TABLE I

DECOMPOSITION OF 1-PHENYL-1-CYCLOHEXYL PERACETATE (I)

Solvent[a]	Reaction time, hr	Product composition, %[b] Phenol	Cyclohexanone	1-Phenoxycyclohexene	Caprophenone	Miscellaneous
Ethanol	62	53	34			[c]
Acetic acid[d]	52	20	30	44		[e]
Acetic acid[f]	72	11	12	72		[g]
Heptane	25			34	58	[h]
Pyridine	22	[i]	[i]	*Ca.* 75	*Ca.* 25	

[a] Reaction was carried out in refluxing solvent, unless otherwise noted. [b] Percentages of peak areas obtained in gc analysis with a Carbowax 20M column at *ca.* 200°. These data do not represent accurate mole per cent composition, but do indicate approximate relative amounts of the indicated products. [c] Two peaks (13%) were found at very short retention times, one of them probably being solvent. [d] Reaction temperature, 80°. [e] 5% phenyl acetate was detected, also unidentified high boiling material, *ca.* 15% of total observed area. [f] Reaction carried out at room temperature (*ca.* 25°). [g] There was also 5% unidentified material. [h] 8% of what appears to be 1-phenylcyclohexanol was detected. Some unidentified higher boiling material was present. [i] Traces of phenol and cyclohexanone were detected.

t-butylperoxy chloroformate, the mechanism of which is solvent dependent.[8] Furthermore, the nature of the ionic products in the decomposition of I depends on the particular solvent employed, as discussed above.

Experimental Section

Gas chromatographic analyses were carried out with a Perkin-Elmer Model 154 instrument using a Carbowax 20M column (10% on 70–80 mesh Anakrom ABS) at 200°, and with an F & M Model 500 instrument using a 2-ft 10% silicone rubber (SE 30) on 60–70 mesh Anakrom ABS column. The F & M instrument was programmed for 70–340° at 21°/min. Peak areas were calculated by the peak height-width at half-height method.

1-Phenyl-1-cyclohexyl Peracetate.—1-Phenylcyclohexyl hydroperoxide was prepared from the corresponding alcohol with 90% (or 70%) hydrogen peroxide using the procedure of Hey, Stirling, and Williams.[5] Reaction of the pure hydroperoxide with acetyl chloride in pyridine gave the liquid peracetate in 87% yield. The identity of the peracetate was confirmed by its infrared spectrum (neat); strong bands at 1754 (C=O), 1183 (C–O), and 754 and 694 cm^{-1} (monosubstituted aromatic). The nmr spectrum (CCl_4) confirmed the structure of the peracetate, showing a multiplet (5 H) in the aromatic region near δ 7.3 ppm and a broad signal for the ring protons from *ca.* 1.4 to 2.3 ppm, which included a sharp singlet for $-OCOCH_3$ at δ 1.72 ppm (total 13 H).

Decomposition of the Peracetate in Ethanol.—1-Phenyl-1-cyclohexyl peracetate (6 g) was heated under reflux for 62 hr in absolute ethanol. The cooled reaction mixture was diluted with salt solution and extracted with ether. The ether solution was washed with sodium bicarbonate and salt solution and dried over $MgSO_4$. An infrared spectrum of the recovered product, 3.7 g, showed no evidence of starting peracetate. Strong hydroxyl and carbonyl (1689 cm^{-1}) bands were present. The product was analyzed by gas chromatography on a Carbowax 20M column at 198° (Table I). Further analysis on the silicone rubber column programmed to 340° confirmed phenol and cyclohexanone as the only significant components in the mixture.

Decomposition of I in Acetic Acid.—Compound I (3 g) was decomposed in 30 ml of glacial acetic acid at 80° for 52 hr. The product (2 g) was worked up as described above, except that methylene chloride was used for extraction. Analysis of the product was carried out by gas chromatography on the Carbowax 20M and silicone rubber columns (Table I).

In a similar decomposition, the crude product was washed with 10% sodium hydroxide and distilled, giving 1-phenoxycyclohexene, bp 66–68° (0.15 mm).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.71; H, 8.09. Found: C, 82.04; H, 8.19.

The infrared spectrum (10% CCl_4) showed bands at 1220 (s) (aromatic ether), 1669 (C=C str), 862 cm^{-1} (=CH out of plane deformation). The structure of the vinyl ether was confirmed by its nmr spectrum, which showed a multiplet (5 H) in the aromatic region near 7 ppm, an olefin proton (multiplet, 1 H) at about δ 4.94 ppm, and the ring methylene protons (8 H) in the range 1.4–2.4 ppm composed of two major overlapped multiplets corresponding to the ring allylic and nonallylic protons. Strong irradiation in the allylic proton region (175.8 cps upfield from the olefin signal) collapsed the olefin proton signal to a broad singlet.

Decomposition of I in Heptane and Pyridine.—Compound I (2 g) was decomposed in 20 ml of refluxing heptane under nitrogen for 25 hr. The product (1.7 g) had an infrared spectrum which showed very little hydroxyl absorption and no cyclohexanone. There was a strong band at 1667 [C_6H_5–C(=O)–] and at 1220 cm^{-1}. Analysis of the product was carried out on the Carbowax 20M and silicone rubber columns (Table I).

The peracetate (1.3 g) was decomposed in 20 ml of refluxing pyridine under nitrogen for 22 hr. The infrared spectrum of the product showed virtually no hydroxyl absorption but showed strong bands at 1667 and 1215 cm^{-1}. Product analysis was carried out on a Carbowax 20M column (Table I).

Registry No.—I, 17012-34-9; 1-phenoxycyclohexene, 17012-35-0.

Acknowledgments.—Thanks are extended to Dr. P. E. Butler of the Analytical Research Division for performing the nmr decoupling experiment and also to Mr. Jack Oliver for his technical assistance.

(8) P. D. Bartlett and H. Minato, *J. Amer. Chem. Soc.*, **85**, 1858 (1963).

Reaction of 2-Acetylcyclohexanone with Malononitrile and Cyanoacetamide

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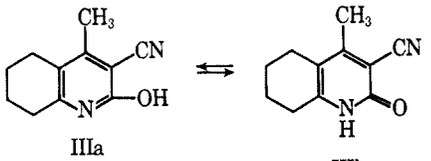
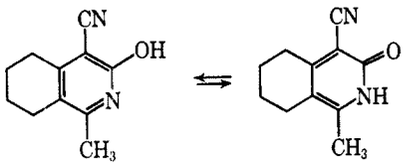
It has been reported,[1,2] without structure proof, that the pyridine-catalyzed reaction of cyanoacetamide (I) and 2-acetylcyclohexanone (II) gave a mixture of 3-cyano-2-hydroxy-4-methyl-5,6,7,8-tetrahydroquinoline (III) and 4-cyano-3-hydroxy-1-methyl-5,6,7,8-tetrahydroisoquinoline (IV). During studies of the reaction of malonic acid derivatives and dicarbonyl compounds, we found that the diethylamine-catalyzed reaction of malononitrile (V) or I with II gave a solid with the empirical formula $C_{11}H_{12}N_2O$. We have shown this product to have structure IV *via* elemental analysis, spectral analyses, and chemical reactivity. Also, we have prepared several previously unknown derivatives of IV. The nmr spectrum of IV in trifluoroacetic acid, which shows resonances at τ 6.98 (m), 7.35 (m), 7.48 (s, C–CH_3), and 8.17 (m), does not distinguish

(1) H. K. Sen-Gupta, *J. Chem. Soc.*, **107**, 1347 (1915).
(2) H. K. Sen and U. Bose, *J. Indian Chem. Soc.*, **4**, 51 (1929).



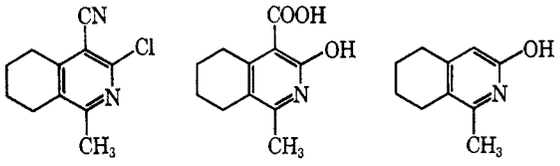
IIIa IIIb



IVa IVb

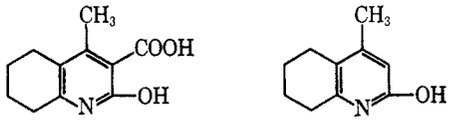
between III and IV nor does the ultraviolet spectrum, which is similar to 3-isoquinolinol,[3] distinguish between III and IV. The infrared spectrum showed absorptions at 4.45 μ (conjugated CN), 6.05 and 6.21 (>C=O ↔ >C–OH), and 8.7 μ (isoquinoline).[4-6]

Phosphorous pentachloride converts IV into a *single* chloride VI. The isoquinoline structure is evident from the infrared band at 8.75 μ and the absence of absorption in the 9.05-μ region.[4,5] The nmr spectrum of VI in $CDCl_3$ showed methylene hydrogens at τ 7.10 (m), 7.38 (m), and 8.16 (m) and methyl hydrogens at 7.75 (s).



VI VII VIII

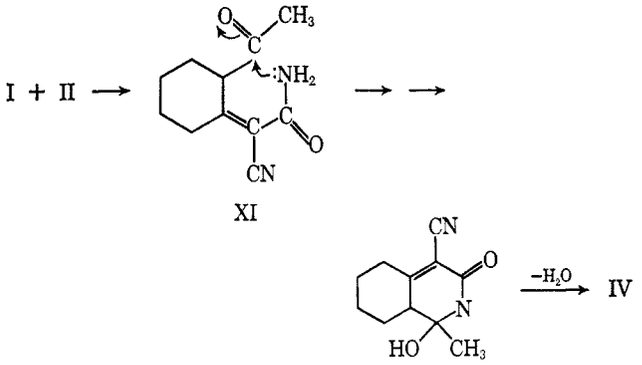
Judicious hydrolysis of IV with 25% potassium hydroxide solution gave a *single* acid VII, mp 259–260° dec, and its decarboxylation product VIII, mp 236–237°, in the same experiment. Dornow and Neuse[4] have reported that the corresponding quinoline isomers, IX and X, melt at 242° and at 217–218°, respectively.



IX X

Both VII and VIII showed the characteristic isoquinoline band in the infrared spectrum at 8.75 and 8.72 μ, respectively. Finally, thermal decarboxylation[7] of VII gave VIII in 73.6% yield. These data are consistent with the formulation of the condensation product as IV.

The mechanism presumably involves attack of the anion derived from I or V at the cyclic carbonyl carbon[8] to give a Knoevenagel condensation product (XI) which cyclizes *via* a nucleophilic attack of the unshared pair of nitrogen electrons at the acyl carbonyl carbon, followed by elimination of water.



XI

This procedure provides a simple and high yield route to otherwise difficulty accessible substituted 5,6,-7,8-tetrahydroisoquinolines. The scope and mechanism of this reaction with divers dicarbonyl compounds and different malonic acid derivatives are being investigated.

Experimental Section

General.—All melting points are uncorrected and were determined on a Thomas–Hoover apparatus. Nmr spectra were taken on a Varian A-60 instrument; infrared spectra were taken on a Baird-Atomic spectrophotometer; and ultraviolet spectra were taken on a Beckman DK-2A. Elemental analyses were performed by G. I. Robertson, Jr., Florsham Park, N. J., and Spang Microanalytical Laboratory, Ann Arbor, Mich.

4-Cyano-3-hydroxy-1-methyl-5,6,7,8-tetrahydroisoquinoline (IV). A. From Cyanoacetamide.—A mixture of 4.6 g (0.05 mole) of 2-acetylcyclohexanone,[9] 1.5 g (0.017 mol) of cyanoacetamide (Aldrich), 50 ml of 95% ethanol, and 0.5 ml of diethylamine (Eastman) was stirred for 18 hr at room temperature. The reaction mixture was filtered and the solid was washed with dilute alcohol and dried to give 2.8 g of IV. The filtrate and the washings gave an additional 0.2 g after standing overnight (crude yield of 90%). Recrystallization from absolute ethyl alcohol gave 2.81 g (85%) of pale yellow needles: mp 357–359° dec; ir (KBr), 4.45 (CN), 6.05, 6.21 (C=O ↔ C–OH), 8.74 μ (isoquinoline); uv max (95% EtOH), 218 mμ (ϵ 18,824), 223 (19,049), 238 (6777), 343 (11,140); nmr (CF_3COOH), τ, 6.98, (m, 2, CH), 7.35 (m, 2, CH), 7.48 (s, 3, CH_3), 8.16 (m, 4, CH_2).

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.88. Found: C, 70.15; H, 6.36; N, 14.70.

B. From Malononitrile.—The procedure was the same as above except that the reaction time was 30 min and the yield was 27%. A mixture melting point determination showed this product to be identical with the product obtained with cyanoacetamide.

3-Chloro-4-cyano-1-methyl-5,6,7,8-tetrahydroisoquinoline (VI) was prepared by the procedure of Mariella and Leech.[10] Recrystallization of the solid from dilute ethanol gave white needles: mp 100–100.5°; ir (KBr), 4.42 (CN), 8.75 (isoquinoline), 13.59 (CCl); nmr ($CDCl_3$), τ 7.10 (m, 2, CH), 7.38 (m, 2, CH), 7.55 (s, 3, CH_3), 8.16 (m, 4, CH_2).

Anal. Calcd for $C_{11}H_{11}N_2Cl$: C, 63.93; H, 5.36; N, 13.55. Found: C, 63.91; H, 5.24; N, 13.60.

4-Carboxy-3-hydroxy-1-methyl-5,6,7,8-tetrahydroisoquinoline (VII) and 3-Hydroxy-1-methyl-5,6,7,8-tetrahydroisoquinoline (VIII).—A solution of 4.0 g (0.021 mol) of IV in 150 ml of 25% potassium hydroxide solution was refluxed for 5 days, cooled, and extracted continuously with ether for 48 hr to remove VIII. The ether was removed through a 14-in. Vigreaux column, and the residue was dissolved in 95% ethanol, treated with Norit, filtered, and cooled to give 0.7 g (21%) of VIII: mp 236–237°; ir (KBr), 8.74 μ (isoquinoline).

(3) H. E. Baumgarten, W. F. Murdock, and J. E. Dirks, *J. Org. Chem.*, **26**, 803 (1961).

(4) A. Dornow and E. Neuse, *Arch. Pharm.*, **287**, 361 (1954).

(5) H. Luther, *ibid.*, **287**, 383 (1954).

(6) H. Junek, *Montash. Chem.*, **95**, 1473 (1964).

(7) H. Hart and F. Freeman, *J. Amer. Chem. Soc.*, **85**, 1161 (1963).

(8) A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 2533 (1928); 1976 (1930). Cyclic ketones generally react faster than acyclic ketones in carbonyl addition reactions.

(9) R. M. Manyik, F. C. Frostick, Jr., J. J. Sandstron, and C. R. Hauser, *J. Amer. Chem. Soc.*, **75**, 5030 (1953).

(10) R. P. Mariella and J. L. Leech, *ibid.*, **71**, 331 (1949).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.53. Found: C, 73.66; H, 8.04; N, 8.55.

The residue from the continuous ether extraction was made acid to congo red with dilute hydrochloric acid and the volume was doubled by the addition of water. The precipitated solid was filtered, dried, transferred to a Soxhlet extractor, and extracted with chloroform for 7 days. Evaporation of the chloroform gave a white solid which was dissolved in absolute ethyl alcohol, treated with Norit, filtered, and cooled to give 2.1 g (50%) of VII: mp 259–260° dec, ir (KBr), 8.75 μ (isoquinoline).

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.52; H, 6.49; N, 6.66.

VIII from VII.—Compound VII was decarboxylated at 264° *via* the procedure of Hart and Freeman.[7] Recrystallization from ethanol gave 0.6 g (73.6%) of white needles of VIII, mp 236–237°. The melting point was undepressed on admixture with the hydrolytic product (*vide supra*).

Registry No.—I, 107-91-5; II, 874-23-7; IVb, 17012-30-5; V, 109-77-3; VI, 17012-31-6; VII, 17012-32-7; VIII, 17012-33-8.

Acknowledgment.—We are indebted to Dr. E. C. Friedrich[11] for some of the nmr spectra and to Mr. R. H. DuBois for certain of the infrared spectra.

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An Unusual Cyclobutane Pyrolysis

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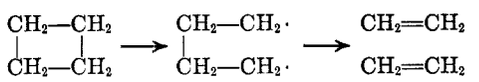
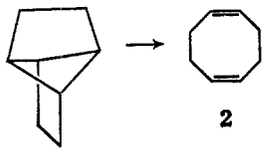
The thermal decomposition of cyclobutane to ethylene[2] is believed to involve the intermediacy of the tetramethylene diradical, which undergoes β scission to yield products (eq 1).[3] Numerous sub-



(1)

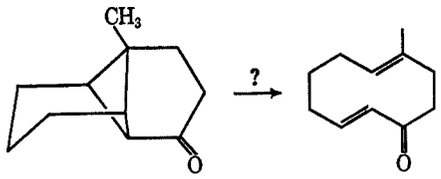
stituted cyclobutanes have been pyrolyzed and almost all undergo the reaction outlined in eq 1, the few exceptions being vinyl and 1,2-divinylcyclobutanes, which rearrange to cyclohexenes and cyclooctadienes, respectively.[3]

Srinivasan and Levi[4] found that tricyclo[3.3.0.0^{2,6}]-octane (**1**) undergoes thermal decomposition in the expected manner to yield 1,5-cyclooctadine (**2**). In connection with another study, we desired a method



1 **2**

for preparing 8-methyl-2,7-cyclodecadien-1-one (**4**). One possibility appeared to be pyrolysis of the readily available tricyclic ketone **3**.[5]



3 **4**

When compound **3** was heated at 360° in a sealed Pyrex vessel, two isomeric products were formed in varying amounts (Table I). The major product was

TABLE I

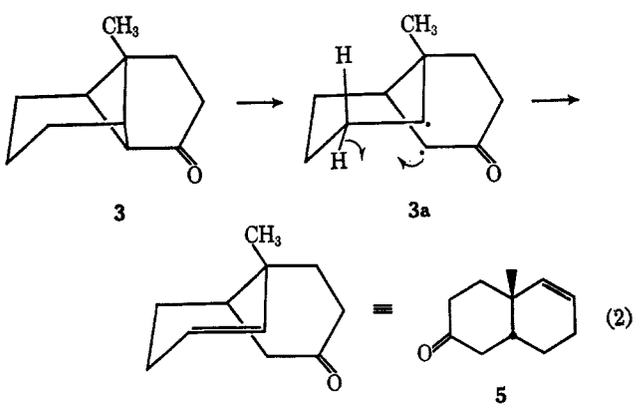
PYROLYSIS OF 1-METHYLTRICYCLO[4.4.0.0^{2,7}]DECAN-8-ONE

Run	Amount of **3**, mg	Reaction mixture analysis, % **3**	**5**	Other product
1	527.5	70.0	24.2	5.6
2	523.4	69.2	24.4	6.3
3	538.9	70.0	23.1	6.8
4	517.1	65.9	27.2	6.8
5	527.9	66.2	25.7	8.0
6	534.0	66.6	25.6	7.8
7	547.6	68.0	24.3	8.1
8	553.2	67.9	24.4	7.7[a]

[a] Analysis by internal standard showed 24.6% of nonvolatile products.

identified as the octalone **5**, by comparison with an authentic sample.[5] The minor product was shown to be a cyclohexanone or cycloheptanone (ν_{max} 1700 cm^{-1}) containing a terminal methylene group (ν_{max} 890 cm^{-1}). Due to the extreme difficulty in isolating this minor product in a pure state, its structure was not further investigated.

The probable mode of formation of **5** is outlined in eq 2. The intramolecular diversion of the postulated



3 **3a** **5** (2)

diradical **3a** lends additional credence to the probable intermediacy of tetramethylene diradicals in cyclobutane pyrolyses.[3] The reason for the different modes of reaction of tricyclic compounds **1** and **3** is not clear.

Experimental Section

Pyrolysis of 1-Methyltricyclo[4.4.0.0^{2,7}]decan-8-one (3).—Approximately 500 mg of ketone **3**[5] was sealed at 1 mm in a 20-ml Pyrex vessel. The tube was heated at 360° for 2 hr, cooled, and opened. Analysis of the reaction mixture by capillary vpc (150

(1) Fellow of the Alfred P. Sloan Foundation.

(2) (a) G. T. Genaux and W. D. Walters, *J. Amer. Chem. Soc.*, **73**, 4497 (1951); (b) F. Kern and W. D. Walters, *Proc. Nat. Acad. Sci. U. S.*, **39**, 937 (1952); (c) F. Kern and W. D. Walters, *J. Amer. Chem. Soc.*, **75**, 6196 (1953).

(3) H. M. Frey, "Gas Phase Pyrolyses of Some Small Ring Hydrocarbons," in Advances in Physical Organic Chemistry, Vol. 4, V. Gold, Ed., Academic Press, New York, N. Y., 1966.

(4) R. Srinivasan and A. A. Levi, *J. Amer. Chem. Soc.*, **86**, 3756 (1964).

(5) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *ibid.*, **89**, 4135 (1967).