tween the two major components. 24-Methylenecholesterol represented 53.3% of the sterols of cockle. The distribution of the zones of scallop and mussel together with that of oyster and clam is shown in Table I.

TABLE I

DISTRIBUTION OF AZOYL ESTERS IN PELECYPODA

	Oyster, %	Clam, %		Scallop, %	Cockle, %
Zone 1	5.0	3.0			
Zone 2	36.1	53.0	Zone 1	34.6	53.3
Zone 3	28.6	21.3	Zone 2	39.4	16.7
Zone 4	30.3	22.7	Zone 3	26.0	30.0

Mussel azoyl esters also separated into three zones on the column. 24-Methylenecholesterol represented 5.4% of the total azoyl esters. Since, however, the commercial sterol mixture had previously undergone crystallization for removal of 7-dehydrosterols[2] no conclusions could be drawn about the original composition of mussel sterols.

Properties of 24-methylenecholesterol and derivatives. Zone 1 azoyl ester from scallop crystallized from benzene-aq. ethanol, m.p. 197°; mixed with azoyl ester of 24-methylenecholesterol from oyster,[1] m.p. 196°. The azoyl ester was hydrolyzed[5] and the acetate was prepared. Ultraviolet absorption and the modified Liebermann-Burchard reaction[6,7] of the crude acetate showed the presence of 2.6% of $\Delta^{5,7}$ sterols (calc'd as ergosterol) which were removed with maleic anhydride in the usual manner.[1] The recrystallized acetate of zone 1 melted at 136°, mixture m.p. 136° with 24-methylenecholesterol, $[\alpha]^{22}_{D}$ $-42.9°$.

Anal. Calc'd for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found: C, 81.71; H, 10.88.

The *acetate* was hydrolyzed and the *sterol* was crystallized from methanol, m.p. 141°, mixture m.p. 141° with 24-methylenecholesterol, $[\alpha]^{22}_{D}$ $-35.7°$.

The *benzoate* melted at 147°, undepressed on admixture with 24-methylenecholesterol benzoate, $[\alpha]^{22}_{D}$ $-14.2°$.

24-Ketocholesteryl acetate and derivatives. The acetate of zone 1 in cold glacial acetic acid-acetic anhydride (1:1) was treated with 2 equivalents of ozone. The ozonolysis product was worked up as previously described.[1] Subsequent crystallization from methanol yielded a substance with the m.p. 127°, $[\alpha]^{22}_{D}$ $-43.1°$. Mixture m.p. with 24-ketocholesterol from oyster and a synthetic product was 127°. *24-Ketocholesterol acetate oxime* was prepared by refluxing with hydroxylamine hydrochloride in pyridine-ethanol. Two recrystallizations from aq. ethanol gave m.p. 169°, mixture m.p. 169° with the synthetic material.

Anal. Calc'd for $C_{29}H_{47}NO_3$: C, 76.10; H, 10.35; N, 3.06. Found: C, 76.34; H, 10.56; N, 2.94.

24-Ketocholesterol acetate 2,4-dinitrophenylhydrazone was recrystallized from ethanol. M.p. 169°, mixture m.p. 169° with the synthetic product.

Anal. Calc'd for $C_{35}H_{50}N_4O_6$: C, 67.50; H, 8.09. Found: C, 67.38; H, 8.22.

24-Methylenecholesterol from cockle and mussel. 24-Methylenecholesterol and derivatives were prepared from zone 1 of cockle and mussel identically as described above for scallop. The preparations contained only insignificant quantities of Δ^7-sterols. The properties of the sterol and of the azoyl ester, acetate, and benzoate were identical with those of 24-methylenecholesterol from oyster, clam, and scallop.

Infrared spectra. The identify of 24-methylenecholesterol from the five sources so far investigated was confirmed by a comparison in detail of their infrared spectra. The spectrum of 24-methylenecholesterol showed the maxima at 890 and 1640 cm^{-1} characteristic of the methylene group.[1] Other changes in the spectrum caused by introduction of the 24 (28) double bond were a sharp (weak) peak at 3050 cm^{-1} and a broader (weak) band at 1750–1790 cm^{-1}. These data were derived from a comparison of the spectrum of 24-methylenecholesterol with those of its neutral reduction product (Adams' catalyst in ethyl acetate) and of campesterol.

The infrared spectra of zone 2 from scallop, cockle, and mussel and the diunsaturated zone 3 from oyster and clam were compared and found to be identical. The second double bond does not introduce any major bands. A comparison with the spectra of Δ^5-sterols showed the following characteristics: Absence of the weak band at 925 cm^{-1}; a dominant shoulder at 965–975 cm^{-1}; absence of the weak peak at 1240 cm^{-1}; shifting of the weak band at 1305 cm^{-1} to 1295 cm^{-1}; absence of the shoulder at 1360 cm^{-1}. The monounsaturated bottom zone from oyster, clam, scallop, cockel, and mussel produced a spectrum typical of Δ^5-sterols. The clam and scallop sterol has been reduced to a stanol with Adams' catalyst in glacial acetic acid but the product and its derivatives do not possess the properties of any previously described unsaturated sterol.

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[5] Idler, Nicksic, Johnson, Meloche, Schuette, and Baumann, *J. Am. Chem. Soc.*, **75**, 1712 (1953).

[6] Idler and Baumann, *J. Biol. Chem.*, **195**, 615 (1952).

[7] Idler and Baumann, *J. Biol. Chem.*, **203**, 389 (1953).

The Addition of Azide Ion to Epoxides[1]

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From the original rate correlation of Swain and Scott[2] in conjunction with work performed at the Jet Propulsion Laboratory on the kinetics of the addition of nitrate ion to the ethylene oxide ring,[3] it was observed that the rate of addition of the azide ion to epoxides is relatively high in comparison with that of other nucleophilic species. Therefore, azidoalcohols may be prepared readily in aqueous solution, under mild conditions by nucleophilic attack of epoxides by azide ions. In a recent publication,[4] the reaction of sodium azide with representative epoxides has been aptly studied, and the structure proof of the resulting azidoalcohols has been presented. The present note contains improved synthetic procedures for the preparation of azidoalcohols by this reaction. In addition, some new compounds, including glycidyl azide, have been prepared.

The relatively harsh conditions employed by

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-Ord 18, sponsored by the Department of the Army, Ordnance Corps.

[2] Swain and Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

[3] Petty and Nichols, *J. Am. Chem. Soc.*, **76**, 4385 (1954).

Vander Werf, *et. al.*,[4] namely, a 16- to 40-hour refluxing period in dioxane without neutralization, of the base formed, led to the production of 1,3-diazidopropanol instead of 1-azido-3-chloro-2-propanol in the reaction of epichlorohydrin and produced an unstable product from the reaction of propylene oxide with sodium azide. Although their 1-azido-2-propanol was well characterized by catalytic hydrogenation to the corresponding amine and subsequent identification of the derivative, the yield on that basis was somewhat low, and the purity of the product was questionable. In the present work three modifications in procedure were employed for the preparation of azidoalcohols. In two of the procedures the hydroxyl ions produced during the course of the reaction were removed as formed, in one case by neutralization with perchloric acid and in the other by precipitation as magnesium hydroxide. In the third procedure the hydroxyl ions were not neutralized until final isolation of the azidoalcohol. In practice it appears necessary to keep the reaction medium neutral or slightly acidic only if it is desired to prepare 1-azido-3-propanol from epichlorohydrin; however, 1-azido-2,3-propanediol was also prepared under neutral conditions. The compounds prepared by procedures given below are shown in Table I.

TABLE I

ORGANIC AZIDE COMPOUNDS PRODUCED BY REACTION OF SODIUM AZIDE WITH EPOXIDES IN AQUEOUS SOLUTION

Compound	Boiling Point (°C)	Boiling Point (mm)	$n_D^{25°}$	d_4^{25} (g./ml.)	Yield, %	Method of Preparation (refer to text)	Analyses: Constituent, Element, or Group	Analyses: Calc'd	Analyses: Found
1-Azido-2-propanol	72–74	21	1.4533	1.060	70	C	Carbon	35.60	35.80
							Hydrogen	6.93	7.07
							Nitrogen	41.57	41.31
1-Azido-2,3-propanediol	92–95	0.3	1.4892	1.2581	65	A	Nitrogen	35.88	36.19
							Vicinal Hydroxyl	100.0	98.8
							Glycerin	none	none
1-Azido-3-chloro-2-propanol	44–48	0.5	1.4918	1.291	60	A	Nitrogen	30.90	30.81
					75	B			
Glycidyl azide	37–39	8	1.4530	1.129	86	D	Carbon	36.36	36.49
							Hydrogen	5.09	5.07
							Nitrogen	42.41	42.19
							Epoxide	100.0	98.0
1-Azido-3-nitrato-2-propanol	88	1	1.4861	1.3636	45	Nonaqueous Nitration	Nitrogen	34.56	34.69
					80	B			

EXPERIMENTAL

A. Procedure for reaction of epoxides with sodium azide and perchloric acid. The reaction was conducted in a 3-liter beaker fitted with a mechanical stirrer, thermometer, and separatory-funnel. A solution of 455 g. (7.0 moles) of sodium azide in 1500 ml. of water was prepared in the beaker. To this solution was added 6.25 moles of epoxide. Provision was made to keep the mixture between 25 and 30°, and 70% aqueous perchloric acid was added slowly over a period of about six hours keeping the solution between *p*H 6 and 9 (or above the neutral point of Congo Red paper and no more than weakly basic to *p*H indicator paper). Attempts to use the *p*H meter were usually unsuccessful since there was apparently some interference at the electrodes which resulted in erroneous readings. The optimum reaction temperature was 25 to 30°. Below 25° it was necessary to add the acid very slowly, a procedure which would take longer than a normal working day. Above 30° the reaction was difficult to control and a drastic temperature rise was possible. After the reaction was about 90% complete as indicated by the quantity of perchloric acid consumed, the mixture was stored at 0° overnight. The lower layer was separated and the aqueous layer was further extracted with methylene chloride. The extracts were combined with the crude azidoalcohol. The solution was evacuated and the product was isolated by remote distillation under reduced pressure to give a 60 to 70% yield of the azidoalcohol.

B. Procedure for reaction of epoxides with a solution of sodium azide and magnesium perchlorate. To 700 ml. of water were added 179 g. (0.8 mole) of magnesium perchlorate and 117 g. (1.8 moles) of sodium azide with appropriate cooling of the mixture. The solution was stirred and cooled to 0 to 5° with an ice-bath and 1.3 moles of epoxide were added rapidly. The mixture was stirred about 20 minutes and stored in a refrigerator overnight. The precipitated magnesium hydroxide was removed by filtration and washed with several portions of methylene chloride, which were combined with the original filtrate. The methylene chloride layer was separated and the aqueous layer was washed with one 200-ml. and two 100-ml. portions of methylene chloride. The extracts were combined and evacuated. The crude product was distilled remotely through a six-inch Vigreux column to give 70 to 75% yields of the azidoalcohol.

C. Procedure for reaction of epoxides with aqueous sodium azide. To a solution of 100 g. (1.54 moles) of sodium azide in 250 ml. of water was added 1 mole of epoxide with stirring. The stoppered flask was stirred magnetically overnight. The reaction mixture was stirred an additional three hours while being heated to 35° the next day. The product was separated and the aqueous layer was washed with one 200-ml. and two 100-ml. portions of methylene chloride. The extracts were combined and evacuated to remove solvent. The crude product was distilled remotely to give a 69% yield in the preparation of 1-azido-2-propanol.

D. Preparation of glycidyl azide and 1-azido-3-nitrato-2-propanol. Glycidyl azide was prepared by exactly the same procedure that was applied to 1-chloro-3-nitrato-2-propanol

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[4] Vander Werf, Heisler, and McEwen, *J. Am. Chem. Soc.*, **76**, 1231 (1954).

for synthesizing glycidyl nitrate in previous work.[3] It was not necessary to distil the 1-azido-3-chloro-2-propanol prepared by procedure A or B above before dehydrohalogenation with aqueous sodium hydroxide. The over-all yield of glycidyl azide based on epichlorohydrin was about 55%. Glycidyl azide may be nitrated to form 1-azido-3-nitrato-2-propanol by conventional procedures.[5]

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(5) Nichols, Magnusson, and Ingham, *J. Am. Chem. Soc.*, **75**, 4255 (1953).

The Ultraviolet Absorption Spectrum of 1,4-Cyclohexadien-1-carboxylic Acid, an Intermediate in the Preparation of 1,4-Cyclohexadienyl Methyl Ketone

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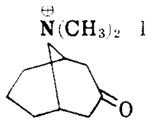
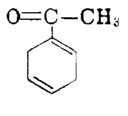
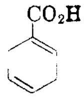
In connection with a study of the "dihydroacetophenone" reported to be formed by treatment of pseudopelletierine methiodide (I) with strong base,[1] we have had occasion to prepare 1,4-cyclohexadienyl methyl ketone (II) by a new route.



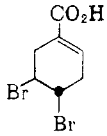
I



II



III



IV

Addition of butadiene to propiolic acid yielded 1,4-cyclohexadien-1-carboxylic acid (III), a compound previously isolated by Alder and Backendorf as a by-product arising from the addition of butadiene to acetylene dicarboxylic acid.[2] The desired ketone (II) was obtained by treatment of the Diels-Alder adduct (III) with lithiummethyl in the standard fashion.

It was of interest to examine the ultraviolet absorption spectrum of the diene acid III, in view of the considerable influence of the *nonconjugated* ethylenic linkage previously demonstrated in the case of II and some of its analogs. Thus, II has been shown to exhibit a $\lambda_{max.}$ at 245 mμ, ϵ 4,000, while 1-cyclohexenyl methyl ketone has a $\lambda_{max.}$ at 232 mμ, ϵ 12,500.[3] The isolated double bond in the carboxylic acid III has now been found to bring about a similar but somewhat larger shift in both wavelength and intensity of maximal absorption. A $\lambda_{max.}$ at 235 mμ, ϵ 2,500 was observed for this acid, while 1-cyclohexen-1-carboxylic acid[4] exhibits a $\lambda_{max.}$ at 212 mμ, ϵ 11,000. Thus in these closely related pairs of molecules, a shift of +23 mμ results from the nonconjugated unsaturation in the carboxylic acid, compared with a shift of +13 mμ in the case of the ketone. *trans*-4,5-Dibromo-1-cyclohexen-1-carboxylic acid (IV), readily produced by addition of bromine to III, showed the expected normal absorption ($\lambda_{max.}$ 212 mμ, ϵ 10,000).

EXPERIMENTAL

Ultraviolet spectra. The spectra were determined in ethanol solutions, using a Beckman DU spectrophotometer equipped with a photomultiplier.

1,4-Cyclohexadien-1-carboxylic acid (III). A solution of propiolic acid (7.5 g.) and butadiene (9.0 g.) in a sealed Pyrex bomb was maintained at 54° for 39 hours. The yield (6.0 g.) of white, crystalline adduct obtained after the usual work-up procedure could undoubtedly have been improved if an attempt were made to find the optimum reaction and isolation conditions. Alternate vacuum sublimation and recrystallization from heptane gave an analytical specimen, m.p. 121-122° (lit. m.p. 123°).

Anal. Calc'd for $C_7H_8O_2$: C, 67.7; H, 6.5. Found: C, 68.0; H, 6.4.

Light absorption. $\lambda_{max.}$ 235 mμ, ϵ 2,500.

1,4-Cyclohexadienyl methyl ketone (II). Following a classical example,[5] 1,4-cyclohexadien-1-carboxylic acid (III) (5.5 g.) and two equivalents of lithiummethyl in ethereal solution were allowed to interact, giving a lemon-colored liquid (4.7 g.) after the usual isolation procedure. Careful distillation yielded colorless 1,4-cyclohexadienyl methyl ketone (II) (2.1 g.), b.p. 71.5°/6.0 mm., n_D^{20} 1.5126 (lit. b.p. 80-81°/14 mm.; n_D^{16} 1.5135).

Light absorption. $\lambda_{max.}$ 245 mμ, ϵ 4,450.

trans-4,5-Dibromo-1-cyclohexen-1-carboxylic acid (IV). The Diels-Alder adduct (III) (0.10 g.) instantly decolorized bromine, added dropwise in carbon tetrachloride solution, giving rise to white crystals. Two crystallizations from carbon tetrachloride, followed by vacuum sublimation, gave the dibromo acid (IV) (0.18 g.), m.p. 152-154°.

Anal. Calc'd for $C_7H_8Br_2O_2$: C, 29.6; H, 2.8; Br, 56.3; Neut. equiv., 284. Found: C, 30.1; H, 3.1; Br, 55.7; Neut. equiv., 283.

Light absorption. $\lambda_{max.}$ 212 mμ, ϵ 10,000.

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(1) Ciamician and Silber, *Ber.*, **26**, 156 (1893).

(2) Alder and Backendorf, *Ber.*, **71**, 2199 (1938).

(3) Bowden and Jones, *J. Chem. Soc.* 52 (1946); Braude, Jones, Sondheimer, and Toogood, *J. Chem. Soc.*, 607 (1949).

(4) Braude and Coles, *J. Chem. Soc.*, 2014 (1950).

(5) van Dorp and Arens, *Rec. trav. chim.*, **65**, 338 (1946).