicka, *et al.*, reported m.p. 184°¹⁰).

Anal. Calcd. for $C_{19}H_{37}N_3O$: C, 70.53; H, 11.53. Found: C, 70.65; H, 11.87.

The conversion of II to IV semicarbazone was 21% while the yield, adjusted for recoverable diketone derivatives, was 80%.

Hydrolysis of 200 mg. of IV semicarbazone with aqueous oxalic acid gave 90 mg. of once sublimed IV, m.p. 68–70° (Ruzicka, *et al.*, reported m.p. 71°¹²).

ITHACA, N. Y.

(11) L. Ruzicka, *et al.*, *Helv. Chim. Acta*, **13**, 1152 (1930).

(12) L. Ruzicka, M. Stoll and H. Schinz, *ibid.*, **9**, 263 (1926).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

1,2-Dimethylenecyclobutane^{1,2}

BY A. T. BLOMQUIST AND JOSEPH A. VERDOL

RECEIVED AUGUST 31, 1954

1,2-Dimethylenecyclobutane has been obtained by thermal decomposition of 1,2-bis-(dimethylaminomethyl)-cyclobutane dimethoxyhydroxide. The latter was synthesized from diethyl 1,2-cyclobutanedicarboxylate by (1) lithium aluminum hydride reduction of the ester to a glycol, (2) bromination of the glycol with phosphorus tribromide, (3) aminolysis of the dibromide with trimethylamine and finally (4) hydrolysis of the bis-quaternary salt with moist silver oxide. That the diene was 1,2-dimethylenecyclobutane was confirmed by its chemical and physical properties, including its infrared and ultraviolet absorption spectra. Normal Diels-Alder adducts of the diene could be obtained only in the presence of a polymerization inhibitor. In their absence the diene polymerized. Treatment of the diene with sulfur dioxide also caused its polymerization, even in the presence of inhibitor. Persulfate initiated polymerization of the diene at 50° for 24 hr. gave a rubber-like soluble high polymer having ca. 80% 1,4-addition polymerization units as indicated by the perbenzoic acid method. Attempts to obtain the diene by pyrolysis of 1,2-bis-(acetoxymethyl)-cyclobutane were unsuccessful. 2-Viny-1,3-butadiene was the only isolable product of this thermal decomposition.

As part of an extensive program in this Laboratory concerned with an investigation of new conjugated diene systems which might be expected to show high reactivity in polymerization reactions, the synthesis and properties of 1,2-dimethylenecy-

clobutane (I) were studied. This particular hydrocarbon with two exocyclic double bonds conjugated through a cyclobutane ring was of especial interest because of its relationship to the conjugated exocyclic dienes in the cyclohexane series studied by Bailey³ and by Wicklatz and Short.⁴ Like the

(1) Presented before the Division of Organic Chemistry at the National Meeting of the American Chemical Society at New York, N. Y., September 12–17, 1954.

(2) The work reported here was done as part of a research program at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Company.

(3) (a) W. J. Bailey and H. R. Golden, Abstracts of the 117th Meeting of the American Chemical Society, March–April, 1950, p. 330; (b) W. J. Bailey and H. R. Golden, *THIS JOURNAL*, **75**, 4780 (1953).

(4) J. R. Wicklatz and J. N. Short, U. S. Patent 2,600,454, June, 1952; *C. A.*, **46**, 11768b (1952).