Our results demonstrate that hydrogen bromide addition to **1a** and **1b** is regiospecific as well as stereospecific, whereas the addition of **1c** is nonregiospecific. The most convincing rationale of our results is depicted in Scheme I. We suggest that **1a** or **1b** reacts with hydrogen bromide in a reversible process to form the corresponding unstable π-proton complex (**2a** or **2b**), which readily breaks up to form a planar resonance stabilized π-allylic cation (**3a** or **3b**). The addition of bromide anion to **3a** or **3b** can give rise to the observed allylic bromide (**4a** or **4b**) in each case. The stereospecificity observed can be explained as the cis configuration of **3a** or **3b** is much more stable than its trans configuration in a nine- or ten-membered ring. In the case of **1c** we argue that the π-proton complex (**2c**) is stable, and it is attacked by the nucleophile (Br^-) both at central and terminal centers to form 1-bromocyclotridecene (**5**) and 3-bromocyclotridecene (**6**), respectively. However, the possibility of the formation of the observed products (**5** and **6**) via nonplanar allylic and vinylic cations cannot be ruled out completely.

In conclusion, the reactions reported here represent the first example of change of orientation of hydrogen bromide addition with change in the ring size. The mode of addition of hydrogen bromide to strain-free 1,2-cyclotridecadiene (**1c**) resembles that of simple 1,3-disubstituted acyclic allenes.[7] We propose that the strain factor could be responsible for the observed difference in behavior of C-9 or C-10 as compared to C-13 allene in hydrogen bromide addition.

Experimental Section

All boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer IR-137 using neat liquids. NMR spectra were recorded on a Varian Model A-60 NMR spectrometer relative to internal standard Me_4Si. The mass spectral measurements were performed by the Mass Spectrometry Laboratory, National Chemical Laboratory, Poona, India. The gas–liquid chromatography utilized a Varian Model 90-P gas chromatograph with a thermal conductivity detector. Elemental analyses were performed by the Microanalysis Laboratory, Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India.

General Procedure for the Addition of Hydrogen Bromide to Cyclic Allenes. The cyclic allene (0.05 mol) was taken in a three-necked round-bottomed flask and cooled to around 15–20° in a nitrogen atmosphere. Hydrogen bromide solution in acetic acid (40% w/v, 12.0 ml, 0.055 mol) was added dropwise with magnetic stirring over a period of 30 min. After the addition was over, it was allowed to stir for another 2 hr. The reaction mixture was poured into 200 ml of water, neutralized carefully with sodium bicarbonate, and extracted with petroleum ether (bp 40–60°). The combined extract was washed thoroughly with water and dried over anhydrous $MgSO_4$. Removal of solvent and distillation under vacuum gave the monobromo adduct.

Addition of Hydrogen Bromide to 1,2-Cyclononadiene. From 1,2-cyclononadiene (6.1 g, 0.05 mol) and hydrogen bromide (0.055 mol), there was obtained 8.8 g (86%) of *cis*-3-bromocyclononene: bp 87–88° (5 mm) [lit.[5] bp 34–35° (0.05 mm)]; ir (neat) 2018, 1635, and 710 cm^{-1}; NMR ($CDCl_3$) δ 5.60 (m, 2 H), 5.00 (br m, 1 H), and 1.00–2.40 (m, 12 H).

Anal. Calcd for $C_9H_{15}Br$: C, 53.20; H, 7.39. Found: C, 53.41; H, 7.21.

Addition of Deuterium Bromide to 1,2-Cyclononadiene. Following the general procedure, the treatment of 1,2-cyclononadiene (1.22 g, 0.01 mol) with deuterium bromide (0.012 mol) in acetic acid-*d* provided 1.5 g (74%) of 3-bromocyclononene-2-*d*: bp 90° (5 mm); ir (neat) 2020, 1636, and 712 cm^{-1}; NMR ($CDCl_3$) δ 5.60 (m, 1 H), 5.00 (br m, 1 H), and 1.00–2.40 (m, 12 H); mass spectrum *m/e* 203 and 205 (M^+) of almost equal intensity.

Addition of Hydrogen Bromide to 1,2-Cyclodecadiene. Treatment of 1,2-cyclodecadiene (6.8 g, 0.05 mol) with hydrogen bromide (0.055 mol) in acetic acid gave 8.0 g (75%) of *cis*-3-bromocyclodecene: bp 91–92° (5 mm) [lit.[5] bp 86–87° (3 mm)]; ir (neat) 2018, 1634, and 712 cm^{-1}; NMR ($CDCl_3$) δ 5.58 (m, 2 H), 5.00 (br m, 1 H), and 1.00–2.42 (m, 14 H).

Anal. Calcd for $C_{10}H_{17}Br$: C, 55.30; H, 7.83. Found: C, 55.13; H, 7.71.

Addition of Hydrogen Bromide to 1,2-Cyclotridecadiene. 1,2-Cyclotridecadiene (9.0 g, 0.05 mol) was treated with hydrogen bromide (0.055 mol) to yield 9.0 g (70%) of a mixture of 3-bromocyclotridecene and 1-bromocyclotridecene, bp 93–101° (1 mm). Careful GLC analysis (10% silicone rubber SE-30, 5 ft × 0.25 in., 100°, 30 ml/min N_2) of the reaction product showed two closely situated peaks having 1-bromocyclotridecene (shorter retention time) and 3-bromocyclotridecene in the ratio 45:55. The two components were separated by GLC and compared with authentic samples.[5,6]

An authentic sample of 3-bromocyclotridecene was prepared from cyclotridecene (cis and trans mixture) and *N*-bromosuccinimide:[5] ir (neat) 2014, 1636, 970, and 710 cm^{-1}; NMR ($CDCl_3$) δ 5.56 (m, 2 H), 4.96 (br m, 1 H), and 0.96–2.45 (m, 20 H). An authentic sample of 1-bromocyclotridecene was made by lithium aluminum hydride reduction of 2,3-dibromocyclotridecene:[6] ir (neat) 2016, 1636, 850, and 820 cm^{-1}; NMR ($CDCl_3$) δ 5.50 (t, J = 7.0 Hz, 1 H) and 0.98–2.54 (m, 22 H).

Anal. Calcd for $C_{13}H_{23}Br$: C, 60.23; H, 8.88. Found: C, 59.98; H, 8.50.

Registry No.—**1a,** 1123-11-1; **1b,** 4415-98-9; **1c,** 5601-67-2; **4a,** 33332-75-1; **4b,** 56412-17-0; **5,** 56412-18-1; **6,** 38916-95-9; hydrogen bromide, 10035-10-6; deuterium bromide, 13536-59-9; 3-bromocyclononene-2-*d*, 56412-19-2; *cis*-cyclotridecene, 2484-66-4; *trans*-cyclotridecene, 2484-65-3; 2,3-dibromocyclotridecene, 34833-29-9; *N*-bromosuccinimide, 128-08-5.

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Sodium Borohydride–Carboxylic Acid Systems. Useful Reagents for the Alkylation of Amines

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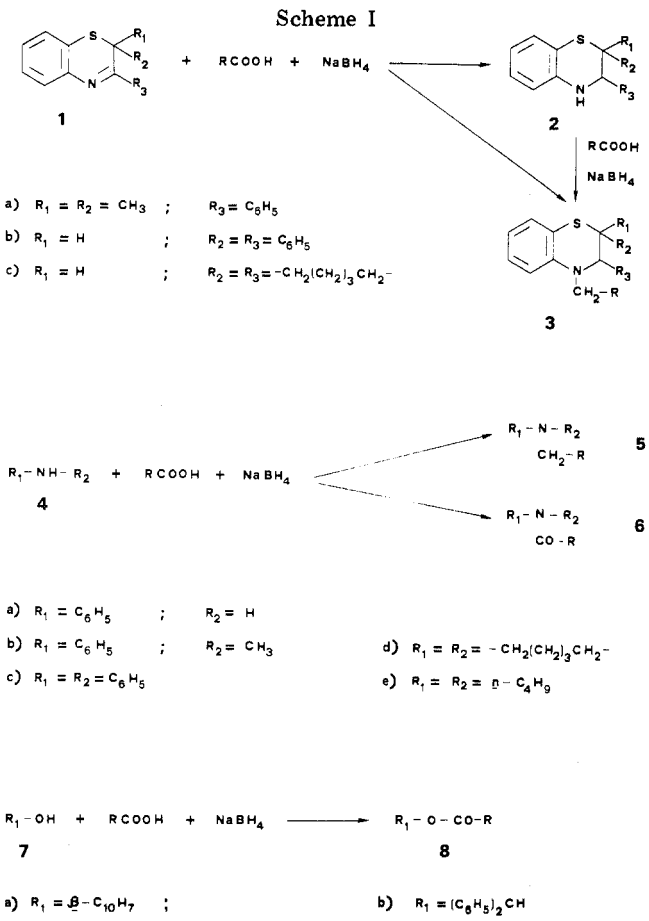
The recent paper by Gribble et al.[1] concerning the alkylation of aromatic amines with liquid carboxylic acids and sodium tetrahydroborate has prompted us to publish our own data on the same reaction, since they not only support the findings of the authors cited, but extend the scope of the reaction to the N-alkylation of amines with *solid* carboxylic acids, and provide further insight on the possible reaction pathway.

In the course of an investigation aimed at determining the reactivity of some 1,4-benzothiazines of structure **1**[2] we observed that their treatment with $NaBH_4$, in neat acetic acid as solvent, gave rise to the expected dihydro-1,4-benzothiazines **2** or to the corresponding *N*-ethyl derivatives **3** (R = CH_3) (Scheme I) depending on the amount of $NaBH_4$ added. The unexpected formation of *N*-alkyl derivatives prompted us to extend the reaction to a number of primary and secondary amines, both aliphatic and aromatic, and to

Scheme I



several liquid carboxylic acids; invariably the corresponding *N*-alkyl derivatives were obtained (Table I).

We noticed that by adding the amine to the $NaBH_4$–carboxylic acid mixture previously refluxed for 3 hr, further heating for a period of 3 hr leads to the formation of *N*-acyl derivatives **6**; addition of an alcohol or a phenol (**7**), in the place of the amine, yields, under the same conditions, the corresponding esters **8**.

In separate experiments, the volume of H_2[1,3] evolved on addition of $NaBH_4$ to neat acetic acid was measured. The results of a number of experiments indicate that 3 mol of H_2 per mole of $NaBH_4$ is immediately evolved at 20°, while approximately a fourth mole of H_2 is evolved very slowly at 20°, and more rapidly on heating at 80°.

The remarkable ease and usefulness of this direct method of alkylating amines by means of the corresponding carboxylic acid has induced us to study the possibility of performing N-alkylations even with solid carboxylic acids dissolved in suitable solvents. In fact, it is clear from what has been reported so far that the method appeared limited to the use of liquid carboxylic acids. It was first checked that the stoichiometry of the evolution of hydrogen was not changed when $NaBH_4$ and carboxylic acid in the molar ratio 1:5 were allowed to react in solvents such as benzene or toluene; in fact, 3 mol of hydrogen per mole of $NaBH_4$ was evolved at 20°, and approximately a fourth mole on heating under reflux. A certain number of reactions have therefore been performed in benzene yielding the *N*-alkyl derivatives **5** (Table II).

The addition of $NaBH_4$ to solutions of the acids in benzene causes, in general, the formation of insoluble compounds very sensitive to moisture. We have isolated those from formic, acetic, monochloroacetic, and benzoic acid; these are high-melting solids (except that obtained from monochloroacetic acid, which decomposes at 120–125°); their ir spectrum exhibits a B–H band between 2480 and 2530 cm^{-1} and two bands in the carbonyl zone. By treatment with water, they rapidly evolve H_2, and yield the carboxylic acid and boric acid in the molar ratio of 2:1, as shown by volumetric[5] and potentiometric[6] titrations; a third mole of carboxylic acid can be freed by addition of strong acids to the hydrolysis reaction mixture.

These products are capable of carrying out N-alkylation reactions, when reacted with amines in solvents such as toluene or benzene (Table III).

Table I
Results Obtained According to Procedure A

Reactants			
Substrate	Carboxylic acid	Reaction products	Yield, %
1a	Acetic	2a	60
1b	Acetic	2b	95
1a	Acetic	3a (R = CH_3)	95
1c	Acetic	3c (R = CH_3)	75
2a	Acetic	3a (R = CH_3)	95
2c	Formic	3c (R = H)	70
4c	Acetic	5c (R = CH_3)	95
4d	Acetic	5d (R = CH_3)	60
4e	Acetic	5e (R = CH_3)	80
4a	Propionic	6a (R = C_2H_5)	95
4c	Acetic	6c (R = CH_3)	40
4d	Propionic	6d (R = C_2H_5)	60
7a	Acetic	8a (R = CH_3)	50
7b	Acetic	8b (R = CH_3)	95

Table II
Results Obtained According to Procedure B

Reactants			
Substrate	Carboxylic acid	Reaction products	Yield, %
4a	Acetic	5a (R = CH_3)	30
4a	Propionic	5a (R = C_2H_5)	60
4a	Propionic	5 (R = C_2H_5, R_1 = C_6H_5, R_2 = n-C_3H_7)	90[a]
4b	Propionic	5b (R = C_2H_5)	65
4b	Palmitic	5b (R = $C_{15}H_{31}$)	70
4b	Benzoic	5b (R = C_6H_5)	20
4c	Acetic	5c (R = CH_3)	70
4c	Propionic	5c (R = C_2H_5)	35
4c	Palmitic	5c (R = $C_{15}H_{31}$)	25
4c	Monochloroacetic	5c (R = CH_2Cl)	35
4c	Monochloroacetic	5c (R = CH_2Cl)	90[b]

[a] Reaction carried out with a molar ratio BH_4^-:substrate of 10:1. [b] Molar ratio BH_4^-:substrate 5:1.

Table III
Results Obtained According to Procedure C

Reactants			
Substrate	Carboxylic acid	Reaction products	Yield, %
4b	Benzoic	5b (R = C_6H_5)	90[a]
4c	Acetic	5c (R = CH_3)	80
4c	Monochloroacetic	5c (R = CH_2Cl)	100
2,2′-Dithiodianiline	Acetic	*N*,*N*′-Diethyl derivative	90[b]
2,2′-Dithiodianiline	Benzoic	*N*,*N*′-Dibenzyl derivative	70[b]

[a] Reaction carried out in toluene under reflux for 15 hr. [b] Reaction carried out with a molar ratio BH_4^-:substrate of 10:1.

While the results so far available can hardly be regarded as conclusive, we feel that the experimental data support the assignment of the triacyloxymonohydroborate structure $Na[(RCOO)_3BH]$ (**9**) to the N-alkylating species we have isolated. This structure agrees with the results of the hydrolysis: in fact, it is obvious that on treatment with water 1 mol of **9** necessarily gives 1 mol of H_2, 1 mol of boric acid, 2 mol of carboxylic acid, and 1 mol of the sodium salt of the carboxylic acid and therefore that the addition of a strong acid is required to displace the third mole of carboxylic acid from the sodium salt. Furthermore, the structure **9** fits the ir spectroscopic data. In particular, the observed high frequency of B–H stretching bands seems appropriate for borohydrides, that can be looked at as adducts of poor Lewis acids like the acyloxyboranes of the present case. This interpretation is consistent with the results in the paper by Rice et al.,[7] correlating the increase in B–H stretching frequency of borane adducts with their lowered stability.

Species **9** can form an aldehyde by intra- or intermolecular hydride reduction; indeed, we have obtained benzyl alcohol on refluxing **9** ($R = C_6H_5$) for 20 hr in toluene and β-monochloroethyl monochloroacetate on refluxing **9** ($R = CH_2Cl$) for 6 hr in benzene. Furthermore, we found that all species isolated from $NaBH_4$ and carboxylic acids are capable of reducing iminium cations. These results seem to support the reaction pathway suggested by Gribble et al.[1]

Concerning the nature of acylating species, the evolution of 4 mol of H_2 per mole of $NaBH_4$ can be reasonably ascribed to the formation of a tetracyloxyborate $Na[B(OCOR)_4]$, **10**.

However, under the experimental conditions used, it is possible that species such as **10** decompose into RCOONa and $B(OCOR)_3$, whose acylating ability has been reported.[1,8]

Experimental Section[9]

N-Alkylation Reactions in Neat Carboxylic Acids. Procedure A. $NaBH_4$ (0.1 mol) was added portionwise to neat carboxylic acid (30 ml), the temperature being kept at 20°; when the lively evolution of H_2 had ceased, the amine (0.02 mol) was added. The reaction mixture was heated at 80° for 3 hr, cooled at room temperature, made alkaline with 2 *N* NaOH, and extracted with CH_2Cl_2. The organic layer was separated, dried (Na_2SO_4), and evaporated; PLC of the residue [light petroleum ether–ethyl acetate (9:1) as solvent] gave the corresponding *N*-alkyl derivative. The results obtained are reported in Table I.

4-Ethyl-2,2-dimethyl-3-phenyl-3,4-dihydro-2*H*-benzo[*b*]-[1,4]thiazine (3a, R = CH_3): mp 103–104° (2-propanol); NMR ($CDCl_3$) δ 7.6–6.6 (group of signals, 9 H, aromatic H), 4.27 (s, 1 H, C_3 H), 3.8–3.0 (m, 2 H, CH_2), 1.52 (s, 3 H, C_2 CH_3), 1.12 (s, 3 H, C_2 CH_3), and 1.12 ppm (t, 3 H, CH_3).

11-Ethyl-5a,6,7,8,9,10,10a,11-octahydrobenzo[*b*]cyclohepta[*e*][1,4]thiazine (3c, R = CH_3): bp 120–122° (0.05 Torr); NMR (CCl_4) δ 7.3–6.4 (group of signals, 4 H, aromatic H), 3.7–3.0 (group of signals, 4 H, NCH_2 + C_{5a} H + C_{10a} H), and 2.5–0.8 ppm [group of signals, 13 H, CH_3 + $(CH_2)_5$].

11-Methyl-5a,6,7,8,9,10,10a,11-octahydrobenzo[*b*]cyclohepta[*e*][1.4]thiazine (3c, R = H): mp 56–57° (EtOH); NMR (CCl_4) δ 7.2–6.5 (group of signals, 4 H, aromatic H), 3.8–3.5 (m, 1, C_{10a} H), 3.5–3.3 (m, 1 H, C_{5a} H), 2.87 (s, 3 H, CH_3), and 2.4–1.2 ppm [group of signals, 10 H, $(CH_2)_5$].

In the case of the imines **1**, if the above procedure (A) is modified by allowing $NaBH_4$ and benzothiazine to react in the molar ratio 1:1 and reducing the heating time to 1 hr, the reaction products are the dihydro derivatives **2**.[2]

The reaction of $NaBH_4$ with neat carboxylic acids at 20° was explored in order to determine the amount of H_2 evolved. In several experiments, it was found that 3.0 ± 0.1 mol of H_2 per mole of $NaBH_4$ was formed. In a typical run, $NaBH_4$ (0.079 g, 2.1 mmol) was added to neat acetic acid (0.8 ml) at 20°; 6.4 mmol of H_2 was immediately evolved.

Acylation Reactions in Neat Carboxylic Acids. $NaBH_4$ (0.1 mol) was added portionwise to neat carboxylic acid (30 ml), the reaction mixture was refluxed for 3 hr, the amine, the alcohol, or the phenol (0.02 mol) was added, and the reflux was prolonged for an additional 3 hr. By working up as above, the corresponding amide or ester was isolated. The results of these reactions are reported in Table I.

The reaction of $NaBH_4$ with liquid carboxylic acids under reflux was explored in order to determine the amount of H_2 evolved. In several experiments, it was found that 3.8 ± 0.1 mol of H_2 per mole of $NaBH_4$ was formed. In a typical run, $NaBH_4$ (0.125 g, 3.3 mmol) was added to neat acetic acid (1.5 ml); after reflux for 3 hr, 12.7 mmol of H_2 was evolved.

N-Alkylation Reactions in Benzene Solution. Procedure B. $NaBH_4$ (0.1 mol) was added to a solution of the carboxylic acid (0.33 mol) in dry benzene (50 ml), the temperature being kept at 20°. When the evolution of H_2 had ceased, the amine (0.05 mol) was added, and the reaction mixture was refluxed for 3 hr, cooled at room temperature, and shaken with 2 *N* NaOH. The organic layer was separated, dried (Na_2SO_4), and evaporated; PLC of the residue [light petroleum ether–ethyl acetate (9:1) as solvent] gave the corresponding *N*-alkyl derivative. The results obtained are reported in Table II. It should be noted that the reported yields were not optimized; in fact, better yields can be attained by raising the BH_4^-:substrate molar ratio and/or the refluxing time, as shown in the case of **5c** ($R = CH_2Cl$), which was obtained in 90% yield using a molar ratio BH_4^-:substrate of 5:1.

***N*-(2-Chloroethyl)-*N*-phenylaniline (5c, R = CH_2Cl):** bp 110–112° (0.1 Torr); NMR (CCl_4) δ 7.2–6.9 (group of signals, 10 H, aromatic H) and 4.3–3.5 ppm (group of signals, 4 H, $-CH_2CH_2-$).

***N*-Hexadecyl-*N*-phenylaniline (5c, R = $C_{15}H_{31}$):** mp 43–44° (EtOH); NMR (CCl_4) δ 7.6–6.9 (group of signals, 10 H, aromatic H), 3.78 (t, 2 H, NCH_2), and 2.0–0.6 ppm (group of signals, 31 H, aliphatic H).

The reaction of $NaBH_4$ with solutions of carboxylic acids in dry benzene or toluene at 20° was explored in order to determine the amount of H_2 evolved. In several experiments, it was found that 3.0 ± 0.1 mol of H_2 per mole of $NaBH_4$ was formed. In a typical run, $NaBH_4$ (0.144 g, 3.8 mmol) was added to a solution of acetic acid (1.5 ml) in dry toluene (10 ml) at 20°; 11.1 mmol of H_2 was evolved.

Sodium Triacyloxymonohydroborates, 9. $NaBH_4$ (0.1 mol) was added portionwise to a solution of the carboxylic acid (0.33 mol) in dry benzene (1 l.), the temperature being kept at 20°. After hydrogen evolution, the precipitate **9** was rapidly collected by suction, washed with ethyl ether, and dried under vacuum. Compounds **9** do not melt up to 300°, except for **9** ($R = CH_2Cl$), which decomposes at 120–125°.

9 ($R = CH_2Cl$): ir 2530 (B–H) and 1735, 1685 cm^{-1} (C=O).

9 (R = H): ir 2480 (B–H) and 1680 cm^{-1} (broad band, C=O).

9 ($R = CH_3$): ir 2480 (B–H) and 1660 cm^{-1} (broad band, C=O).

9 ($R = C_6H_5$): ir 2490 (B–H) and 1670, 1635 cm^{-1} (C=O).

A suspension of **9** ($R = C_6H_5$) in dry toluene (50 ml) was refluxed for 20 hr and cooled at room temperature, and the solid was filtered off. The presence of benzyl alcohol in the filtrate was monitored by vapor phase chromatography. Similarly, β-monochloroethyl monochloroacetate was formed by refluxing a suspension of **9** ($R = CH_2Cl$) in dry benzene for 6 hr, and monitored by vapor phase chromatography.

Compounds **9** are capable of reducing imonium cations. In a typical run, **9** ($R = CH_3$) (0.22 g) was added to a stirred suspension of **1a HCl** (0.29 g) in dry benzene (50 ml) at room temperature. After 10 min, the reaction mixture was shaken with 2 *N* NaOH, and the organic layer was separated, dried (Na_2SO_4), and evaporated to give **2a** (0.25 g).

Hydrolysis of the Triacyloxymonohydroborates 9. On reaction with an excess of water, **9** promptly release hydrogen; in a typical run, 0.400 g of **9** ($R = C_6H_5$) (1.00 mmol) evolves 0.98 mmol of H_2.

The hydrolysis mixtures were examined by potentiometric titration with 0.1 *N* NaOH; a molar ratio of carboxylic acid to boric acid of 1.95 ± 0.05:1 was determined.

In the case of benzoic acid derivative (**9**, $R = C_6H_5$) a gravimetric determination was also accomplished. **9** ($R = C_6H_5$) (3.91 g) was hydrolyzed in hot water (150 ml); after cooling, the reaction mixture was extracted with CCl_4, and the organic layer was separated, dried (Na_2SO_4), and evaporated; a residue of benzoic acid (2.26 g) was obtained. The aqueous layer was strongly acidified with HCl, and extracted with CCl_4; the organic phase was separated, dried (Na_2SO_4), and evaporated; a residue of benzoic acid (1.25 g) was obtained.

N-Alkylation Reactions Carried Out with 9. Procedure C.

The amine and **9** in the molar ratio 1:5 were refluxed in dry benzene for 6 hr. By working up as for the above procedure (B) the corresponding *N*-alkyl derivatives were isolated. The results obtained are reported in Table III.

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Registry No.—**1a,** 49634-65-3; **1b,** 19195-32-5; **1c,** 25069-59-4; **2a,** 49634-66-4; **2b,** 25069-68-5; **2c,** 25069-64-1; **3a** (R = CH_3), 56553-67-4; **3c** (R = H), 49634-64-2; **3c** (R = CH_3), 56553-68-5; **4a,** 62-53-3; **4b,** 100-61-8; **4c,** 122-39-4; **4d,** 110-89-4; **4e,** 111-92-2; **5** (R = Et; R_1 = Ph; R_2 = Pr), 2217-07-4; **5a** (R = CH_3), 103-69-5; **5a** (R = C_2H_5), 622-80-0; **5b** (R = C_2H_5), 13395-54-5; **5b** (R = C_6H_5), 614-30-2; **5b** (R = $C_{15}H_{31}$), 56553-69-6; **5c** (R = CH_3), 606-99-5; **5c** (R = CH_2Cl), 42393-65-7; **5c** (R = $C_{15}H_{31}$), 51580-76-8; **5d** (R = CH_3), 766-09-6; **5e** (R = CH_3), 4458-33-7; **6a** (R = C_2H_5), 620-71-3; **6c** (R = CH_3), 519-87-9; **6d** (R = C_2H_5), 14045-28-4; **7a,** 135-19-3; **7b,** 91-01-0; **8a** (R = CH_3), 1523-11-1; **8b** (R = CH_3), 954-67-6; **9** (R = H), 56553-59-4; **9** (R = CH_3), 56553-60-7; **9** (R = CH_2Cl), 56553-61-8; **9** (R = C_6H_5), 56553-62-9; acetic acid, 64-19-7; formic acid, 64-18-6; propionic acid, 79-09-4; palmitic acid, 57-10-3; benzoic acid, 65-85-0; monochloroacetic acid, 79-11-8; 2,2′-dithiodianiline, 56553-70-9; *N,N′*-diethyl-2,2′-dithiodianiline, 1141-88-4; *N,N′*-dibenzyl-2,2′-dithiodianiline, 56553-71-0.

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(5) W. Gerrard, M. F. Lappert, and R. Shafferman, *J. Chem. Soc.*, 3648 (1958).
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(8) A. Pelter and T. E. Levitt, *Tetrahedron,* **26,** 1899 (1970).
(9) All melting points (determined on a Kofler apparatus) and boiling points are uncorrected. The compounds previously described were compared with authentic samples. All new compounds, but **9,** gave satisfactory elemental analyses. Ir spectra as Nujol mulls were recorded on a Perkin-Elmer Model 257 grating spectrophotometer. NMR spectra were obtained on a Jeol 60 spectrometer, using Me_4Si (δ 0 ppm) as internal standard. The reaction products were isolated by preparative thin layer chromatography (PLC) on Merck PF_{254} silica gel coated plates. Commercial $NaBH_4$ was recrystallized according to Brown et al.[10]
(10) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77,** 6209 (1955).

Synthesis of 3,11-Dimethyl-2-nonacosanone, a Contact Courting Pheromone of the German Cockroach[1]

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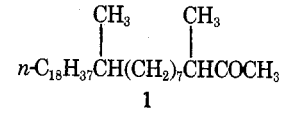
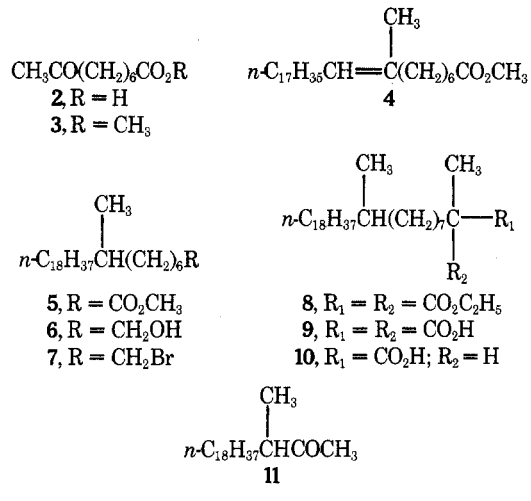
From the cuticle of sexually mature female German cockroaches (*Blattella germanica*), Ishii and coworkers recently isolated a contact chemoreceptive agent, identified as 3,11-dimethyl-2-nonacosanone (**1**), which was shown to elicit typical courting behavior, including wing raising, in males.[2] As part of a program of research on the properties and functions of cockroach pheromones,[3] we undertook and now describe a synthesis of **1**. After completion and submission of this work for publication, an account with limited experimental details of a synthesis of **1** along somewhat similar lines by Ishii and coworkers appeared.[4]



1

As starting material in our synthesis we employed 8-oxononanoic acid (**2**), prepared from ϵ-caprolactone by modifications of the route of Kameoka et al.[5] via 6-bromohexanoic acid, esterification, and acetoacetic ester synthesis. Treatment of the methyl ester **3** in polar solvent with the Wittig reagent derived from octadecyltriphenylphosphonium bromide gave, in 48% yield, methyl 8-methyl-8-hexacosenoate (**4**), apparently mainly (by GLC) the *Z* isomer.[6] Hydrogenation of **4** afforded the saturated ester **5**, which, after $LiAlH_4$ reduction to the corresponding alcohol **6** and conversion into the bromide **7**, was used to alkylate diethyl methylmalonate. Hydrolysis of the resulting diester **8** and decarboxylation of the acid **9** gave 2,10-dimethyloctacosanoic acid (**10**), which, with two widely separated asymmetric centers, was undoubtedly a mixture of the two possible diastereoisomers. Treatment of **10** with 2 mol of methyllithium then furnished the desired ketone **1**, mp 28–31° (lit.[4] 29–31°), in 50% overall yield from the Wittig product **4**.



2, R = H
3, R = CH_3

4

5, R = CO_2CH_3
6, R = CH_2OH
7, R = CH_2Br

8, R_1 = R_2 = $CO_2C_2H_5$
9, R_1 = R_2 = CO_2H
10, R_1 = CO_2H; R_2 = H

11

Although spectral data indicate that the synthetic and natural ketones are structurally identical, our method of synthesis, like that of Ishii and coworkers,[4] undoubtedly afforded a mixture of the two possible diastereoisomers of **1**. It is not surprising, therefore, that the natural product has a different melting point (45–46°), even though it appears to be optically inactive.[2,4]

Previous studies have shown that courting behavior in the German cockroach includes antennation (antennal stroking) of the female by the male, presumably allowing the latter to perceive sex pheromone on the cuticular surface of the female.[7] In our bioassay of synthetic **1** we used antennae ablated from American cockroaches (*Periplaneta americana*) to eliminate any possible stimuli associated with German cockroach antennae. Control antennae, dipped only in carbon tetrachloride, evoked no response. Antennae dipped in a 70 μg/ml solution of synthetic **1** in carbon tetrachloride elicited typical wing raising and other features of courting display[7] in 5% of a group of males (n = 60) kept isolated from females. At a higher concentration of 500 μg/ml the response was 70% in a group of isolated