very large peak with a retention time identical with that of acetanilide.

Pyrolysis of N-(*n*-Butyl)-N-formylacetamide. Copper Tube.—The imide (228 mg, 1.59 mmol) was injected in 50-μl aliquots. The products (186 mg) were collected in ice and analyzed by glpc. Product weight corrected for carbon monoxide loss from 85% of the starting material was 224 mg.

Glass Tube.—The imide (228 mg, 1.59 mmol) was injected in 50-μl aliquots. The products (195.5 mg) were collected in ice and analyzed by glpc. Product weight corrected for carbon monoxide loss from 85% of the starting material was 234 mg.

Pyrolysis of N-(*sec*-Butyl)-N-formylacetamide.—The imide (461 mg, 3.22 mmol) was injected in 45-μl aliquots. The products (433 mg) were collected in ice and analyzed by glpc. The product weight corrected for carbon monoxide loss with 33% unreacted starting material and 57% of the reacted imide decarbonylating was 467 mg.

Pyrolysis of N-Cyclohexyl-N-formylacetamide.—The imide (980 mg, 5.80 mmol) was injected in 45-μl aliquots. The products (802 mg) were collected in ice and analyzed by glpc. The weight corrected for carbon monoxide loss with 8% unreacted starting material and 51% of the reacted imide decarbonylating was 880 mg.

Registry No.—N-(*n*-Butyl)-N-formylacetamide, 17604-86-3; N-(*sec*-butyl)-N-formylacetamide, 17604-87-4; N-cyclohexyl-N-formylacetamide, 17604-88-5.

Acknowledgment.—Elemental analyses were performed by the Analytical Chemistry Department, Chemical Research Laboratory, Edgewood Arsenal.

Synthetic Routes to Cyclopropyl-Substituted Azoalkanes. Some Reactions of Cyclopropylcarbinyl Cyanates, Isocyanates, Benzoates, and *p*-Nitrobenzoates

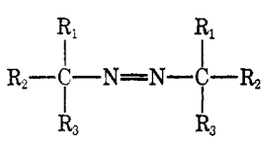
JACK W. TIMBERLAKE AND J. C. MARTIN

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801

Received January 29, 1968

The syntheses of substituted azomethanes with one, two, and three cyclopropyl substituents on each methyl carbon (**1a–e**) have been approached *via* a variety of pathways starting from the appropriate cyclopropylcarbinols. We discuss complicating reactions which arise from the ready ionization of compounds such as tricyclopropylcarbinyl isocyanate and from ring-opening reactions of cyclopropyl carbonium ions. The most generally successful route to these azoalkanes involved ammonolyses of cyclopropylcarbinyl esters followed by oxidative coupling of the resulting amines by treatment with iodine pentafluoride. A second promising synthetic route converts a ketone into an azine to which chlorine is added to give an azo-α-chloroalkane. Replacement of the chlorine by an alkyl substituent occurs readily with alkylmagnesium bromides, under conditions which lead to regeneration of the azine on treatment with the corresponding alkylmagnesium iodide.

In connection with a kinetic study of the rates of formation of substituted cyclopropylcarbinyl radicals,[1] we have synthesized the following tertiary alkylazo compounds: 2,2′-dicyclopropyl-2,2′-azopropane (**1a**), 1,1,1′,1′-tetracyclopropyl-1,1′-azoethane (**1b**), 1,1,1′,1′-tetracyclopropyl-1,1′-azoisobutane (**1c**), and 1,1,1,1′,-1′,1′-hexacyclopropylazomethane (**1e**). This paper describes the synthesis of these compounds and the attempted synthesis of 1,1′-dicyclopropyl-1,1′-diisopropyl-1,1′-azoisobutane (**1d**).



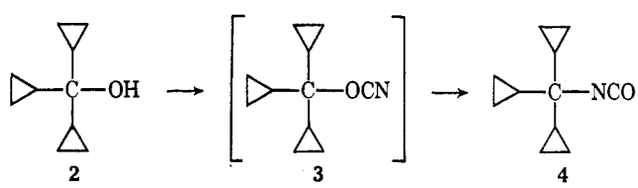
1a, $R_1 = R_2 = CH_3$; R_3 = cyclo-C_3H_5
b, $R_1 = CH_3$; $R_2 = R_3$ = cyclo-C_3H_5
c, $R_1 = i$-C_3H_7; $R_2 = R_3$ = cyclo-C_3H_5
d, $R_1 = R_2 = i$-C_3H_7; R_3 = cyclo-C_3H_5
e, $R_1 = R_2 = R_3$ = cyclo-C_3H_5
f, $R_1 = R_2 = R_3 = CH_3$
g, $R_1 = R_2 = CH_3$; $R_3 = C_6H_5$

Two possible synthetic approaches were considered likely to provide attractive routes to compounds such as **1**. The method of Esser, Rastadter, and Reuter[2] involves treatment of the appropriate isocyanate with excess hydrogen peroxide and leads directly to the azo compound. The method of Stevens[3] involves oxidative coupling of the appropriate amine with iodine pentafluoride. The latter method has been used to prepare the tertiary alkyl-substituted azo compounds 2,2′-azoisobutane[3,4] (**1f**) and azocumene[4] (**1g**).

Kauer and Henderson[5] have developed a method for preparation of isocyanates which involves treatment of an alcohol with sodium hydride followed by cyanogen chloride to give the aliphatic cyanates. The cyanates rearrange to the isocyanates on treatment with boron trifluoride etherate or, in some cases, simply on distillation.

$$ROH \xrightarrow{NaH} RO^-Na^+ \xrightarrow{ClCN} ROCN \xrightarrow{BF_3\cdot Et_2O} RNCO$$

Amine Syntheses.—Employing the method of Kauer and Henderson,[5] with only slight modification, we were able to prepare tricyclopropylcarbinyl isocyanate (**4**). The rapid rearrangement of **3** to **4** is suggested by our failure to detect any cyanate (**3**). Treatment of the isocyanate with hydrogen peroxide did not yield the desired azo compound. Instead, an almost quantitative yield of tricyclopropylcarbinol (**2**) was returned.



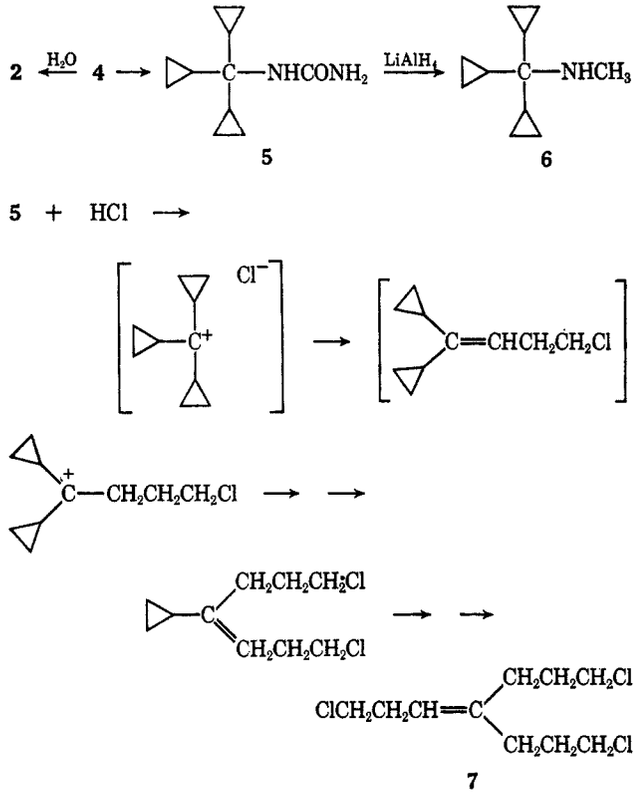
2 **3** **4**

It is possible that the isocyanate is hydrolyzed in the aqueous hydrogen peroxide solution even though attempts were made to remove all water. Hydroly-

(1) J. C. Martin, John E. Schultz, and Jack W. Timberlake, *Tetrahedron Lett.*, 4629 (1967).
(2) H. Esser, K. Rastadter, and G. Reuter, *Chem. Ber.*, **89**, 685 (1956).
(3) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).
(4) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).
(5) J. C. Kauer and W. W. Henderson, *ibid.*, **86**, 4732 (1964).

sis of the isocyanate in water–tetrahydrofuran also gave only **2**. The ionization of alkyl isocyanates is usually not rapid enough to compete with attack of nucleophile at the isocyanate carbon. In this case, however, the great stability of the tricyclopropyl carbonium ion apparently provides sufficient driving force to effect the ionization.[6] It was hoped that because of the facile ionization of **4**, treatment with ammonia would give tricyclopropylcarbinylamine. Instead, the isocyanate reacted in the manner usual for isocyanates, and the only isolated product was the substituted urea (**5**). The urea was unreactive toward dilute aqueous acid, and treatment with concentrated acid solution gave only 1,7-dichloro-4-(3-chloropropyl)-3-heptene (**7**), probably by the sequence of steps outlined in Scheme I.

SCHEME I

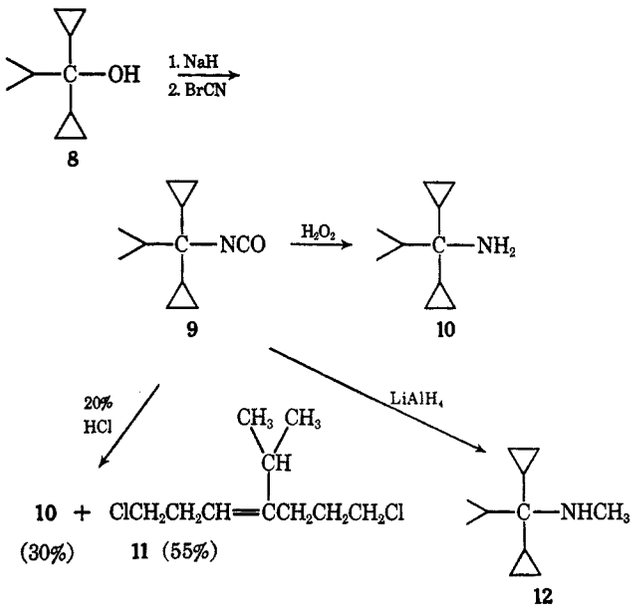


Isocyanate **4** was reduced by lithium aluminum hydride to yield N-methyl-N-tricyclopropylcarbinylamine (**6**).

Isopropyldicyclopropylcarbinyl isocyanate (**9**) was prepared in the same manner as tricyclopropylcarbinyl isocyanate. Again, isomerization of the cyanate intermediate was so rapid that its isolation was impossible. Treatment of the isocyanate with hydrogen peroxide did not yield the desired azo compound, nor did it hydrolyze in an analogous manner to **2** to isopropyldicyclopropylcarbinol (**8**). Instead, the only isolated product was isopropyldicyclopropylcarbinylamine (**10**). In contrast to **4**, **9** is unreactive toward water in refluxing tetrahydrofuran, and treatment with 20% hydrochloric acid yields a mixture of **10** (30%) and 1,7-dichloro-4-isopropyl-3-heptene (**11**, 55%). Isocyanate **9** was also reduced to the corresponding

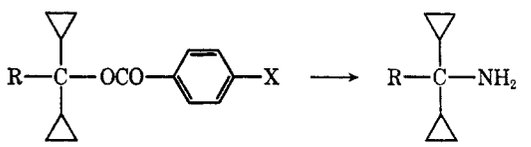
(6) R. Breslow in "Molecular Rearrangement," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 4.

SCHEME II



methylamine (**12**) by action of lithium aluminum hydride (Scheme II).

Although hydrolysis of **9** gave low yields of **10**, a more convenient route was found which not only gave **10** in high yield but which could be adapted for synthesis of tricyclopropylcarbinylamine (**16**) and methyldicyclopropylcarbinylamine (**17**). Ammonolysis of benzoate (**13**) or *p*-nitrobenzoate esters (**14** and **15**) in anhydrous liquid ammonia at room temperature gave the corresponding amines **16**, **10**, and **17** in high yield. The driving force provided by the cyclopropyl substituents apparently makes ionization to the carbonium ion more rapid than nucleophilic attack on the carbonyl group by ammonia.



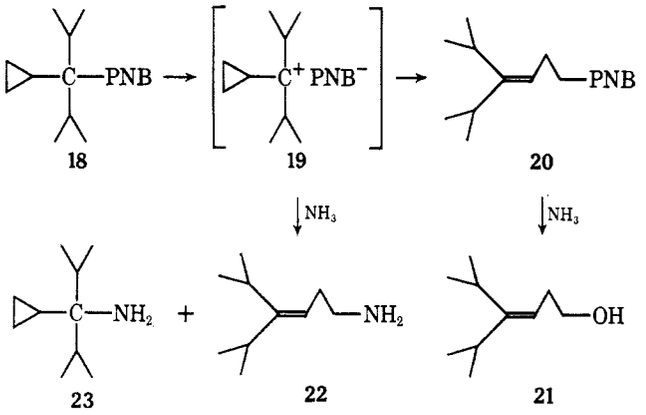
13, R = cyclo-C_3H_5; X = H
14, R = *i*-C_3H_7; X = NO_2
15, R = CH_3; X = NO_2

16, R = cyclo-C_3H_5
10, R = *i*-C_3H_7
17, R = CH_3

Significantly different results were obtained from the ammonolysis of diisopropylcyclopropylcarbinyl *p*-nitrobenzoate (**18**) in liquid ammonia. The ester was less reactive, and the ammonia solution had to be heated to 50° before appreciable disappearance of ester could be observed. The product yields were determined by glpc to be 36% 5-methyl-4-isopropyl-3-hexenol (**21**), 42% 6-amino-2-methyl-3-isopropyl-3-hexene (**22**), and 17% diisopropylcyclopropylcarbinylamine (**23**) (Scheme III). There was also one other amine component present in about 2% yield which was not identified. The structure of **21** is apparent from its elemental analysis and spectral data. Carbinol **21** has been reported as a product from the hydrolysis of 5-methyl-4-isopropyl-3-hexenyl *p*-nitrobenzoate (**20**).[7] The structural proof for amines **22** and **23**, although less rigorous, is evident from consideration of the spectral data. A mixture of the two amines, after

(7) H. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, **81**, 320 (1959).

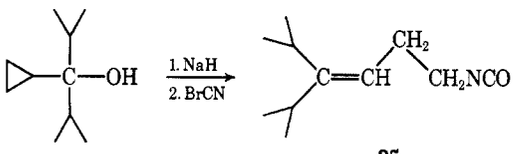
SCHEME III



purification by glpc, gave a satisfactory elemental analysis. The nmr of 6-amino-2-methyl-3-isopropyl-3-hexene (**22**) shows a single-proton triplet at δ 5.0 (vinyl proton), a three-proton multiplet at 2.38–3.10 (the methylene protons are adjacent to the amine group and the methine proton is on the isopropyl group which is *cis* to the vinyl proton),[8,9] a three-proton multiplet at 1.91–2.37 (the methylene protons are α to the double bond and the methine proton on the isopropyl group is *trans* to the vinyl proton), a two-proton broad peak at 1.54 (amine protons), and a twelve-proton doublet at 0.96 (methyl protons on the isopropyl groups).

Although the higher temperature employed for ammonolysis of **18** may have some effect in determining the different product distribution, the most important factor is more likely to be the greater difference in charge distribution in the carbonium ion formed by ionization of ester **18** relative to the ions from esters **13–15**. The formation of carbinol **21** is best accounted for by postulating internal return from the ion pair (**19**) to form the ring-opened *p*-nitrobenzoate ester (**20**) which then undergoes ammonolysis by attack at the carbonyl position to give the cleavage products 5-methyl-4-isopropyl-3-hexenol and *p*-nitrobenzamide. Hart[7] has found the same behavior for solvolysis of diisopropylcyclopropylcarbinyl *p*-nitrobenzoate in a variety of solvents. He found that the amount of rearranged ester (**20**) decreases as the dissociating power of the solvent increases. Although it is possible that all three products, carbinol **21** and amines **22** and **23**, arise from the rearranged ester **20**,[10] it is more likely that amines **22** and **23** arise from competition of ammonia with the *p*-nitrobenzoate anion for the initially formed cyclopropylcarbinyl cation. This is in accord with the observed lack of reactivity of 5-methyl-4-isopropyl-3-hexenyl *p*-nitrobenzoate (**20**), and supports the rationale that once formed it reacts *via* carbonyl attack of ammonia to yield carbinol. The preponderance of ring-opened amine in the ammonolysis of **13–15** appears to parallel the amount of positive charge expected on the methylenes in the cyclopropyl rings of the carbonium ions. The two isopropyl groups in **19** may also be so much more sterically demanding than cyclopropyl groups that attack by nucleophile on the ring becomes favored over attack at the tertiary carbon atom.

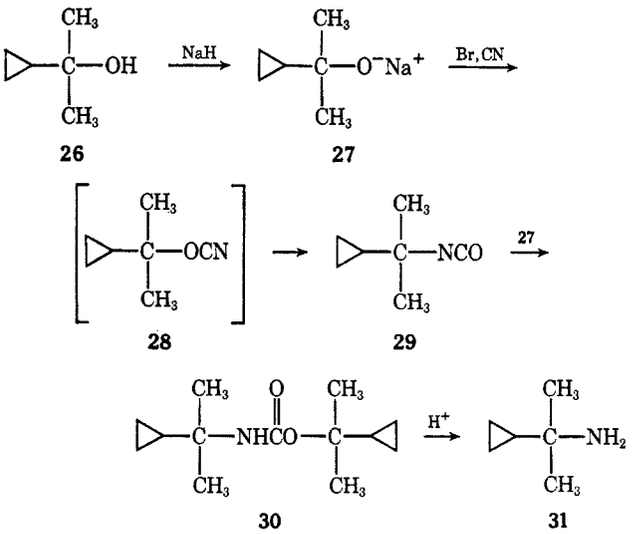
An attempted preparation of diisopropylcyclopropylcarbinylamine *via* the isocyanate was also unsuccessful. Treatment of diisopropylcyclopropylcarbinol with sodium hydride and cyanogen bromide gave a mixture of unstable products. The only component which was isolated (38%) was tentatively identified as 5-methyl-4-isopropyl-3-hexenyl isocyanate (**25**) from its ir and



nmr spectra. The ir spectrum showed intense absorption at 2260 cm^{-1} (NCO). The nmr showed a single-proton triplet at δ 5.08 (vinyl proton), a two-proton triplet at 3.24 (methylene protons α to the isocyanate group), a four-proton multiplet at 1.81–2.94 (methylene protons α to the double bond and the isopropyl methine protons), a doublet at 1.01, (J = 7 cps, methyl protons), and a small absorption from an impurity at 0.45. The impurity (less than 5%) could be diisopropylcyclopropylcarbinyl isocyanate.

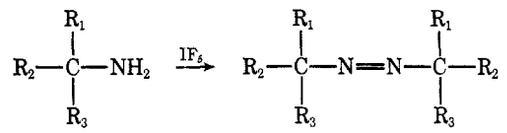
Dimethylcyclopropylcarbinylamine (**31**) was prepared by acid hydrolysis of the carbamate (**30**) produced from treatment of the carbinol (**26**) with sodium hydride and cyanogen bromide. It is noteworthy that, even though there is only one cyclopropyl group to delocalize the charge in the rearrangement of cyanate to isocyanate, no ring-opened products are formed. Apparently the less sterically demanding methyl groups (relative to isopropyl) allow attack by NCO^- at the tertiary carbon atom rather than on the ring. The isocyanate, once formed, is not appreciably sterically hindered toward attack by the unreacted alkoxide (**27**), and the major product is the carbamate (**30**) (Scheme IV). In the earlier isocyanate preparations no carbamate was observed.

SCHEME IV



(8) R. B. Bates, R. H. Carnighan, R. O. Rakutis, and H. J. Schauble, *Chem. Ind.* (London), 1020 (1960).
(9) R. B. Bates, and D. M. Gale, *J. Amer. Chem. Soc.*, **82**, 5949 (1960).
(10) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331 (1965).

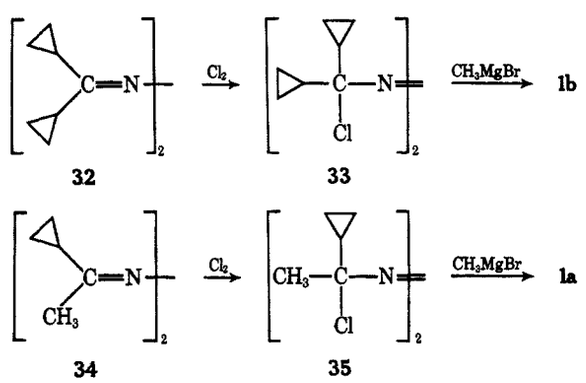
Azo Compounds.—In all cases the amines (**10, 16, 17,** and **31**) underwent oxidative coupling to the corresponding azo compounds **1a–c** and **1e** by treatment with iodine pentafluoride.



10, 16, 17, 31 **1a–c, 1e**

Compounds **1a** and **1b** were also prepared from the appropriate chloroazo compounds, **33** and **35**. Such compounds can readily be prepared by the method of Goldschmidt and Acksteiner[11,12] and Benzing[13] by action of chlorine on the azine. Compounds **33** and **35** were prepared in this manner from the corresponding ketazines **32** and **34**. Treatment of **33** with methylmagnesium iodide did not provide the desired azo compound, **1b**. Instead, the chloroazo compound was transformed into ketazine **32**. It was found that use of methylmagnesium bromide instead of methylmagnesium iodide did give **1b** from **33** and **1a** from **35** (Scheme V).

SCHEME V



32 **33**

34 **35**

It is possible that, in cases where the desired amines are difficult or impossible to prepare, this may be the preferred method for preparation of tertiary alkylazo compounds of type **1**.

Experimental Section

Tricyclopropylcarbinyl Isocyanate (**4**).—The method of Hart and Sandri[14] was used to prepare tricyclopropylcarbinol, **1**, bp 85° (10 mm) [lit.[14] bp 85° (10 mm)], in 83% yield. The isocyanate was prepared according to the general method of Kauer and Henderson[5] with several modifications.

To 3.5 g (0.146 mol) of sodium hydride in 30 ml of tetrahydrofuran was added dropwise tricyclopropylcarbinol (10.2 g, 0.067 mol) in 20 ml of tetrahydrofuran. After the addition (2 hr) the reaction mixture was refluxed for 8 hr. The mixture was cooled in an ice bath, and a tetrahydrofuran solution of cyanogen bromide (20.0 g, 0.189 mol) was added. The mixture was stirred at room temperature for 1 hr and suction filtered. Solvent removal and distillation gave 9.5 g of clear liquid, bp 74–76° (2.5 mm). Analysis by glpc (SE-30 on Chromosorb W, column temperature 140°) showed the liquid to be a 4:1 mixture of isocyanate **4** and tricyclopropylcarbinol which was not separated by a second, more careful distillation. Attempted column chromatography on silica gel and elution with benzene resulted in an increase in the amount of carbinol from hydrolysis of the isocyanate on the column. A small sample was purified for analytical and spectroscopic purposes by glpc, but for the reactions listed below samples of 80–90% purity were used [nmr ($CDCl_3$) δ 0.75–1.24 (m, 3.7, methine cyclopropyl protons), 0.27–0.69 (m, 11.83, methylene cyclopropyl protons)].

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.91. Found: C, 74.50; H, 8.58; N, 8.11.

To the above mixture of **4** and **1** (500 mg) was added 1.5 ml of water and 5 ml of tetrahydrofuran. The mixture was refluxed with stirring for 11 hr. The reaction mixture was extracted with ether and dried over magnesium sulfate. After removal of the ether and tetrahydrofuran *in vacuo* there remained 480 mg of a liquid whose ir and nmr spectra and glpc retention time, under conditions which would allow tricyclopropylcarbinylamine, tricyclopropylcarbinol, and tricyclopropylcarbinyl isocyanate to be distinguished, were identical with those of an authentic sample of tricyclopropylcarbinol.

N-Methyl-N-tricyclopropylcarbinylamine (**6**).—To lithium aluminum hydride (0.8 g, 0.021 mol) in 25 ml of sodium-dried ether was added tricyclopropylcarbinyl isocyanate of approximately 90% purity (2.07 g, 0.0117 mol, assuming 100% isocyanate) in 10 ml of ether. The solution was refluxed for 90 min, then hydrolyzed with water. The ether layer was dried, and hydrogen chloride gas passed over the surface. The resulting white salt was filtered, washed with several small portions of ether, and dissolved in 30% potassium hydroxide solution. Ether extracts of the basic solution were dried over magnesium sulfate, and the ether was removed *in vacuo*. The resulting yellow liquid was purified by preparative glpc on a 5-ft column of Carbowax 20M at 150° to give 1.32 g (68%) of amine **6**: nmr ($CDCl_3$) δ 3.39 (s, 2.88, $-CH_3$), 0.08–0.85 (m, 16.12, NH_2 and cyclopropyl protons, integral reduced to 15.08 on shaking with D_2O).

Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.47. Found: C, 80.19; H, 11.44; N, 8.18.

Tricyclopropylcarbinylurea (**5**).—To an isocyanate mixture of approximately 90% purity (3.45 g, 0.0195 mol) in a Carius tube was added approximately 20 ml of anhydrous ammonia. The tube was sealed and allowed to stand at room temperature for 50 hr. After evaporation of the ammonia the oily solid that remained was recrystallized three times from a 4:1 mixture of hexane and chloroform. There was obtained 2.78 g (69%) of tricyclopropylcarbinylurea as colorless needles: mp 120.5–121°; nmr ($CDCl_3$) δ 4.88–5.30 (broad signals, 2.77, NH_2 and NH), 0.72–1.23 (m, 3.03, methine protons), and 0.14–0.69 (m, 11.98, methylene protons).

Anal. Calcd for $C_{11}H_{18}N_2O$: C, 68.01; H, 9.35; N, 14.42. Found: C, 67.89; H, 9.34; N, 14.49.

Tricyclopropylcarbinylurea (1.15 g, 5.93 mmol) was stirred for 10 hr with 20 ml of concentrated hydrochloric acid. The reaction was made basic and extracted with ether. The ether layer was dried and removed *in vacuo* to yield 1.40 g of crude 1,7-dichloro-4-(3-chloropropyl)-3-heptene identified by comparison of ir and nmr spectra with those of an authentic sample (*vide infra*).

1,7-Dichloro-4-(3-chloropropyl)-3-heptene (**7**).—To tricyclopropylcarbinol (5.07 g, 0.03 mol) was added 25 ml of concentrated hydrochloric acid. The suspension was stirred at room temperature for 8 hr and extracted with ether. The ether layer was dried over magnesium sulfate and removed *in vacuo*. After distillation through a 30-cm Holzman column, there was obtained 5.54 g (76%) of 1,7-dichloro-4-(3-chloropropyl)-3-heptene: bp 110–112° (0.25 mm); nmr ($CDCl_3$) δ 5.27 (t, 1.02, J = 7.0 Hz, vinyl proton), 3.50 (t, 5.88, J = 6.0 Hz, $-CH_2-$ α to chlorine), 1.55–2.70 (m, 10.01, $-CH_2-$ β to chlorine and $-CH_2-$ γ to chlorine).

Anal. Calcd for $C_{10}H_{17}Cl_3$: C, 49.30; H, 7.03. Found: C, 49.60; H, 7.06.

Isopropyldicyclopropylcarbinyl Isocyanate (**9**).—Isopropyldicyclopropylcarbinol was prepared according to the method of Hart and Sandri in 74% yield, bp 77–78° (10 mm) [lit.[7] bp 75° (10 mm)]. The isocyanate was prepared by the same procedure used for tricyclopropylcarbinyl isocyanate. After chromatography on silica gel there was obtained a 68% yield of the isocyanate contaminated with 5% (by glpc) of an unknown impurity. Preparative glpc on a 5-ft 20% SE-30 on Chromosorb W column at 120° was used to prepare a sample for elemental and spectroscopic analyses: nmr ($CDCl_3$) δ 1.72–2.22 [m, 1.0, $-CH(CH_3)_2$], 1.02 [d, $CH(CH_3)_2$] superposed on 0.68–1.20 (m,

(11) S. Goldschmidt and B. Acksteiner, *Chem. Ber.*, **91**, 502 (1958).
(12) S. Goldschmidt and B. Acksteiner, *Ann. Chem.*, **618**, 173 (1958).
(13) E. Benzing, *ibid.*, **631**, 1 (1960).
(14) H. Hart and J. M. Snadri, *Chem. Ind.* (London), 1014 (1956).

cyclopropyl methine protons) (total integral 8.0), 0.22–0.53 (m, 8.0, cyclopropyl $-CH_2-$).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.97; H, 9.45; N, 8.05.

A small sample of isopropyldicyclopropylcarbinyl isocyanate was shown to be stable toward water in refluxing tetrahydrofuran by reisolating the sample and examining its nmr and ir spectra and glpc retention time on a Carbowax 20M column, under conditions which would allow the carbinol, amine, and isocyanate to be distinguished.

To an ether solution of hydrogen peroxide (2 ml of 83% H_2O_2 dissolved in 40 ml of ether and dried over sodium sulfate)[15] was added 2 drops of triethylamine and 256 mg (1.43 mmol) of isopropyldicyclopropylcarbinyl isocyanate. The reaction was stirred at room temperature for 4 hr. After extracting the mixture with three 20-ml portions of water, the ether layer was dried over magnesium sulfate and concentrated. There was obtained in this manner 190 mg (87%) of a liquid whose nmr and ir spectra were identical with those of isopropyldicyclopropylcarbinylamine, *vide infra*.

1,7-Dichloro-4-isopropyl-3-heptene (11).—To 11.2 g (0.0625 mol) of isopropyldicyclopropyl isocyanate in 30 ml of tetrahydrofuran was added 15 ml of 20% hydrochloric acid. The solution was refluxed for 36 hr. The tetrahydrofuran solution was concentrated, and the acidic solution was extracted with ether. The ether layer was washed with 5% sodium hydroxide and dried, and the ether removed *in vacuo*. The dark red-brown oil was distilled to give 8.0 g (65%) of a colorless liquid identified as 1,7-dichloro-4-isopropyl-3-heptene: nmr ($CDCl_3$) δ 4.98–5.47 (m, 0.95, C=CH—), 3.30–3.77 (m, 3.88, CH_2 α to chlorine), 1.58–3.02 [m, 7.24, CH_2 α to double bond, plus CH_3 α to double bond and β to chlorine plus —CH(CH_3)$_2$], 1.02 [d, 5.95, J = 7.0 Hz, —CH(CH_3)$_2$].

Anal. Calcd for $C_{10}H_{18}Cl_2$: C, 57.42; H, 8.67. Found: C, 57.18; H, 8.68.

The acid solution was made basic and extracted with ether. The ether layer was dried, and hydrogen chloride gas was passed over the surface. The resulting white solid was filtered, washed with ether, and dissolved in 30% aqueous potassium hydroxide. The amine was extracted with ether. After drying the ether and removing it *in vacuo*, there remained 2.90 g (29%) of isopropyldicyclopropylcarbinylamine (**10**), *vide infra*.

N-Methyl-N-isopropyldicyclopropylcarbinylamine (12).—To 0.6 g (0.0158 mol) of lithium aluminum hydride in 30 ml of sodium dried ether was added 1.1 g (6.14 mmol) of isopropyldicyclopropylcarbinyl isocyanate in 10 ml of ether. The reaction was refluxed for 4 hr and hydrolyzed with 30 ml of water. The ether layer was dried over magnesium sulfate and concentrated. The clear liquid was purified by preparative glpc on a 3.5-ft SE-30 on Chromosorb W column at 120° to give 790 mg (77%) of the amine, **12**: nmr ($CDCl_3$) δ 2.30 (s, 2.96, NCH_3), 1.97 [quintet, 0.99, J = 7.0 Hz, -CH(CH_3)$_2$], 0.98 [d, 6.21, J = 7.0 Hz, -CH(CH_3)$_2$], 0.08–0.80 (m, 10.90, cyclopropyl protons plus NH).

Anal. Calcd for $C_{11}H_{21}N$: C, 78.97; H, 12.65; N, 8.37. Found: C, 78.90; H, 12.57; N, 8.57.

Tricyclopropylcarbinylamine (16).—Crude tricyclopropylcarbinyl benzoate, **13**, was prepared in 90% yield according to the method of Hart and Law[16] and was used without further purification. Into each of four Carius tubes (30 cm in length and 25 mm in diameter), containing equal portions of 20.28 g (0.0793 mol) of this ester, was condensed approximately 25 ml of anhydrous ammonia. After standing at room temperature for 10 days, the tubes were opened, and the ammonia was allowed to evaporate. The residue was taken up in 400 ml of ether and extracted with several portions of 10% sodium hydroxide. The ether layer was dried over magnesium sulfate and concentrated to yield 12.0 g (100%) of a yellow liquid. The amine was converted into its hydrochloride salt and reconverted into the amine with 30% potassium hydroxide. There was obtained after distillation 10.9 g (91%) of tricyclopropylcarbinylamine, bp 85° (11 mm). The nmr spectrum shows continuous absorption between 9.00 and 9.90.

Anal. Calcd for $C_{10}H_{17}N$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.15; H, 11.25; N, 9.08.

A small portion of the hydrochloride salt was recrystallized from a 4:1 mixture of ethyl acetate and ethanol.

Anal. Calcd for $C_{10}H_{18}NCl$: C, 63.98; H, 9.67; N, 7.46. Found: C, 64.03; H, 9.61; N, 7.49.

1,1,1,1′,1′,1′-Hexacyclopropylazomethane (1e).—The general method used was that of Stevens[3] with several modifications.

Tricyclopropylcarbinylamine (3.84 g, 0.0265 mol) in 20 ml of olefin-free pentane was added dropwise to a solution of iodine pentafluoride (2.0 ml, 0.026 mol) and pyridine (10.25 g, 0.130 mol) in 75 ml of pentane cooled to 0° in an ice bath. After the addition, the solution was stirred at 0° for 15 min and then at room temperature for 45 min. Work-up was effected by adding 40 ml of a 10% potassium hydroxide solution and separation of the hydrocarbon layer. The aqueous layer was extracted with several 50-ml portions of pentane. After washing the pentane extracts with two 50-ml portions of water, two 50-ml portions of 5% sodium thiosulfate solution, and two additional 50-ml portions of water, the solution was dried over magnesium sulfate and the pentane removed *in vacuo*. The viscous yellow oil was chromatographed on 120 g of base washed alumina, eluting with hexane. The resulting yellow oil was recrystallized from a methanol–ether mixture (10:1) by cooling in Dry Ice and centrifuging the crystals. After three recrystallizations there was obtained 1.45 g (38%) of 1,1,1,1′,1′,1′-hexacyclopropylazomethane: mp 17–18.5°; bp 100° (0.25 mm) dec; uv max (cyclohexane) 386 mμ (ϵ 41); nmr ($CDCl_3$) δ 0.65–1.09 (m, 5.7, cyclopropyl methine), 0.12–0.64 (m, 24.3, cyclopropyl methylene).

Anal. Calcd for $C_{20}H_{30}N_2$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.24; H, 9.94; N, 9.52.

Further elution of the column with ethyl acetate gave 1.6 g (42%) of tricyclopropylcarbinol which was identified by comparison of its ir and nmr spectra with those of an authentic sample.

Isopropyldicyclopropylcarbinylamine (10).—To a suspension of potassium metal (5.3 g, 0.135 g-atom) in 300 ml of ether was added dropwise isopropyldicyclopropylcarbinol (20.86 g, 0.135 mol) dissolved in 50 ml of ether. The mixture was stirred at room temperature for 18 hr. The flask was cooled in an ice bath and *p*-nitrobenzoyl chloride (25.1 g, 0.1355 mol) in 100 ml of ether was added rapidly. The solution was stirred at room temperature for 1 hr and suction filtered. The solvent was removed, and the solid was recrystallized from hexane to yield 30.2 g (74%) of isopropyldicyclopropyl *p*-nitrobenzoate, mp 108–110° (lit.[7] mp 114–1151).

The same ammonolysis procedure was followed as was employed to make tricyclopropylcarbinylamine.

From 29.03 g (0.0784 mol) of the *p*-nitrobenzoate, there was obtained 10.8 g (90%) of pure isopropyldicyclopropylcarbinylamine: bp 86–87° (10 mm); nmr ($CDCl_3$) δ 1.55 [m, 0.99, -CH(CH_3)$_2$] 1.00 [d, 6.24, -CH(CH_3)$_2$], 0.45–0.85 (m, 2.34, cyclopropyl methine), 0.05–0.40 (m, 9.43, cyclopropyl methylene plus N-H).

Anal. Calcd for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found: C, 78.11; H, 12.37; N, 9.05.

A small amount of the amine hydrochloride salt was recrystallized from an ethyl acetate and ethanol mixture (8:1).

Anal. Calcd for $C_{10}H_{20}NCl$: C, 63.30; H, 10.63; N, 7.38. Found: C, 63.39; H, 10.59; N, 7.48.

1,1,1′,1′-Tetracyclopropyl-1,1′-azoisobutane (1c).—The azo compound was prepared in an identical manner with that described for 1,1,1,1′,1′,1′-hexacyclopropylazomethane.

From 6.12 g (0.04 mol) of isopropyldicyclopropylcarbinylamine, 3.3 ml (0.042 mol) of iodine pentafluoride, and 16.6 g (0.21 mol) of pyridine there was obtained, after chromatography and two recrystallizations from methanol–ether (9:1), 3.62 g (60%) of 1,1,1′,1′-tetracyclopropyl-1,1′-azoisobutane: nmr ($CDCl_3$) δ 2.00 [m, 2.17, CH(CH_3)$_2$], 0.95 [d, 12.11, -CH(CH_3)$_2$], 0.10–0.85 (m, 19.72, cyclopropyl protons).

Anal. Calcd for $C_{20}H_{34}N_2$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.37; H, 11.23; N, 9.51.

Methyldicyclopropylcarbinyl *p*-Nitrobenzoate (15).—Methyldicyclopropylcarbinol was prepared by the method of Hart and Sandri in 85% yield, bp 64° (15 mm) [lit.[7] bp 45° (4 mm)]. The *p*-nitrobenzoate was prepared by the same method used for synthesis of isopropyldicyclopropylcarbinyl *p*-nitrobenzoate.

From 24.2 mg (0.192 mol) of methyldicyclopropylcarbinol, 7.51 g (0.192 g-atoms) of potassium, and 35.52 g (0.192 mol) of *p*-nitrobenzoyl chloride was obtained, after recrystallization from hexane, 32.5 g (62%) of methyldicyclopropylcarbinyl *p*-nitrobenzoate as fluffy colorless needles: nmr ($CDCl_3$) 8.03–8.52 (m, 4.07, phenyl C-H), 1.52 (s, 3, CH_3), 1.60–1.80 (m,

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(16) H. Hart and P. S. Law, *J. Amer. Chem. Soc.*, **86**, 1957 (1964).

1.8, cyclopropyl methine), 0.30–0.80 (m, 8.15, cyclopropyl methylene). The ester has no well-defined melting point. It changes crystalline structure between 100 and 165°, from needles to plates, the latter melting at 225–230°.[17]

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.63; H, 6.26; N, 5.18.

Methyldicyclopropylcarbinylamine (17).—The same procedure was followed that was employed for tricyclopropylcarbinylamine.

From 25 g (0.095 mol) of methyldicyclopropylcarbinyl *p*-nitrobenzoate there was obtained 9.22 g (82%) of methyldicyclopropylcarbinylamine: bp 50° (12 mm); nmr ($CDCl_3$) δ 0.96 (s, 3.38, CH_3), 0.40–0.95 (m, 3.86, cyclopropyl methine plus N–H), 0.29 and 0.20 (m, 7.81, cyclopropyl methylenes).

Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.07; N, 11.19. Found: C, 76.90; H, 12.19; N, 11.13.

1,1,1′,1′-Tetracyclopropyl-1,1′-azoethane (1b).—The compound was prepared in an identical manner with that described for 1,1,1,1′,1′,1′-hexacyclopropylazomethane.

From methyldicyclopropylcarbinylamine (5.75 g, 0.046 mol), iodine pentafluoride (3.8 ml, 0.05 mol), and pyridine (19.75 g, 0.25 mol) there was obtained, after chromatography and two recrystallizations from absolute methanol at −80°, 3.17 g (56%) of 1,1,1′,1′-tetracyclopropyl-1,1′-azoethane: bp 80–81° (0.25 mm); uv max (cyclohexane) 378 mμ (ϵ 34); nmr ($CDCl_3$) δ 0.82 (s, 6.10–CH_3), 0.75–1.25 (m, 3.9, cyclopropyl methine), 0.10–0.55 (m, 16.0, cyclopropyl methylene).

Anal. Calcd for $C_{16}H_{26}N_2$: C, 77.99; H, 10.64; N, 11.37. Found: C, 78.17; H, 10.82; N, 11.45.

Diisopropylcyclopropylcarbinyl *p*-Nitrobenzoate (18).—Diisopropylcyclopropyl carbinol was prepared in 66% yield by the method of Hart and Sandri, bp 70–73° (10 mm) [lit.[7] bp 75° (10 mm)]. The corresponding *p*-nitrobenzoate was prepared by a slight modification of the method used for preparation of isopropyldicyclopropylcarbinyl *p*-nitrobenzoate.

From 3.12 g (0.02 mol) of diisopropylcyclopropylcarbinol, 1.0 g (0.0417 mol) of sodium hydride, and 3.7 g (0.02 mol) of *p*-nitrobenzoyl chloride there was obtained, after recrystallization from hexane, 4.0 g (66%) of diisopropylcyclopropylcarbinyl *p*-nitrobenzoate, mp 90–92° (lit.[7] mp 91–92°).

Ammonolysis of Diisopropylcyclopropylcarbinyl *p*-Nitrobenzoate (18).—The method employed was similar to the one used for preparation of isopropyldicyclopropylcarbinylamine.

Diisopropylcyclopropylcarbinyl *p*-nitrobenzoate (4.0 g, 0.0131 mol) was sealed in two Carius tubes with approximately 25 ml of anhydrous ammonia in each. After heating in a water bath at 50° for 10 days, the tubes were opened and the ammonia was allowed to evaporate. The residue was taken up in 200 ml of ether and washed with several portions of 10% potassium hydroxide solution. The ether layer was dried over magnesium sulfate and concentrated to give 1.91 g of yellow liquid. The mixture was analyzed on an Aerograph A-90-P3 glpc employing a 3-ft column packed with 20% diisodecylphthalate on base-washed firebrick at 146° with a helium flow rate of 50 cc/min. The mixture consisted of three major components (94.3%), identified in order of increasing retention times as, 6-amino-2-methyl-3-isopropyl-3-hexene (45%), diisopropylcyclopropylcarbinylamine (12.9%), and 5-methyl-4-isopropyl-3-hexenol-1 (36.4%). No diisopropylcyclopropylcarbinol was detected.

The carbinol was separated by chromatography of a small portion of the mixture on a silica gel column (50:1 weight ratio) by eluting with benzene–ethyl acetate (2:1). The clear liquid that eluted first was purified by preparative glpc on a 5-ft 20% Carbowax 20M on Chromosorb W column. It was identified as 5-methyl-4-isopropyl-3-hexenol[7] (21): nmr ($CDCl_3$) δ 5.11 (t, 1.00 J = 7.5 Hz; C=C**H**), 3.29–3.69 (m, 300 —CH_2**OH**), 2.57–3.07 [m, 1.12, —C**H**(CH_3)$_2$ *cis* to vinyl C—H],[8,9] 2.05–2.50 [m, 3.00, allylic CH_2 plus CH_2 plus C**H**(CH_3)$_2$ *trans* to vinyl C—H],[8,9] 1.02 [d, 11.88, J = 7.0 Hz, —CH(CH_3)$_2$].

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.83; H, 12.89.

The amine portion of the original mixture was purified by conversion into the hydrochloride salts and reconversion into the amines. The amines were collected by preparative glpc on a Carbowax 20M column.

Anal. Calcd for $C_{10}H_{21}N$: C, 77.34; H, 13.63; N, 9.02. Found: C, 77.23; H, 13.70; N, 9.24.

Purification of 6-amino-3-isopropyl-2-methyl-3-hexene was carried out by preparative glpc on a 3-ft 20% diisodecylphthalate on base-washed firebrick column: nmr ($CDCl_3$) ϵ 5.10 (t, 0.95 C=C**H**), 2.38–2.10 [m, 2.95 —CH_2—N plus —C**H**(CH_3)$_2$ *cis* to vinyl C—H], 1.91–2.37 [m, 2.95 allylic CH_2 plus C**H**(CH_3)$_2$ *trans* to vinyl C—**H**], 1.54 (m, 2.05, N—**H**), 0.96 [d, 12.13, —CH(CH_3)].

Purification of diisopropylcyclopropylcarbinylamine was effected using the same base-washed diisodecylphthalate column; nmr ($CDCl_3$) δ 1.53–2.17 [m, 2.17, -C**H**(CH_3)$_2$], 1.38 (m, 1.80 -N**H**), 0.94 and 0.90 [pair of doublets, 11.80, J = 7.0 Hz, two -CH(CH_3)$_2$].

5-Methyl-4-isopropyl-3-hexenyl Isocyanate (25).—The method was similar to that used for preparation of **4**.

From diisopropylcyclopropylcarbinol (5.2 g, 0.0333 mol), sodium hydride (2.4 g, 0.1 mol), and cyanogen bromide (12 g, 0.112 mol) was obtained, after work-up, 5.5 g of viscous red liquid.

The nmr of this liquid shows less than 15% of the molecules to have the cyclopropyl rings still intact.

A portion of the product (2.5 g) was chromatographed on 88 g of silica gel and eluted with benzene. The component which eluted first (1.19 g) was flash distilled to give 1.05 g (38%) of a colorless liquid which gradually turned red upon standing. The nmr and ir spectra are consistent for 5-methyl-4-isopropyl-3-hexenyl isocyanate: nmr ($CDCl_3$) δ 5.08 (t, 0.95, C=C**H**), 3.24 (t, 1.99 —CH_2NCO), 1.81–2.94 [m, 4.07, allylic CH_2 plus C**H**(CH_3)$_2$], 1.01 [d, 11.97, J = 7 Hz, —CH(CH_3)$_2$], 0.45 (impurity, less than 5%, probably diisopropylcyclopropylcarbinyl isocyanate).

Dimethylcyclopropylcarbinyl-N-(dimethylcyclopropylcarbinyl)-carbamate (30).—Dimethylcyclopropylcarbinol was prepared according to literature methods in 73% yield, bp 120–123° (760 mm) [lit.[18,19] bp 121–122°, 123–124° (760 mm)]. The carbinol (5.0 g, 0.05 mol) in 5 ml of tetrahydrofuran was added to sodium hydride (2.4 g, 0.1 mol) suspended in 50 ml of tetrahydrofuran. After refluxing for 10 hr, a solution of cyanogen bromide (15 g, 0.14 mol) in 50 ml of tetrahydrofuran was added rapidly to the ice-cooled alkoxide solution. The reaction was stirred at room temperature for 1 hr. After suction filtration, the tetrahydrofuran and excess cyanogen bromide were removed *in vacuo*, and the resulting viscous dark red liquid was vacuum distilled through a 30-cm Holzman column. After collecting 1.8 g of forerun, presumably dimethylcyclopropylcarbinyl isocyanate (the forerun showed a very strong infrared absorption at 2240 cm^{-1}), we collected 3.1 g (55%) of dimethylcyclopropylcarbinylcarbamate as a colorless viscous liquid: bp 95–96° (1.8 mm); nmr ($CDCl_3$) δ 4.45 (m, 0.82–N**H**) 1.17 and 1.31 (two singlets, 12.73, -CH_3), 1.17 (m, 12.23, -CH_3), 0.69–1.17 (m, 1.86, cyclopropyl methine), 0.30–0.41 (m, 8.09, cyclopropyl methylene).

Anal. Calcd for $C_{13}H_{53}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.34; H, 10.40; N, 6.61.

Dimethylcyclopropylcarbinylamine (31).—The most facile procedure for isolating the amine was to hydrolyze the crude carbamate described above before distillation.

From 30 g (0.3 mol) of dimethylcyclopropylcarbinol, 12 g (0.5 mol) of sodium hydride, and approximately 70 g of cyanogen bromide was isolated 28.6 g of dark red liquid. To the crude carbamate, cooled in an ice bath, was added approximately 50 ml of concentrated hydrochloric acid. The reaction was magnetically stirred and heated at 60° for 8 hr, cooled, and washed with three 50-ml portions of ether. The acid layer was cooled in an ice bath and made basic (pH > 11) with potassium hydroxide pellets. After extraction with ether and concentration by distillation through a Vigreux column, the amine was converted into the hydrochloride salt and recrystallized from ethyl acetate–ethanol, 8.05 g (53%): mp 223–225° dec; nmr ($CDCl_3$) δ 5.15 (s, 2.75, -N**H**), 1.75 (s, 6.30, CH_3), 0.95–1.30 (m, 0.75 cyclopropyl methine), 0.40–0.72 (m, 4.20, cyclopropyl methylene).

Anal. Calcd for $C_6H_{14}NCl$: C, 53.13; H, 10.40; N, 10.33. Found: C, 53.15; H, 10.64; N, 10.11.

1,1′-Dicyclopropyl-2,2′-azopropane (1a).—Dimethylcyclopropylcarbinylamine hydrochloride (7 g, 0.0518 mol) was dissolved in 20 ml of water, made basic (pH > 11) with potassium hydroxide pellets, and extracted with 50 ml of olefin-free hexane.

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The hexane was dried over magnesium sulfate, filtered, and added dropwise to an ice-cooled mixture of iodine pentafluoride (4.7 ml, 0.061 mol) and pyridine (24.1 g, 0.305 mol). After work-up, chromatography on 200 g of base-washed alumina, and distillation, there was obtained 2.23 g (44%) of 1,1′-dicyclopropyl-2,2′-azopropane: bp 43–45° (1.0 mm); uv max (cyclohexane) 372 mμ (ε 22); nmr ($CDCl_3$) δ 1.03 (s, CH_3), superposed on 0.77–1.38 (m, total 14.10, cyclopropyl methine), 0.25–0.32 (m, 7.90, cyclopropyl methylene).

Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.14; H, 11.44; N, 14.63.

Cyclopropylmethylcarbinylazine (34).—To cyclopropyl methyl ketone (8.4 g, 0.1 mol) in 30 ml of pentane was added anhydrous hydrazine (1.7 ml, 0.053 mol). The solution was refluxed for 24 hr and dried over calcium chloride, and the pentane was removed *in vacuo*. Distillation gave 4.44 g (54%) of cyclopropylmethylcarbinylazine: bp 76° (1.5 mm); nmr ($CDCl_3$) δ 1.76 (s, 5.6, $-CH_3$) 1.18–1.70 (m, 2.4, cyclopropyl methine), 0.50–0.90 (m, 8.0, cyclopropyl methylene).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06. Found: C, 73.01; H, 9.84; N, 17.20.

1,1′-Dichloro-1,1′-dicyclopropyl-1,1′-azoethane (35).—The azo compound was prepared by the method of Goldschmidt and Acksteiner.[11,12] After three recrystallizations from pentane at −30° there was obtained a 57% yield of the azo compound, mp 43–50°, presumably as a mixture of isomers: nmr ($CDCl_3$) δ 1.82 (s, 6.05, $-CH_3$), 1.30–1.75 (m, 1.95, cyclopropyl methine), 0.40–0.80 (m, 8.00, cyclopropyl methylene).

Anal. Calcd for $C_{10}H_{16}N_2Cl_2$: C, 51.07; H, 6.86; N, 11.91. Found: C, 50.91; H, 6.73; N, 11.83.

Dicyclopropylcarbinylazine (32).—The azine was prepared according to the method of Hart and Curtis in 78% yield, mp 91–91.5° (lit.[20] mp 92–93°).

1,1′-Dichloro-1,1,1′,1′-tetracyclopropylazomethane (33).—The azo compound was prepared in 72% yield by the procedure described for 1,1′-dichloro-1,1′-dicyclopropyl-1,1′-azoethane: mp 48–52°; nmr ($CDCl_3$) δ 1.32–1.90 (m, 4.09, cyclopropyl methines), 0.35–0.85 (m, 15.91, cyclopropyl methylenes).

Anal. Calcd for $C_{14}H_{20}N_2Cl_2$: C, 58.54; H, 7.02; N, 9.75. Found: C, 58.52; H, 7.14; N, 9.72.

Reaction of 1,1′-Dichloro-1,1,1′,1′-tetracyclopropylazomethane with Methylmagnesium Bromide.—To 1,1′-dichloro-1,1,1′,1′-tetracyclopropylazomethane (250 mg, 0.871 mmol) in 20 ml of sodium-dried ether was added methylmagnesium bromide (2 ml of approximately 3 *M* solution, 6 mmol). The solution was stirred at room temperature for 30 min and treated with water. The ether layer was dried, and the ether was removed *in vacuo*. The resulting liquid was chromatographed on 20 g of base-washed alumina to give 110 mg (51%) of a compound whose nmr and ir spectra were identical with those of 1,1,1′,1′-tetracyclopropyl-1,1′-azoethane.

It was found that addition of the chloroazo compound to a Grignard reagent generated from methylmagnesium iodide gave only dicyclopropylcarbinylazine in 85% yield.

Reaction of 1,1′-Dichloro-1,1′-dicyclopropyl-1,1′-azoethane with Methylmagnesium Bromide.—To 1,1′-dichloro-1,1′-dicyclopropyl-1,1′-azoethane (1.17 g, 5 mmol) in 35 ml of sodium-dried ether was added excess methylmagnesium bromide (5 ml of approximately 3 *M* solution, 15 mmol). After a slight induction period the reaction refluxed gently for several minutes. The solution was stirred for 2 hr at room temperature and hydrolyzed with water. The ether layer was dried over magnesium sulfate, concentrated, and chromatographed on 100 g of base-washed alumina to give 710 mg (73%) of a compound whose nmr and ir spectra were identical with those of 1,1′-dicyclopropyl-2,2′-azopropane.

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Registry No.—**1a**, 17396-98-4; **1b**, 17396-99-5; **1c**, 17397-00-1; **1e**, 17397-01-2; **4**, 17397-02-3; **5**, 17397-03-4; **6**, 17397-04-5; **7**, 17397-05-6; **9**, 17397-06-7; **10**, 17397-07-8; **11**, 17397-08-9; **12**, 17397-09-0; **15**, 17414-37-8; **16**, 17397-21-6; **17**, 17397-10-3; **18**, 17397-11-4; **21**, 17396-20-2; **25**, 17396-19-9; **30**, 17397-12-5; **31** HCl, 17397-13-6; **33**, 17397-14-7; **34**, 17397-15-8; **35**, 17397-16-9; **10** HCl, 17397-17-0; **16** HCl, 17397-18-1; 6-amino-2-methyl-3-isopropyl-3-hexene, 17397-19-2; diisopropylcyclopropylcarbinylamine, 17397-20-5.

Acknowledgments.—This work was supported in part by a grant from the U. S. Public Health Service, GM-12296. Predoctoral fellowship support for J. W. T. was provided by the Rohm and Haas Co. and the National Institutes of Health. Fellowship support for J. C. M. was provided by the Alfred P. Sloan Foundation and the John Simon Guggenheim Memorial Foundation.

Alkyl-Substitution Effects in the Photochemistry of 2-Cyclohexenones[1]

WILLIAM G. DAUBEN, GARY W. SHAFFER,[2] AND NOEL D. VIETMEYER

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

Received April 12, 1968

The scope of photochemical lumirearrangement in alkyl-substituted 2-cyclohexenones has been investigated. The rearrangement occurs only if the fourth carbon atom of the 2-cyclohexenone ring is fully alkyl substituted. If this requirement is not met, photodimers are the major products. The substituent requirement is necessary but not sufficient to ensure rearrangement as the presence of other substituents either retard or inhibit the reaction.

Photochemical Reactions of Conjugated Ketones.—In recent years the scope and mechanistic aspects of conjugated ketone photochemistry has received a great deal of attention. Photoreactions involving *cis–trans* isomerization,[3,4] molecular rearrangement,[5] dimerization,[6,7] solvent addition,[8] cycloaddition,[9] and reduction[10] have been reported.

The most widely investigated group of compounds possessing this chromophore has been the substituted cyclohexenone type, and in this series the characteristic rearrangements are the lumirearrangement[5] and cyclo-

(1) This work was supported in part by Public Health Service Grant No. G 0709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) National Institutes of Health Predoctoral Fellow, 1965–1967.

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