Anal. Calcd for $C_{20}H_{38}O_2$: C, 77.36; H, 12.34; mol wt, 310.5. Found: C, 76.60; H, 12.48; mol wt, 314 (thermistor).

Copper Chelate.—Hot aqueous cupric acetate and an ethanolic solution of the keto aldehyde were combined and cooled to deposit blue-green crystals of the chelate: mp 128–129°; uv 245 mμ (*E* 7300), 302 (8900); ir, 1585, 1498, 1445, 1350 cm^{-1} (CHCl$_3$).

Anal. Calcd for $C_{40}H_{74}O_4Cu$: C, 70.39; H, 10.93. Found: C, 70.53; H, 10.94.

Dechelation.—A solution of the chelate in warm chloroform was shaken with 0.1 *N* hydrochloric acid, and the chloroform layer was washed with water, dried (sodium sulfate), and evaporated to yield a residue of the free keto aldehyde identical in properties with the sample described above.

3-Oxooctadecanal.—By a method analogous to procedure C, vinyl palmitate was converted to the C-18 3-keto aldehyde: mp 51.5–52.2° (lit.[10] mp 47°); ir and uv very like those of the C-20 compound; copper chelate, mp 125–126.5°.

3-Oxotetradecanal.—By a method analogous to procedure C, vinyl laurate was converted to the C-14 3-keto aldehyde: mp 32.5–33.0°; ir and uv very similar to those of the C-18 and C-20 homologs. The pure crystalline compound was not stable to storage.

The copper chelate had mp 126.8–127.4°.

Anal. Calcd for $C_{28}H_{50}O_4Cu$: C, 65.38; H, 9.82. Found: C, 65.38; H, 9.81.

Reaction of Vinyl Alkanoate with Aluminum Chloride to Form β Diketones. Procedure D. 18,20-Dioxoheptatriacontane (Distearoylmethane).—Vinyl stearate (23.4 g, 0.075 mol) in 200 ml of olefin-free hexane was treated with 10.15 g (0.075 mol) of aluminum chloride, and the mixture was refluxed for 2 hr, cooled, quenched by agitation with dilute hydrochloric acid, and dried (sodium sulfate), and the solvent was removed *in vacuo*. The residue weighed 8.5 g and more material (10 g) was recovered from the aqueous acid by methylene chloride–ether extraction.

The residues were combined, dissolved in hot 95% ethanol, and treated with an excess of hot aqueous curpic acetate to deposit a 73% yield of the lilac chelate identical with the preparation described above. [Where mixtures of the keto aldehyde and diketone were obtained as, for example, in intermediate reaction times (compare procedures C and D), separation was effected by chromatography of the mixed chelates on Florisil. Elution with hot benzene gave a forerun of the lilac chelated distearoylmethane followed by the blue-green chelated 3-oxoeicosanal. Additional chelated keto aldehyde was eluted with chloroform.]

16,18-Dioxotritriacontane (Dipalmitoylmethane).—In a manner analogous to the above (procedure D) vinyl palmitate was converted to dipalmitoyl methane.

12,14-Dioxopentacosane (Dilauroylmethane).—In a manner analogous to the above, vinyl laurate was converted to dilauroylmethane.

Ethyl Palmitoacetate and Ethyl Dipalmitoacetate.—Acetoacetic ester (3.6 ml, 0.028 mol) and 7.62 g of palmitoyl chloride (0.028 mol) in 50 ml of olefin-free hexane were treated with 3.7 g (0.028 formula wt) of aluminum chloride added in one portion. The pasty mixture was warmed for 2 hr at 70° during which time all solids dissolved. The mixture was cooled, poured into iced dilute hydrochloric acid, and extracted into ether. A little ethanol was used to break emulsions. The organic layer was dried (sodium sulfate), solvents were removed, and the product was chromatographed on Florisil. The first pentane eluates contained 1 g of dipalmitoylacetic ester purified by recrystallization of the copper chelate from ethanol: mp 91.9–92.3°; uv 297 mμ (*E* 26,000), 241 (18,000).

Anal. Calcd for $C_{72}H_{134}O_8Cu$: C, 72.58; H, 11.34. Found: C, 72.88; H, 11.34.

Dechelation with hydrochloric acid gave the free dipalmitoylacetic ester, mp 42–43°, uv 280 mμ (*E* 92000) (EtOH). Further elution of the column with methylene chloride gave palmitoacetic ester which, after recrystallization from hexane, melted from 38.7 to 39.2°, copper chelate mp 112–114° (lit.[16] mp 37–38 and 111°, respectively).

Registry No.—I, 6136-89-6; vinyl stearate, 111-63-7; diethyl 2-stearoylmalonate, 24514-82-7; 3,4-dimethylstearophenone, 24514-83-8; 8,10-dioxoheptadecane, 24514-84-9; copper chelate of 8,10-dioxoheptadecane, 24523-20-4; 18,20-dioxoheptatriacontane, 24514-85-0; copper chelate of 18,20-dioxoheptatriacontane, 24515-38-6; 16,18-dioxotritriacontane, 24514-86-1; copper chelate of 16,18-dioxotritriacontane, 24515-39-7; 3-oxoeicosanal, 24514-87-2; copper chelate of 3-oxoeicosanal, 24515-40-0; 3-oxotetradecanal, 24514-88-3; copper chelate of 3-oxotetradecanal, 24515-41-1; ethyl dipalmitoacetate, 24514-89-4; copper chelate of ethyl dipalmitoacetate, 24515-42-2.

Insertion of Ethylene Oxide into the Carbon–Chlorine Bond of Benzyl Chloride

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The synthesis of β-chloroethyl benzyl ethers from benzyl chlorides and ethylene oxide is described. Benzyl chlorides rapidly polymerize, releasing hydrogen chloride, in the presence of Friedel–Crafts catalysts or metal oxides. The chlorides, however, give only small quantities of polymer when N,N-dimethylformamide, N,N-dimethylacetamide, or acetonitrile is added to the system, and β-chloroethyl benzyl ethers can be prepared by adding ethylene oxide to the mixture. The reaction mechanism is discussed.

There are several reports describing the insertion reactions of epoxides into the carbon–chlorine bond.[1–5] Recently, Klamann and coworkers have shown that tetraethylammonium bromide and metallic copper are excellent catalysts for this reaction.[6] On the other

hand, it has been reported that benzyl halides easily polymerize in the presence of Friedel–Crafts catalysts or certain metal oxides.[7,8]

We have now shown that the presence of certain solvents in a zinc chloride–benzyl chloride–ethylene oxide system depresses the condensation–polymerization reaction of benzyl chloride and permits the insertion of ethylene oxide into the carbon–chlorine bond to form β-chloroethyl benzyl ethers. This dramatic solvent effect is observed when N,N-dimethyl-

(1) H. Hoff, U. S. Patent 2,241,200 (1940).

(2) H. Howell, G. B. Butler, and H. H. Sisler, *J. Org. Chem.*, **27**, 1709 (1962).

(3) B. A. Arbuzov and O. N. Nuretdinova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 783 (1963).

(4) P. Weyerstahl, D. Klamann, C. Finger, F. Nerdel, and J. Buddrus, *Chem. Ber.*, **100**, 1858 (1967).

(5) U. Beyer, F. H. Müller, and H. Ringsdorf, *Makromol. Chem.*, **101**, 74 (1967).

(6) D. Klamann, P. Weyerstahl, and F. Nerdel, *Ann. Chem.*, **710**, 59 (1967).

(7) W. C. Overhults and A. D. Ketley, *Makromol. Chem.*, **95**, 143 (1966).

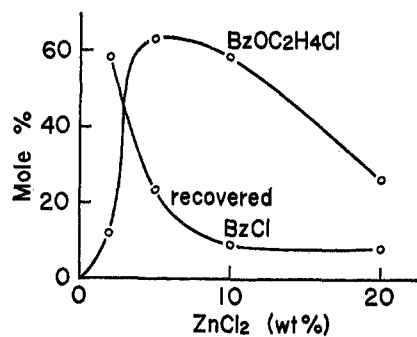(8) D. B. V. Parker, W. G. Davies, and K. D. South, *J. Chem. Soc., B*, 471 (1967).

Figure 1.—Variation of generated BzOC₂H₄Cl and recovered BzCl vs. ZnCl₂ amount. Reaction conditions: BzCl; 4.0 g of DMA; 2.0 g of EO; 50–55 ml/min, 140°, 1 hr. Bz = C₆H₅CH₂–, DMA = N,N-dimethylacetamide, EO = ethylene oxide.
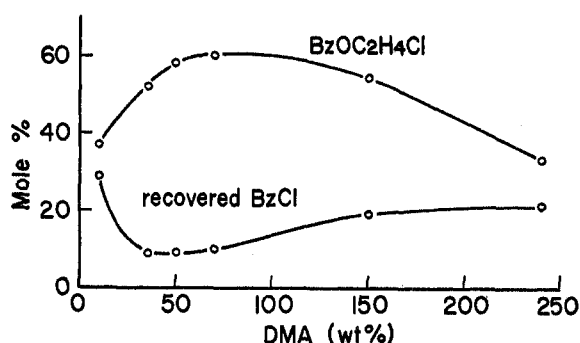

Figure 2.—Variation of generated BzOC₂H₄Cl and recovered BzCl vs. DMA. Reaction conditions: BzCl; 4.0 g of ZnCl₂; 0.4 g of EO; 50–55 ml/min, 140°, 1 hr.

formamide, N,N-dimethylacetamide, or acetonitrile is used.

Results and Discussion

In the reaction of ethylene oxide and benzyl chlorides, condensation of benzyl chlorides, formation of ethylene chlorohydrin, or complicated reactions with solvent may occur. The various factors affecting this reaction were studied.

Catalysts.—Several Friedel–Crafts type catalysts were compared with each other using benzyl chloride in sealed-tube reactions. The results are shown in Table I. Zinc chloride and cupric chloride give the highest yields.

TABLE I

INSERTION OF ETHYLENE OXIDE INTO BENZYL CHLORIDE[a]

Catalyst	Yield, mol % of C₆H₅CH₂OC₂H₄Cl	Recovered benzyl chloride, mol %
AlCl₃	Trace	100
FeCl₃	5.2	81
SnCl₄	Trace	81
BiCl₃	3.7	54
ZnCl₂	14.7	33
CuCl₂	11.0	63
CuCl₂[b]	6.3	53

[a] Reaction conditions: catalyst, 0.001 mol; N,N-dimethylacetamide, 0.01 mol; benzyl chloride, 0.01 mol; ethylene oxide, 0.01 mol; 140°; 1 hr. [b] Without solvent.

As shown in Figure 1, when zinc chloride is used as the catalyst (5 wt % based on benzyl chloride), the maximum yield is 63 mol %). When more catalyst is
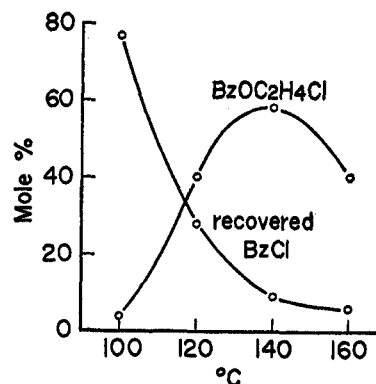

Figure 3.—Variation of generated BzOC₂H₄Cl and recovered BzCl vs. temperature. Reaction conditions: BzCl; 4.0 g of DMA; 2.0 g of ZnCl₂; 0.4 g of EO; 50–55 ml/min, 1 hr.

used, the yield of both β-chloroethyl benzyl ether and the recovery of benzyl group[9] decrease owing to condensation polymerization.

Solvent.—N,N-Dimethylacetamide, N,N-dimethylformamide, acetonitrile, dimethyl sulfoxide, nitrobenzene, nitromethane, and nitroethane were examined. When either N,N-dimethylacetamide, N,N-dimethylformamide, or acetonitrile was used, the insertion reaction occured. Without the solvent, however, a glassy polymer is obtained on heating the mixture with or without ethylene oxide. The yield of β-chloroethyl benzyl ether under optimum conditions increases in the following order, acetonitrile < N,N-dimethylformamide < N,N-dimethylacetamide, with N,N-dimethylacetamide giving the least by-product.

Under the same reaction conditions as in Table I, the results in Table II are obtained.

TABLE II

INSERTION REACTION IN SEALED-TUBE REACTION[a]

Solvent	Yield of C₆H₅CH₂OC₂H₄Cl, mol %
Acetonitrile	7.6
N,N-Dimethylformamide	15.0
N,N-Dimethylacetamide	14.0

[a] Reaction conditions: same as in Table I.

Nitroalkanes, though effective solvents in Friedel–Crafts reactions, give no insertion product. This may be attributed to the poor solubility of the catalyst. Dimethyl sulfoxide gives various by-products but not the desired product.

The conversion of benzyl chloride, the recovery of benzyl group, and the yield of β-chloroethyl benzyl ether were also determined vs. the amount of N,N-dimethylacetamide. As shown in Figure 2, use of 50–70 wt % N,N-dimethylacetamide to benzyl chloride gives the maximum yield of β-chloroethyl benzyl ether. With more solvent, the recovery of benzyl group as well as the yield of the ether decreases.

Reaction Temperature.—As shown in Figure 3, the reaction starts at about 100°, and at 140° the maximum yield is obtained.

(9) Recovery of the benzyl group means the mole summation of β-chloroethyl benzyl ether and unreacted benzyl chloride.

Water.[10]—The presence of water causes the formation of the by-product polyethylene glycol. Moreover, the appearances of reaction mixtures differ from each other owing to the amount of water. The reaction mixture is homogeneous when the solvent contains 0.07–0.4 wt % water. When the solvent is dehydrated as completely as possible (0.03 wt %) with calcium hydride or azeotropically, or when the solvent contains much more water (1.9 wt %), the mixture is heterogeneous.

As shown in Figure 4, the yield of the insertion product decreases to 37% when the system contains 1.9% water, and the recovery of the benzyl group decreases also. The formation of by-products as well as of polyethylene glycol is effected by water.

When the water content is as low as 0.03%, the yield of β-chloroethyl benzyl ether is 44%, and the recovery of benzyl group is 54%. This suggests that the reaction is depressed by low solubility of the catalyst in this system, and that a certain amount of water is necessary to promote the insertion reaction, since the recovery of benzyl group decreases also.

Substitution on the Benzene Ring.—In the reaction of ethylene oxide and benzyl chloride, the intermediate benzylcarbonium ion may form. Therefore, we examined several benzyl chlorides having alkyl, chloro, nitro, and methoxy group substituents. Reactivity of chloromethylated toluene with ethylene oxide increases in the following order as shown in Figure 5: o-CH$_3$ > p-CH$_3$ > m-CH$_3$.

This fact may be explained as follows. When the insertion reaction proceeds *via* a carbonium ion intermediate, the cation from the *meta* derivative may be less stable than that from the *ortho* or *para* derivative. Yields of *ortho* derivative product decrease after 70 min which may also be explained by assuming that the *ortho* derivative may be easily attacked sterically by a benzyl carbonium ion to become polybenzyl.
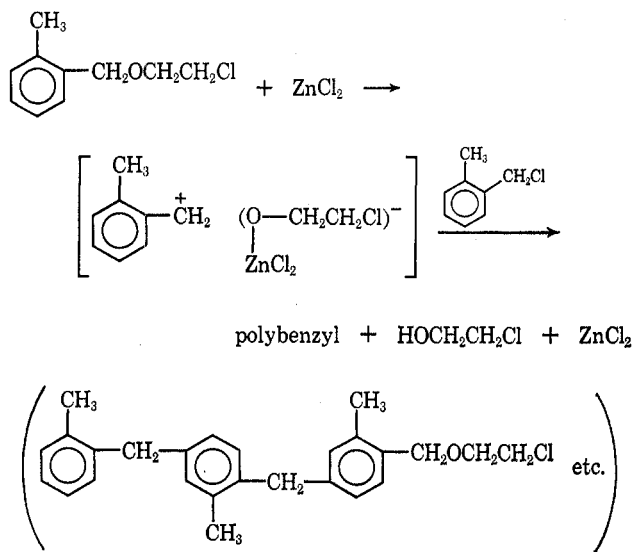
The yields of insertion products from other *para*-substituted benzyl chlorides are shown in Table III. Yields from p-methoxy, p-methyl (Figure 5), and p-nitro derivatives are comparable to their σ values.

(10) Water content in the solvent and benzyl chloride was determined by means of the Karl–Fisher titration.
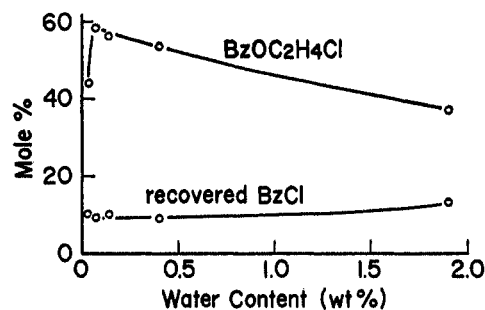

Figure 4.—Variation of generated BzOC$_2$H$_4$Cl and recovered BzCl *vs.* water content. Reaction conditions: BzCl; 4.0 g of DMA; 2.0 g of ZnCl$_2$; 0.4 g of EO; 50–55 ml/min, 140°, 1 hr.
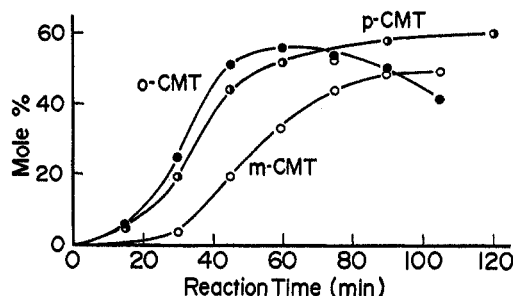

Figure 5.—Progress of insertion product of chloromethylated toluene. Reaction conditions: CMT; 8.0 g of DMA; 4.0 g of ZnCl$_2$; 0.8 g of EO; 55 ml/min, 140°.

The p-chloro derivative, however, shows a high yield despite its positive σ value, 0.226. This fact may be accounted for by its large resonance effect rather than its inductive effect.

Table III

INFLUENCE OF *para* SUBSTITUENTS[a]

Substituent, p-X	Yield of p-XC$_6$H$_4$CH$_2$OC$_2$H$_4$Cl, mol %	σ value
H	14.7	0
CH$_3$	24.9	−0.170
Cl	34.5	+0.226
CH$_3$O	39.3	−0.268
NO$_2$	0	+0.778

[a] Benzyl chloride–ethylene oxide = 1.0; zinc chloride, 10% by weight of benzyl chloride; 140°; 1 hr.

The insertion reaction is applied to higher alkyl derivatives. Thus, dodecylbenzyl chlorides were examined. Products were purified by vacuum distillation, but small amounts of contamination cannot be removed because of their high viscosities and molecular weights. Results are shown in Table IV.

Table IV

INSERTION PRODUCTS FROM n-DODEC-Y-YLBENZYL CHLORIDE[a]

Y	Yield of R-C$_6$H$_4$CH$_2$OC$_2$-H$_4$Cl, %	Bp, °C (0.008 mm)	C	H	Cl[12]
1	41	160–170	73.96	10.86	10.0
2	45	159–165	74.17	10.94	10.6
6	51	153–157	74.14	10.54	9.8

[a] Calcd for C$_{21}$H$_{35}$OCl: C, 74.41; H, 10.41; Cl, 10.46.

Probable Mechanism of Insertion Reaction.—The insertion reaction may proceed through a free benzyl-carbonium ion or a solvated or nearly σ-bonded ion[8]

TABLE V

INSERTION PRODUCTS FROM SUBSTITUTED BENZYL CHLORIDES

$$X-\underset{}{\bigcirc}CH_2OC_2H_4Cl$$

Substrate		Calcd %			Found %		
X	Bp, °C (mm)	C	H	Cl	C	H	Cl[a]
o-CH₃	85–87 (3)	65.04	7.10	19.2	65.18	7.10	18.7
m-CH₃	96–97 (3)	65.04	7.10	19.2	65.20	7.31	19.3
p-CH₃	101–102 (3)	65.04	7.10	19.2	64.92	7.23	19.7
p-Cl	105 (1)	52.71	4.92	34.6	52.95	5.04	34.1
p-CH₃O	108–110 (1)	59.86	6.53	17.7	59.66	6.38	17.7

[a] Reference 12.

to the solvent. The intermediate, stabilized by solvation, may then react with ethylene oxide (route a) to form the ether. Another benzyl chloride may be attacked by the solvated cation to form polymer
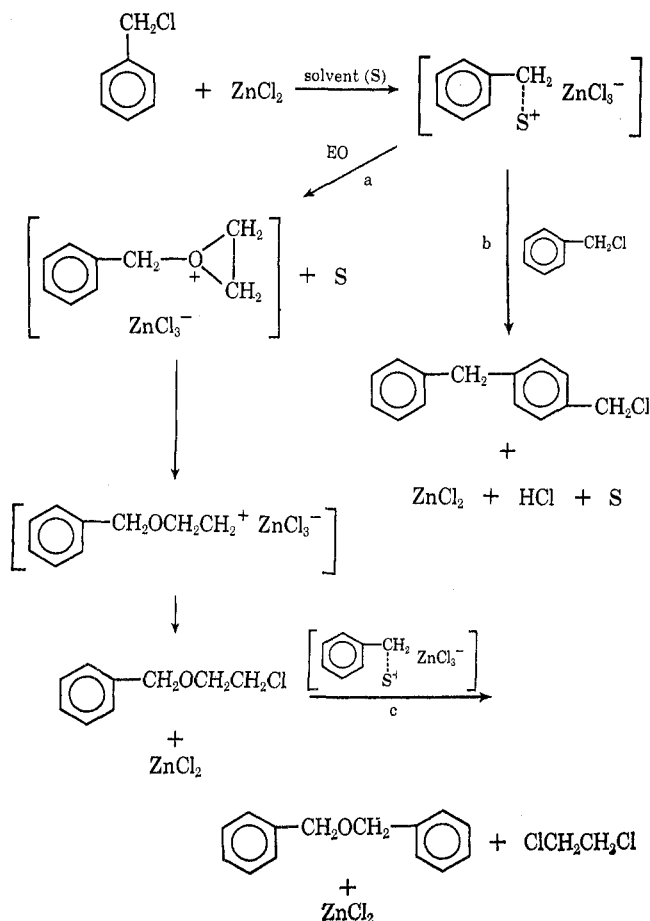
(route b), since a small amount of polymer was detected in all experiments. Dibenzyl ether may be generated by attack of a benzyl cation on β-chloroethyl benzyl ether or benzyl alcohol (route c).

Experimental Section

Reaction of Ethylene Oxide (EO) and Benzyl Chloride.— In the typical run, 2.0 g of N,N-dimethylacetamide (DMA) was added to a vessel containing 0.4 g of freshly dried ZnCl₂. After dispersion of ZnCl₂ by warming, 4.0 g of benzyl chloride was added, and EO, 50–55 ml/min, was bubbled in at 140° for 1 hr. Products were separated by distillation after washing with 1 N HCl and H₂O. The main product, bp 52–53° (1 mm), showed a characteristic infrared band at 1115 cm⁻¹ besides those owing to the phenyl group; nmr (15% CCl₄ solution) τ 6.47[11]

(4 H), 5.57 (2 H), 2.87 (5 H). *Anal.* Calcd for C₉H₁₁OCl C, 63.35; H, 6.50; Cl, 20.8. Found: C, 63.04; H, 6.64; Cl,[12] 20.8. Comparing with the authentic sample synthesized from benzyl alcohol and ethylene oxide in the presence of sodium benzyl alcoholate, followed by chlorination of the hydroxyl group by thionyl chloride, which showed the same ir, nmr spectrum, and boiling point, the main product was identified as β-chloroethyl benzyl ether.

The yield of β-chloroethyl benzyl ether was 63 mol % by glpc.[14] Ethylene chlorohydrin was detected by glpc from the crude product before washing with 1 N HCl. Small amounts of dibenzyl ether, benzyl alcohol, and benzyl formate (when N,N-dimethylformamide was used as a solvent) were also shown by glpc.

Reaction of Substituted Benzyl Chlorides.—To compare reactivities of benzyl chlorides, a mixture of ZnCl₂ (0.2 g), DMA (1.4 g), substituted benzyl chloride (0.016 mol), and EO (0.7 g, 0.016 mol) was heated in a sealed tube at 140° for 1 hr. These β-chloroethyl ethers were isolated by the same procedure as in the case of β-chloroethyl benzyl ether. The substituted β-chloroethyl ethers were also analyzed by glpc.[15]

Phenyldodecanes. 1-Phenyldodecane (I).[16]—I was prepared from lauroyl chloride and benzene by a Friedel–Crafts reaction[17] followed by Clemensen reduction;[18] bp 120–125° (1 mm); yield, 72% based on lauroyl chloride; nmr (neat) τ 9.17 (3 H), 8.73 (18 H), 8.35 (2 H), 7.57 (2 H), 2.96 (5 H). *Anal.* Calcd for C₁₈H₃₀: C, 87.73; H, 12.27. Found: C, 87.55; H, 12.20.

2-Phenyldodecane (II).—After dehydration of methyldecylcarbinol[16] (prepared from decyl bromide[19] and acetophenone) by refluxing with 90% formic acid for 20 hr, the olefin [bp 120–130° (1 mm), two components detected by glpc] was hydrogenated to II in ethanol in the presence of 5% Pd–carbon and 25–30 kg/cm² of hydrogen at room temperature for 4 hr: bp 115–118° (0.8 mm); yield, 52% based on decyl bromide; nmr (neat) τ 9.14 (3 H), 8.85 (3 H), 8.80 (16 H), 8.55 (2 H), 7.45 (1 H), 2.90 (5 H). *Anal.* Calcd for C₁₈H₃₀: C, 87.73; H, 12.27. Found: C, 87.54; H, 12.43.

6-Phenyldodecane (III).—III was prepared by a procedure similar to that used for II, with the olefins [bp 111–120° (0.8 mm), two components detected by glpc] through pentylhexylphenylcarbinol[16] prepared from hexyl bromide and pentyl phenyl ketone[17] obtained from caproyl chloride: bp 115–117° (1 mm); yield, 66% based on pentyl phenyl ketone; nmr (neat) τ 9.20 (6 H), 8.82 (14 H), 8.45 (4 H), 7.60 (1 H), 2.95 (5 H). *Anal.* Calcd for C₁₈H₃₀: C, 87.73; H, 12.27. Found: C, 87.75; H, 12.08.

Chloromethylated Dodecylbenzenes.—Phenyldodecanes were chloromethylated[20] with paraformaldehyde and hydrogen chloride. In the chloromethylation reaction of alkylbenzenes, mixtures of ring-position isomers are generally obtained. In the case of alkylbenzene having bulky alkyl moiety, the genera-

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(11) This was considered to be the superimposed signal of four methylene protons in the β-chloroethyl group, because of the same chemical shifts of protons.

(12) Determined by modified semimicro butanol–Na method.[13]

(13) W. Kimura, *Kogyo Kagaku Zasshi*, **37**, 1310 (1934).

(14) Apiezon L grease 10% on Diasolid, 1 m, 140°, H₂ 70 ml/min. By making a calibration curve between the isolated product and the internal standard, the yield based on benzyl chloride was determined (internal standard, N,N-diethylaniline).

(15) Triton X-305 10% on Diasolid L, 180°; internal standard methyl benzoate for C₆H₅CH₂Cl, lauryl acetate for p-CH₃C₆H₄CH₂Cl, CH₃(OCH₂CH₂)₃OH for p-CH₃OC₆H₄CH₂Cl and p-ClC₆H₄CH₂Cl.

(16) E. R. Lynch and E. B. McCall, *J. Chem. Soc.*, 1254, (1960).

(17) F. L. Breusch and M. Oguzer, *Chem. Ber.*, **87**, 1225 (1954).

(18) "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 444.

(19) Reference 18, Coll. Vol. I, 1941, p 30.

(20) S. K. Freeman, *J. Org. Chem.*, **26**, 212 (1961).

TABLE VI
PROPERTIES OF CHLOROMETHYLATED DODECYLBENZENES

Phenyldodecane	Bp, °C (1 mm)	Cl, % (calcd)
I	158–162	11.9 (12.0)
II	145–148	11.6 (12.0)
III	138–142	11.5 (12.0)

tion ratio of the *para* derivative becomes great, but the compositions of chloromethylated dodecylbenzenes for the insertion reaction cannot be determined by ir, nmr, or glpc. The yields of chloromethylated dodecylbenzenes are low[20] in every case; so raw dodecylbenzenes must be treated repeatedly to obtain chloromethylated compounds. Their properties are shown in Table VI.

Reactions of Chloromethylated Dodecylbenzenes.—The procedure was similar to the case of benzyl chloride, except for the reaction time, 3 hr, and the reactant ratio, dodecylbenzyl chloride:ZnCl₂:DMA = 10:1:10 by weight. The properties of the insertion products are shown in Table IV.

Bridged Polycyclic Compounds. LXI. Synthesis and Some Properties of Tribenzobicyclo[3.2.2]nonatriene (Homotriptycene) and Derivatives[1]

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A preparation of homotriptycene (1) was conducted *via* ring expansion of tribenzobicyclo[2.2.2]octatrienylcarbinyl cation. Alkyl cations from 1 (*i.e.*, 2 and 7) do not rearrange to each other, but the 2-tribenzobicyclo[3.2.2]nonatrienyl cation (2) is an intermediate whose degeneracy was demonstrated with the aid of deuterium labeling. Pmr spectra of some homotriptycenes and triptycenes are recorded.

A natural extension of work in this laboratory on bridged polycyclic systems centered about tribenzobicyclo[3.2.2]nonatriene (1) and some of its derivatives, in particular, the carbonium ion 2. For reasons of simplicity 1 will be referred to as homotriptycene, as it

1

2   **3**
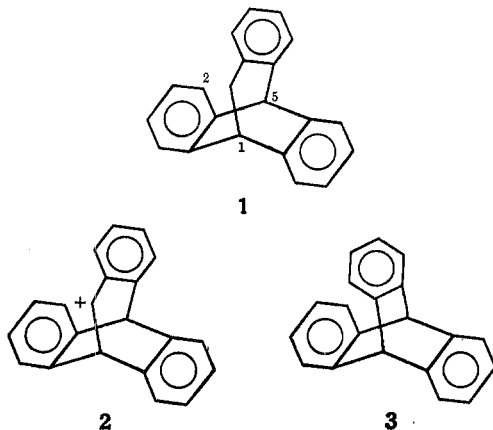
is the next higher homolog of 9,10-dihydro-9,10-*o*-benzenoanthracene, or triptycene (3). Within the last few years syntheses of bicyclo[3.2.2]nonatriene[2] and one of its mono-[3] and both of its dibenzo-substituted[4] derivatives have been described. We now describe another member of this bicyclic family, tribenzobicyclo[3.2.2]-nonatriene.

The key to the synthesis of the homotriptycene ring system appeared to us to be a ring expansion reaction of some derivative of 1-methyltriptycene. As 1-aminomethyltriptycene (4) was known,[5] this appeared to be a very reasonable precursor. In accord with our expectations, nitrous acid in glacial acetic acid converted 4 into a mixture representing a 42% yield of 1-tribenzobicyclo[3.2.2]nonatrienol (5-OH) and a 56%

4

5   **6**

yield of the corresponding acetate (5-OAc).[6] We did not find any alcohol or acetate with unrearranged carbon skeleton (*i.e.*, 6-OH or 6-OAc). Neither 5-OH nor 5-OAc seemed to be an ideal precursor of 1, as 5-OH
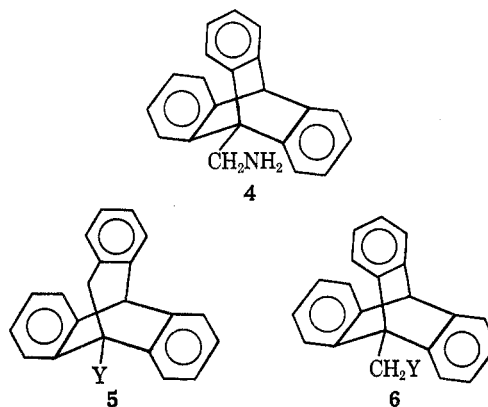
(1) Paper LX: S. J. Cristol, M. A. Imhoff, and D. C. Lewis, *J. Org. Chem.*, **35**, 1722 (1970).

(2) (a) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4413 (1965); (b) M. Jones, Jr., and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 3935 (1967); (c) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).

(3) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *ibid.*, **89**, 2778 (1967).

(4) (a) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); (b) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *ibid.*, **90**, 5564 (1968); (c) S. J. Cristol, G. O. Mayo, and G. A. Lee, *ibid.*, **91**, 214 (1969).

(5) E. C. Kornfeld, P. Barney, J. Blankley, and W. Faul, *J. Med. Chem.*, **8**, 342 (1965).

(6) The presence of large amounts of alcohols from diazotization reactions in acetic acid has been noted before.[7]

(7) (a) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961); (b) P. S. Bailey and J. G. Burr, Jr., *J. Amer. Chem. Soc.*, **75**, 2951 (1953); (c) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (d) H. Felkin, *Bull. Soc. Chim. Fr.*, 1582 (1960); (e) J. R. Mohrig, Ph.D. Thesis, University of Colorado, 1963; (f) G. T. Tiedeman, Ph.D. Thesis, University of Colorado, 1964.