5,5-Diphenylcyclononanol tosylate (I), m.p. 103–104°, was prepared by the method of Brown and Ham[6] and crystallized from petroleum ether.

Anal. Calcd. for $C_{28}H_{32}O_3S$: C, 74.96; H, 7.19; S, 7.15; sapn. equiv., 448.6. Found: C, 75.20; H, 7.36; S, 7.16; sapn. equiv., 445.7.

Kinetic Measurements and Product Analysis.—The rate constant for the acetolysis of 2.026 g. of I was determined at 35° according to the procedure of Winstein, *et al.*,[7] using 120 ml. of anhydrous acetic acid[6] as solvent. Upon completion of the reaction the mixture was diluted with water and the products were extracted with ether. After drying and evaporation of solvent, 1.05 g. of the resultant colorless oil was subjected to chromatography on alumina. Elution with petroleum ether effected separation into two components. Both were crystallized from petroleum ether as white solids; the first (0.75 g., 71%) had m.p. 87–88° and the second (0.21 g., 20%) had m.p. 96–97°. This latter compound was shown by means of mixed melting point and infrared absorption spectrum determinations to be identical with the acetate IV, described above.

The infrared absorption spectrum of the first crystalline fraction, diphenycyclonene (III), showed *inter alia* bands at 10.09 and 13.78 μ. The ultraviolet spectrum of III, in isooctane solution, showed two bands, λ_{max} 260 mμ, log ε 2.93, and λ_{max} 270 mμ, log ε 2.86.

Anal. Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.40; H, 8.75.

When 0.10 g. of the olefin III in ethyl acetate solution was hydrogenated over palladium–carbon catalyst, 9.1 ml. (100 %) of hydrogen was taken up at 740 mm. and 26°. The product, 1,1-diphenylcyclononane, after evaporation of solvent and crystallization from petroleum ether, had m.p. 92°.

Anal. Calcd. for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.48; H, 9.47.

Oxidation of III.—Finely ground potassium permanganate (0.75 g.) was added in small portions to a vigorously stirred solution of III (0.20 g.) and sodium bicarbonate (0.1 g.) in acetone (20 ml.). The mixture was stirred for 2 hr., acidified with dilute sulfuric acid and treated with sulfur dioxide until a clear solution was obtained. The products of oxidation were separated into neutral and acidic fractions in the usual way and the acidic fraction (1.4 g., 57%), after crystallization from glacial acetic acid, had m.p. 213–214°, underpressed on admixutre with authentic δ,δ-diphenylazelaic acid.[1]

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

Many-membered Carbon Rings. XX. Azacyclohendecane *via* Reduction of Cyclodecanone Oxime[1,2]

BY A. T. BLOMQUIST, B. F. HALLAM[3] AND A. D. JOSEY[4]

RECEIVED AUGUST 11, 1858

N,N-Dimethyl-9-decenylamine has been identified as an accessory product (*ca.* 10%) in the preparation of cyclodecene by pyrolysis of trimethylcyclodecylammonium hydroxide. It is proposed that this unsaturated amine arises as a result of rearrangement of cyclodecanone oxime to azacyclohendecane during reduction with lithium aluminum hydride.

trans-Cyclononene and *trans*-cyclodecene have been prepared[5,6] by the pyrolysis of the corresponding trimethylcycloalkylammonium hydroxides, obtained by a route involving the lithium aluminum hydride reduction of the cyclic ketoximes, cyclononanone oxime and cyclodecanone oxime. During the course of this work it was noted that the cycloalkenes were always contaminated with a substantial amount (*ca.* 10%) of an unsaturated amine.

It has been reported[7] earlier that the reduction of acetophenone oxime with lithium aluminum hydride yields a quantity (16%) of N-ethylaniline in addition to the expected α-phenylethylamine and under similar conditions proprionophenone oxime afforded a 14% yield of N-*n*-propylaniline. These N-alkylanilines were considered to arise by rearrangement of the oxime, under the conditions of the reaction, to an amide which was then reduced to a secondary amine.[7,8] In view of these reports it was considered desirable to establish the structure of the unsaturated amines formed as accessory products in the preparation of cyclononene and cyclodecene and a detailed study was made of the by-product formed in the case of the latter preparation.

The unsaturated amine I was separated from cyclodecene in the usual way and distilled as a colorless liquid, b.p. 91–94° (6 mm.), $n^{25}\text{D}$ 1.4404, which gave a picrate derivative, m.p. 53–54°, and a methiodide derivative, m.p. 151–152°. The infrared spectrum of the amine showed strong absorption at 10.98 μ and medium absorption at 6.08 μ, consistent with the presence of a terminal vinyl group in the molecule.[9] Catalytic reduction of the amine I resulted in the absorption of the theoretical amount of hydrogen required for the presence of one carbon–carbon double bond, and the saturated amine II obtained gave a picrate derivative, m.p. 45–46°, and a methiodide derivative, m.p. 199–200°. This amine II was shown to be N,N-dimethyldecylamine by comparison of its infrared spectrum with that of an authentic specimen and by means of mixed melting point determinations on the picrate and methiodide derivatives. Authentic II was prepared for comparative purposes

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(1) For the preceding paper in this series, see A. T. Blomquist and B. F. Hallam, THIS JOURNAL, **81**, 676 (1959).

(2) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) This author wishes to thank the U. S. Educational Commission in the United Kingdom for the award of a Fulbright Travel Grant.

(4) This article is in part abstracted from the dissertation presented by A. D. Josey in February, 1958, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(5) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

(6) A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

(7) D. Smith, M. Maienthal and J. Tipton, *J. Org. Chem.*, **17**, 294 (1952).

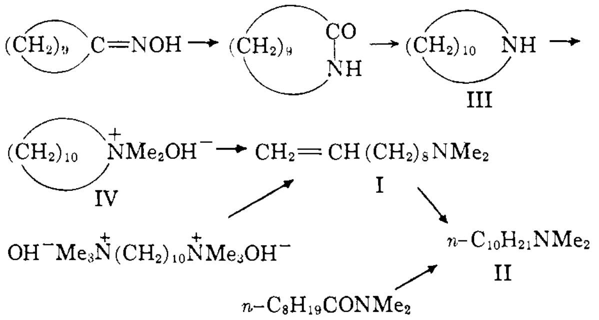
(8) N. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 751.

(9) L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 42.

by the reduction of N,N-dimethylcapramide with lithium aluminum hydride.

Conclusive proof of the identity of the unsaturated amine I was obtained when the quaternary ammonium hydroxide from azacyclohendecane[10] (III) was subjected to pyrolysis. The infrared spectrum of the resulting N,N-dimethyl-9-decenylamine was identical with that of I and mixed melting points of their picrates and methiodides showed no depression. Pyrolysis of decamethylene bis-(trimethylammonium hydroxide) had previously been reported to yield the amine I, together with 1,9-decadiene and decamethylene bis-(dimethylamine).[11] According to this earlier work, Compound I afforded a picrate derivative, m.p. 137°, and a methiodide derivative, m.p. 137–140°, and in view of the discrepancy in melting point data, the work was repeated. The amine I prepared according to v. Braun, however, proved to be identical in every respect with that prepared from azacyclohendecane and no plausible explanation of the previously reported erroneous data can be offered.

The formation of N,N-dimethyl-9-decenylamine (I) as an accessory product to cyclodecene can best be explained on the basis of the formation of azacyclohendecane (III) during the reduction of cyclodecanone oxime by lithium aluminum hydride, followed by degradation according to the scheme



It is probable that a similar side reaction occurs in the reduction of cyclononanone oxime and this is currently under investigation.

Experimental Part[12]

N,N-Dimethyl-9-decenylamine (I).—The residue and distillate obtained from thermal decomposition of 155 g. (0.47 mole) of cyclodecyltrimethylammonium hydroxide[13,14] were combined and extracted with dilute hydrochloric acid. The acid extract, after being washed with ether, was made alkaline with dilute sodium hydroxide solution and extracted with ether. Evaporation of the ether, after drying over potassium hydroxide pellets, afforded a colorless oil (12.3 g., 10% from the quaternary base) which on distillation through a 30-inch Podbielniak column gave 8.9 g. of I, b.p. 90–94° (6 mm.), $n^{25}\mathrm{D}$ 1.4402.

The picrate derivative of I, prepared in the usual way and crystallized from 95% ethanol, had m.p. 53–54°.

Anal. Calcd. for $C_{18}H_{28}N_4O_7$: C, 52.41; H, 6.84; N, 13.59. Found: C, 52.56; H, 6.87; N, 13.66.

The methiodide derivative of I, crystallized from methanol–ether had m.p. 151–152°.

Anal. Calcd. for $C_{13}H_{28}NI$: C, 47.99; H, 8.68; N, 4.31. Found: C, 48.06; H, 8.80; N, 4.50.

N-Methylazacyclohendecane Methiodide (V).—Azacyclohendecane (III)[10] (5.3 g., 0.035 mole) was dissolved in 100 ml. of absolute methanol. Anhydrous potassium carbonate (7.3 g.) and 30 g. of methyl iodide were added and the mixture was heated under reflux on the steam-bath for 18 hr. Filtration and evaporation of solvent gave white crystals (10.4 g., 98%) of the quaternary iodide which, after crystallization from methanol, had m.p. 249–250°.

Anal. Calcd. for $C_{12}H_{26}NI$: C, 46.29; H, 8.43; N, 4.50. Found: 46.05; H, 8.55; N, 4.27.

Thermal Decomposition of N-Methylazacyclohendecane Methohydroxide (IV).—Freshly precipitated silver oxide (prepared from 15.5 g. of silver nitrate and 12.5 g. of potassium hydroxide) was added to a solution of 9.5 g. (0.03 mole) of V in a minimum quantity of water. After stirring for 3 hr., the solution was filtered and evaporated under vacuum on the steam-bath. The resultant colorless oil (10.5 g.) was pyrolyzed at 90–120° under 20 mm. pressure and the distillate and residue were extracted with dilute hydrochloride acid. The acidic extract was washed with ether, made alkaline with dilute sodium hydroxide and then extracted with ether. Evaporation of the ether gave 3.2 g. (57%) of a colorless oil. Distillation of this through a 30-inch Podbielniak column gave the amine I (1.8 g.), b.p. 80° (2.7 mm.), $n^{25}\mathrm{D}$ 1.4379. The infrared absorption spectrum of this amine was identical with that of the amine described above and mixed melting points of the picrate and methiodide derivatives of the two amines showed no depression.

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.61; H, 13.75; N, 7.64. Found: C, 78.72; H, 13.83; N, 7.88.

N,N-Dimethyldecylamine (II). (A) By Reduction of I.—Hydrogenation of 0.367 g. (0.002 mole) of I in ethyl acetate and in the presence of 0.02 g. of Adams catalyst led to the uptake of 46.0 ml. of hydrogen at 24° and 751 mm. (93% of theoretical). The amine obtained by evaporation of solvent gave a picrate, m.p. 46°, and a methiodide, m.p. 199–200°; both derivatives showed no depression of melting points on admixture with the corresponding derivatives described below. The infrared absorption spectrum of the amine was identical with that of the amine described below.

(B) From N,N-Dimethylcapramide.—Reduction of N,N-dimethylcapramide (20.0 g., 0.1 mole) with lithium aluminum hydride (3.0 g.) in ether solution, followed by workup in the usual way gave the amine II (18.8 g.), b.p. 81° (3.2 mm.), $n^{25}\mathrm{D}$ 1.4293.

Anal. Calcd. for $C_{12}H_{27}N$: C, 77.75; H, 14.74; N, 7.51. Found: C, 78.05; H, 14.48; N, 7.76.

The picrate derivative of II, prepared in the usual manner and crystallized from 95% ethanol, had m.p. 46°.

Anal. Calcd. for $C_{18}H_{30}N_4O_7$: C, 52.16; H, 7.29; N, 13.52. Found: C, 52.15; H, 7.53; N, 13.75.

The methiodide derivative of II, crystallized from methanol–ether, had m.p. 200°. (von Braun and co-workers[15] reported a melting point of 191° for the above methiodide and described the picrate as oily.)

Anal. Calcd. for $C_{13}H_{30}NI$: C, 47.70; H, 9.24; N, 4.28. Found: C, 47.95; H, 9.44; N, 4.03.

Decamethylene Bis-(trimethylammonium Bromide).—A sealed Pyrex bomb containing 70 g. (0.23 mole) of 1,10-dibromodecane, 59 g. (1 mole) of trimethylamine and 25 ml. of methanol was allowed to stand at room temperature for 2 weeks. Evaporation of solvent afforded 95 g. (97%) of the quaternary ammonium salt, m.p. 268–270° dec., after crystallization from methanol–acetone.

Anal. Calcd. for $C_{16}H_{38}N_2Br_2$: N, 6.70. Found: N, 6.91.

Thermal Decomposition of Decamethylene Bis-(trimethylammonium Hydroxide).—The quaternary ammonium hydroxide was prepared in the usual way from 95 g. of the above dibromide and freshly precipitated silver oxide (from 223 g. of silver nitrate and 179 g. of potassium hydroxide). Decomposition at 100–130° (20 mm.) gave a mixture of basic

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[10] L. Ruzicka, M. Kobelt, O. Häfliger and V. Prelog, *Helv. Chim. Acta*, **32**, 1544 (1949).

[11] J. v. Braun, *Ann.*, **386**, 273 (1911).

[12] All melting points and boiling points are uncorrected.

[13] See A. Goldstein, Thesis, Cornell University, 1954, for the preparation of this quaternary base.

[14] Thermal decomposition was effected at 85–105° at 10–15 mm. pressure.

[15] J. v. Braun, W. Teuffert and K. Weisslack, *Ann.*, **472**, 121 (1929).

material and 1,9-decadiene. The basic fraction was worked up in the manner previously described and distilled at 138–139° (50 mm.) (literature[11] b.p. 118–120° (17 mm.)). The resultant colorless liquid (6.5 g.) showed an infrared absorption spectrum identical with that of I and formed a picrate derivative, m.p. 54°, and a methiodide derivative, m.p. 150°, both indistinguishable by mixed melting point determinations from the corresponding derivatives of I.

The residue from distillation (1.1 g.) showed no double bond absorption in the infrared region and was presumably decamethylene bis-(dimethylamine).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Synthesis of Glycidic Esters by Epoxidation of α,β-Unsaturated Esters with Peracetic Acid

BY DONALD L. MACPEEK, PAUL S. STARCHER AND BENJAMIN PHILLIPS

RECEIVED AUGUST 4, 1958

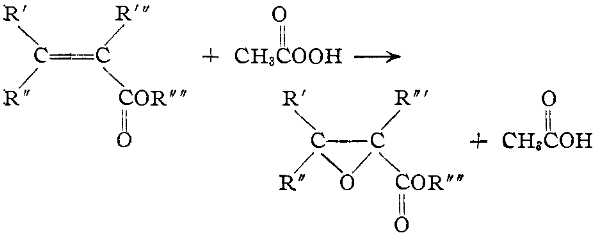
An efficient, single step synthesis of glycidic esters *via* the epoxidation of α,β-unsaturated esters with peracetic acid is described. The method is characterized by the ease of following the reaction and by the general applicability of the procedure. In this way, novel types of glycidic esters were prepared.

The first synthesis of a glycidic ester was reported in 1892 by Erlenmeyer,[1] who prepared ethyl 2,3-epoxy-3-phenylpropionate by the condensation of benzaldehyde and ethyl chloroacetate in the presence of sodium. Darzens[2] expanded the scope of this general method of synthesis which now bears his name. This route and its more recent modifications have been reviewed by Newman and Magerlein.[3]

Several investigators have studied the action of perbenzoic acid on α,β-unsaturated acids and esters. Braun,[4] in 1930, succeeded in epoxidizing crotonic acid by the use of perbenzoic acid in chloroform solution, but the yield of epoxy acid was low, and the reaction conditions—three months at room temperature—were clearly indicative of the slow reaction rate. Other early work has been reviewed by Swern,[5] who concluded that the reaction of an organic peracid with an olefin is slowed down considerably or completely suppressed by the presence of a carboxyl or carboalkoxy group in close proximity to the double bond. More recent studies by Dry and Warren[6] and Plisov and Bykovets,[7] confirmed these conclusions.

In 1955, Emmons and Pagano[8] reported the successful preparation of glycidic esters from acrylic, methacrylic and crotonic esters by an epoxidation procedure employing peroxytrifluoroacetic acid in a system buffered with disodium hydrogen phosphate. The success of this technique was ascribed to the great difference in acidity between peroxytrifluoroacetic acid and the coproduct trifluoroacetic acid. This made it possible, by proper buffering, to neutralize the trifluoroacetic acid as rapidly as it was formed without making the reaction mixture so basic as to affect the stability of the peracid.

The suitability of any peracid solution as an epoxidation reagent depends, among other things, on its purity. Traces of ions of heavy metals, for example, can catalyze peracid decomposition, and if such ions are present and improperly sequestered, a severe limitation on reaction temperature is imposed. Other impurities, including mineral acids, salts, water and excessive concentrations of carboxylic acids, can destroy the epoxide products by participating in or catalyzing the opening of the oxirane rings. It therefore appeared desirable to study the feasibility of making glycidic esters through the use of peracetic acid solutions containing a minimum of these objectionable impurities and without the use of a buffering agent. Such solutions were obtained for the present study by the acetaldehyde-oxidation method.[9] Using peracetic acid solutions in either ethyl acetate or acetone it was found possible to prepare glycidic esters from α,β-unsaturated esters in good yield and under convenient operating conditions. This general reaction may be represented by the equation



wherein the groups R′, R″, R‴ and R⁗ represent a wide variety of alkyl, aryl and oxygen-containing substituents normally unreactive to peracids.

The conventional Darzens condensation is not a completely general synthesis. For example, when formaldehyde is used as the carbonyl component of the reaction, the yields of the desired glycidic esters are low.[10] With normal alkanals the competing aldol condensation causes unsatisfactory results.[10,11] Likewise, the self-condensation of ketones[12] may adversely influence the yield of desired products, and in addition the alkylation of the

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[1] E. Erlenmeyer, Jr., *Ann.*, **271**, 161 (1892).

[2] G. Darzens, *Compt. rend.*, **139**, 1214 (1904).

[3] M. S. Newman and B. J. Magerlein, "Organic Reactions," Vol. V, J. Wiley and Sons, Inc., New York, N. Y., 1949, p. 413.

[4] G. Braun, THIS JOURNAL, **52**, 3185 (1930).

[5] D. Swern, *Chem. Revs.*, **45**, 1 (1949).

[6] L. J. Dry and F. L. Warren, *J. S. African Chem. Inst.*, **6**, 14 (1953).

[7] A. K. Plisov and A. I. Bykovets, *J. Gen. Chem. USSR*, **24**, 852 (1954).

[8] W. D. Emmons and A. J. Pagano, THIS JOURNAL, **77**, 89 (1955).

[9] B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *ibid.*, **79**, 5982 (1957).

[10] G. Darzens, *Compt. rend.*, **142**, 214 (1906).

[11] B. N. Rutowski and N. A. Dajew, *Ber.*, **64**, 693 (1931).

[12] H. A. Weidlich and G. H. Daniels, *ibid.*, **72**, 1596 (1939).