of 3-ethyl-5-*n*-propyltetrahydropyran-4-one, bath temperature 80° (1.5 mm.), $n^{25}D$ 1.4481.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.28; H, 10.59.

The 2,4-dinitrophenylhydrazone (mixture of geometric isomers) was prepared in the usual manner and was fractionally crystallized from 95% ethanol to yield 346 mg. (38%) of an isomer m.p. 147–148°, $\lambda_{\max}^{\text{EtOH}}$ 362 mμ, log ε 4.7.

Anal. Calcd. for $C_{16}H_{22}N_4O_5$: C, 54.84; H, 6.33: N, 15.99. Found: C, 54.92; H, 6.40; N, 15.73.

A second isomer, melting at 122–123.5°, was recovered from the mother liquors, $\lambda_{\max}^{\text{EtOH}}$ 362 mμ, log ε 5. The yield was 265 mg. (29%).

Anal. Calcd. for $C_{16}H_{22}N_4O_5$: C, 54.84; H, 6.33; N, 15.99. Found: C, 54.89; H, 6.55; N, 15.55.

When the oxidation was carried out with chromic acid-pyridine complex, the ketone *14* was obtained in 80% yield. Preparation and crystallization of the 2,4-dinitrophenylhydrazones gave 50% of the isomer melting at 147–148° and 20% of the isomer melting at 122–123.5°.

Equilibration of 3-Ethyl-5-*n*-propyltetrahydropyran-4-one.—To a 50-ml. flask equipped with a condenser was added 500 mg. (0.003 mole) of 3-ethyl-5-*n*-propyltetrahydropyran-4-one followed by 20 ml. of benzene and 20 mg. of *p*-toluenesulfonic acid and the mixture was heated to reflux for 3 hr. After the usual work-up, distillation of the product afforded 450 mg. (90%) of *cis*-3-ethyl-5-*n*-propyltetrahydropyran-4-one. This product showed one peak on gas chromatography.

The **2,4-dinitrophenylhydrazone** (a mixture of geometric isomers) was prepared in the usual manner and was fractionally crystallized from 95% ethanol to yield 80 mg. (20%) of an isomer, m.p. 147–148°.

The second isomer, melting at 111–115°, was recovered from the mother liquors. The yield was 200 mg. (50%).

3-*n*-Propyl-4-propionyltetrahydrofuran.—A sample of 3-*n*-propyl-4-(1′-hydroxy-1′-propyl)tetrahydrofuran (500 mg., 0.003 mole) was oxidized with chromium trioxide–pyridine in the usual manner. Distillation afforded 310 mg. (75%) of 3-*n*-propyl-4-propionyltetrahydrofuran, bath temperature 110–120° (2 mm.), $n^{25}D$ 1.4494.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.32; H, 10.58.

The **2,4-dinitrophenylhydrazone** (a mixture of geometric isomers) was prepared and was fractionally crystallized from 95% ethanol to yield 175 mg. (54%) of pure isomer, m.p. 95.5–97°.

Anal. Calcd. for $C_{16}H_{22}O_5N_4$: C, 54.84; H, 6.33; N, 15.99. Found: C, 54.64; H, 6.42; N, 15.55.

A second isomer, melting at 84–86°, was recovered from the mother liquors. The yield was 86 mg. (26%).

Anal. Calcd. for $C_{16}H_{22}O_5N_4$: C, 54.84; H, 6.33; N, 15.99. Found: C, 55.00; H, 6.28; N, 15.85.

Hydroboration of 3-*n*-Propyl-4-(*trans*-1′-propenyl)tetrahydrofuran.—3-*n*-Propyl-4-(*trans*-1′-propenyl)tetrahydrofuran (90 mg. 0.006 mole) was hydroborated in diglyme with sodium borohydride and boron trifluoride etherate.[17] After oxidation with 30% hydrogen peroxide, the mixture was poured into water. The product was extracted with ether, and the residual diglyme was removed by several washings with ice–water. Distillation followed by further purification by means of gas chromatography yielded 43 mg., 90% yield (based on recovered starting material) of 3-*n*-propyl-4-(1′-hydroxy-1′-propyl)tetrahydrofuran. Gas chromatography showed this material to be homogeneous with a retention time of 9.75 min. at 170° and 8 p.s.i.g.

The *p*-nitrobenzoate was prepared in the usual manner in 15% yield after recrystallization from 95% ethanol, m.p. 88–93°, m.m.p. 88–93°.

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Azo Compounds. XLI.[1] Decomposition of 2,2′-Azobis-2-cyclopropylpropionitrile. A Possible Rearrangement of a Cyclopropylcarbinyl Free Radical

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Solution decomposition of 2,2′-azobis-2-cyclopropylpropionitrile has been shown to yield predominantly polymer along with *sym*-dimethyldicyclopropyl succinonitrile and 1-methylcyclopenten-5-one azine, whereas solid state decomposition gives predominantly dinitrile, some polymer and no azine. Proof of structure of the azine was obtained through spectral evidence along with unequivocal synthesis. Formation of azine is postulated as arising from rearrangement of a cyclopropylcarbinyl free radical in the form of its ketenimine resonance hybrid. Differences in product composition arising from solution *vs.* bulk decompositions are explained as being due to restricted motion of free radicals in the solid state.

The rate of thermal decomposition of azonitriles has been shown to be relatively insensitive to structural variations.[3–5] Throughout the course of their decomposition, solutions have been observed to remain clear and colorless, yielding upon work-up predominantly the correspondingly substituted succinonitriles.[3–7] However, 2,2′-azobis-2-cyclopropylprionitrile I has been found to decompose at an anomalously rapid rate,[4,5] forming colored solutions in the process. In an attempt to elucidate the reasons for this behavior, the nature of the decomposition products under various conditions was investigated.

Results

Decomposition of 2,2′-azobis-2-cyclopropylpropionitrile I[3–5] in hexane at 69° gave predominantly an unidentified brown polymeric material of low molecular weight. This material gradually decomposed upon heating to 300° without exhibiting a definite melting point. It was insoluble in all common organic solvents except acetic acid and did not reprecipitate from solution upon dilution with water unless basified. The solid gradually evolved ammonia upon standing. Infrared and n.m.r. spectra showed the presence of the cyclopropyl group and the absence of unsaturation. The infrared spectrum also showed the presence of the

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[1] This is the 41st in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and G. Kesslin, *J. Org. Chem.*, **27**, 3898 (1962).

[2] Taken from the dissertation submitted by Martin Tobkes to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1963, and from the thesis of Arnold Zweig for the degree of Bachelor of Science in Chemistry, 1955.

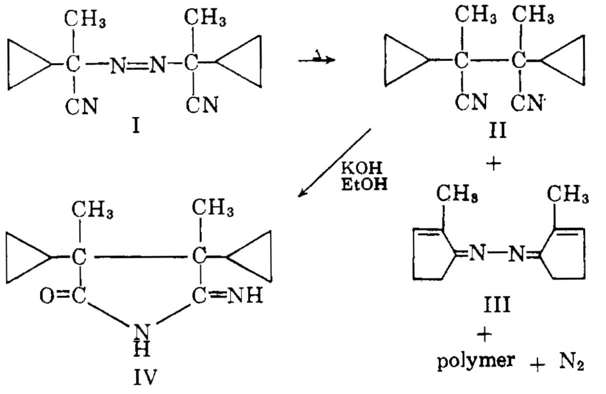
[3] C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949).

[4] C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951).

[5] C. G. Overberger and A. Lebovits, *ibid.*, **76**, 2722 (1954).

[6] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

[7] A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).



nitrile group. This material was not investigated further.

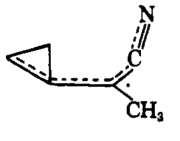
The normal coupled product II was isolated in 19% yield. Its infrared and n.m.r. spectra and elemental analysis were consistent with the expected structure. Saponification with 40% ethanolic potassium hydroxide afforded 3,4-dimethyl-3,4-dicyclopropyl-5-iminopyrrolidin-2-one IV, whose structure was confirmed by elemental analysis and ultraviolet and infrared spectra.

A yellow crystalline solid could be sublimed from the decomposition products in 7.4% yield. Its n.m.r. spectrum exhibited split peaks centered at 3.69 τ (vinyl protons), 7.45 τ (methylene protons) and 8.17 τ (methyl protons) with peak area ratios of 1.0:4.0:3.0, respectively. Elemental analysis indicated the empirical formula $C_{12}H_{16}N_2$. In contradistinction to the coupled dinitrile II (which is transparent in the ultraviolet), the yellow material exhibited strong ultraviolet absorption, with a triplet peak at 298, 287, and 277 mμ (22,600; 27,200; 23,200) and shoulders at 311, 267, and 257 mμ (10,400; 17,300; 14,200). Nitrile and cyclopropyl absorptions were absent in the infrared spectrum and a strong peak (with shoulder) was present at 1635 cm.$^{-1}$ (C=N and C=C). These data lent strong support to the belief that the yellow solid was probably 1-methylcyclopenten-5-one azine III. The compound was prepared unequivocally by the reaction of 1-methylcyclopenten-5-one[8] with hydrazine hydrate. The ultraviolet, infrared, and n.m.r. spectra of the two materials were superimposable and the mixture melting point was undepressed.

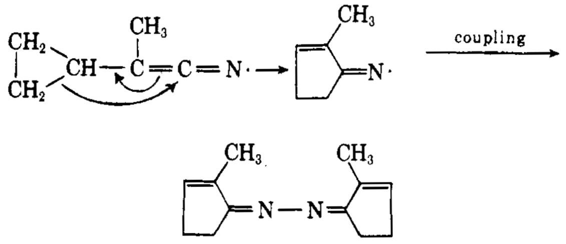
Solution decomposition of the azonitrile at 40° gave comparable yields of all three products. However, decomposition at the same temperature in the solid state afforded no azine, gave greater yields (63%) of coupled dinitrile, and yielded lower quantities of polymer. Essentially the same results were obtained from bulk decomposition at 25°.

Discussion

The anomalously rapid rate of decomposition of 2,2′-azobis-2-cyclopropylpropionitrile has already been shown not to be due to steric factors but has been explained by the suggestion of transition state resonance involving delocalization of the carbon–carbon bonds of the cyclopropyl ring.[4,5] This may be represented as



Electron distributions involving ketenimine free radicals $(\mathrm{R{-}\overset{R'}{\overset{|}{C}}{=}C{=}N\cdot})$ have been shown to make a significant contribution to the transition state in azonitrile decompositions.[9,10] It is possible that formation of azine III arises through rearrangement of such a ketenimine free radical.



III

The driving forces for the rearrangement may be the release of the strain in the cyclopropyl ring and the formation of a more highly conjugated system.

The formation of 3,4-dimethyl-3,4-dicyclopropyl-5-iminopyrrolidin-2-one IV upon saponification of the coupled dinitrile II is unusual, although the same type of product has been demonstrated to be formed upon alkaline peroxide hydrolysis of a related *vic*-dinitrile.[11] The ultraviolet and infrared spectra of our product exhibited the same salient features as that of the aforementioned workers.

The difference in proportions of dinitrile, azine, and polymer obtained from solution compared to bulk decompositions may be explained on the assumption of "freezing" of free radicals in the latter case. In solution the free radicals have the opportunity to leave the solvent cage, allowing sufficient time for rearrangements and other side reactions to occur before an appreciable amount of coupling can take place. On the other hand, in the solid state the free radicals are frozen in close proximity to one another, thus allowing coupling to be the favored process.

Experimental[12]

Decomposition of 2,2′-Azobis-2-cyclopropylpropionitrile (I).—A. In Hexane at 69°.—A solution of 18.7 g. (0.0865 mole) of 2,2′-azobis-2-cyclopropylpropionitrile[4] (m.p. 63.4–64.1°) in 625 ml. of hexane was stirred at reflux for a period of 4 hr. Nitrogen evolution had ceased by this time. The tan suspension was cooled to room temperature and filtered, giving 10.9 g. of a tan solid which had no definite melting point but gradually decomposed upon heating to 300°. The product was insoluble in all common organic solvents except acetic acid. Solutions in this solvent failed to reprecipitate product upon dilution with water but precipitation occurred upon addition of base. The intrinsic viscosity of the product in acetic acid at 30° was 0.07. The infrared spectrum (KBr disk) exhibited a nitrile peak at 2230 cm.$^{-1}$, cyclopropyl peaks at 3070 and 1025 cm.$^{-1}$, and other main absorption peaks at 3350, 2960, 1740, 1665–1630, 1450,

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[8] I. N. Nazarov, L. D. Bergel'son, I. V. Torgov, and S. N. Ananchenko, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 787 (1953).

[9] M. Talât-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3710, 3712 (1955).

[10] G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, *ibid.*, **81**, 4878 (1959).

[11] C. G. Overberger, G. Kesslin, and P.-T. Huang, *ibid.*, **81**, 3779 (1959).

[12] All melting points are corrected. Analyses by Schwarzkopf Microanalytical Laboratory Woodside, 77, N. Y. Ultraviolet absorption spectra were obtained on a Cary Model 14 spectrophotometer, infrared spectra on a Perkin–Elmer Model 21 spectrophotometer, and n.m.r. spectra on a Varian Associates Model HR-60 spectrometer.

and 1375 cm.$^{-1}$. The n.m.r. spectrum in trifluoroacetic acid exhibited broad absorption from 6.0–9.6 τ with main peaks at 8.33 τ (methyl protons) and 9.57 τ (cyclopropyl protons).

Anal. Found: C, 67.29; H, 7.45; N, 6.26.

Because the compound lost ammonia on standing, too much significance should not be placed upon the analytical results.

The filtrate from the decomposition was distilled, yielding 3.08 g. (18.9%) of *sym*-dimethyldicyclopropyl succinonitrile (II), b.p. 81–83°/0.4 mm, n^{25}D 1.4723, d^{25}_{4} 0.9857. The compound exhibited no ultraviolet absorption above 200 mμ. In the infrared (neat) characteristic peaks were present at 3080, 1027, and 868 cm.$^{-1}$ (cyclopropyl), 2230 cm.$^{-1}$ (nitrile), and 2870 and 1377 cm.$^{-1}$ (C—CH$_3$). The n.m.r. spectrum (CCl$_4$) showed split peaks centered at 8.46 τ (methyl protons) and 9.28 τ (cyclopropyl protons) with peak areas in the ratio of 2.9:5.0, respectively.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.84; H, 8.43; N, 15.16.

The residue from the distillation of the dinitrile was sublimed at 80°/0.02 mm, yielding 1.21 g. (7.4%) of the pale yellow 1-methylcyclopenten-5-one azine III, m.p. 96–101°. Analytically pure material, m.p. 101–103°, was obtained upon crystallization from ether. The ultraviolet spectrum in ether exhibited a triplet peak at 298, 287, and 277 mμ (22,600; 27,200; 23,200) with inflections at 311 (10,400), 267 (17,300) and 257 mμ (14,200). The infrared spectrum in carbon tetrachloride showed no absorption at 2200–2300 cm.$^{-1}$ (C≡N) and exhibited a strong shouldered peak at 1635 cm.$^{-1}$ (C═C, C═N). The n.m.r. spectrum in carbon disulfide showed split peaks centered at 3.69 τ (vinyl protons), 7.45 τ (methylene protons), and 8.17 τ (methyl protons) with peak areas in the ratio 1.0:4.0:3.0, respectively. No peaks above 9.0 τ (cyclopropyl protons) were observed.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.71; H, 8.71; N, 14.62.

B. In Hexane at 40°.—From 2.18 g. (0.0101 mole) of I in 50 ml. of hexane at 40°, there was obtained 1.41 g. of polymer. Spectral analysis of the filtrate from the decomposition showed the presence of 6.2% azine III and 14% dinitrile II.

C. In the Solid State at 25°.—After 9 months at 25°, 17.3 g. (0.0800 mole) of I gave 2.70 g. of polymer, 12.0 g. (80%) of dinitrile II, and no azine.

D. In the Solid State at 40°.—After 1 week at 40° there was obtained from 2.18 g. (0.0101 mole) of I, 0.596 g. of polymer, 1.19 g. (62.9%) of dinitrile II, and less than 0.5% azine III. Upon chilling a hexane solution of II, a small quantity of solid, m.p. 45–46°, was obtained. Its infrared spectrum was identical with the analytically pure sample of the liquid isomeric dinitrile mixture, strongly suggesting that it was one of the stereoisomers of the dinitrile.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.34; H, 8.72; N, 14.80.

3,4-Dimethyl-3,4-dicyclopropyl-5-iminopyrrolidin-2-one (IV).—A solution of 1.88 g. (0.010 mole) of *sym*-dimethyldicyclopropyl succinonitrile (II) and 5.6 g. (0.10 mole) of potassium hydroxide in 8.4 g. of 95% ethanol was refluxed for a period of 10 hr. After removal of solvent *in vacuo* the residue was suspended in 20 ml. of water and extracted several times with methylene chloride. The organic layer, after drying, was concentrated to a small volume and pentane was added. The yield of precipitated solid was 1.08 g. (52.3%), m.p. 204–212°. Several crystallizations from toluene and from ethyl acetate were necessary in order to obtain sharp-melting product, m.p. 231.5–232°. The infrared spectrum (KBr disk) showed the characteristic absorption of a monosubstituted amide with singlet peaks at 3333, 1670, and 1527 cm.$^{-1}$. The compound exhibited an ultraviolet absorption maximum (H$_2$O) at 231 mμ (17,200).

Anal. Calcd. for $C_{12}H_{18}N_2O$: C, 69.87; H, 8.80; N, 13.58. Found: C, 69.75; H, 8.85; N, 13.50.

2-Methylcyclopentanone.—The procedure followed was a modification of that of Hückel and Kindler,[13] using for the preparation of the intermediate 2-methyl-2-carbethoxycyclopentanone, methyl iodide in place of methyl bromide and vacuum distilling most of the solvent prior to drowning the reaction mixture in ice water.

From 474 g. (6.96 moles) of sodium ethoxide (prepared from 160 g. of sodium and 2600 ml. of absolute ethanol), 1000 g. (6.40 moles) of 2-carbethoxycyclopentanone (Arapahoe Chemicals, Inc.) and 1363 g. (9.60 moles) of methyl iodide there was obtained 675 g. (62%) of 2-methyl-2-carbethoxycyclopentanone, b.p. 122–124°/25 mm, n^{22}D 1.4458 (70%, 106°/14 mm.[13]; n^{20}D 1.4465[8]).

From 178.6 g. (1.05 mole) of 2-methyl-2-carbethoxycyclopentanone and 900 ml. of 20% aqueous perchloric acid there was obtained after 4 hr. of refluxing, 68.9 g. (66.9%) of 2-methylcyclopentanone, b.p. 139–141°/769 mm., n^{23}D 1.4332 (80%, 140°/758 mm., n^{20}D 1.4347[13]).

1-Methylcyclopenten-5-one.—Using the procedure of Nazarov, *et al.*,[8] there was obtained from the bromination of 49.0 g. (0.50 mole) of 2-methylcyclopentanone with 76 g. (0.48 mole) of bromine in the presence of 31 g. (0.37 mole) of magnesium carbonate followed by dehydrohalogenation with 80 ml. (0.50 mole) of diethylaniline, 9.0 g. (18%) of unchanged starting material, b.p. 139–141°, n^{25}D 1.4340 (17%, b.p. 37–39°/15 mm., n^{21}D 1.4360[8]) and 17.5 g. (36.4%) of 1-methylcyclopenten-5-one, b.p. 159–161°, n^{25}D 1.4767 (42%, 52–53°/15 mm., n^{22}D 1.4770[8]; 158–161°, n^{20}D 1.4771[14]). Correcting for recovery of unchanged starting material, the yield was 44.7% (51%[8]).

1-Methylcyclopenten-5-one Azine.—To 1.60 g. (0.0167 mole) of pure (by vapor phase chromatography) 1-methylcyclopenten-5-one stirred in a nitrogen atmosphere at 80° there was added dropwise over the course of 0.5 hr. a solution of 0.416 g. (0.00832 mole) of hydrazine hydrate in 5 ml. of absolute ethanol containing 1 drop of glacial acetic acid. After completion of the addition the solution was refluxed 0.5 hr. longer and then stirred overnight at room temperature. After removal of solvent *in vacuo* 1.41 g. (90%) of crude pale yellow solid remained. Vacuum sublimation followed by crystallization from ether afforded the pure product as yellow needles, m.p. 101.6–102.3°. A mixture melting point with azine III isolated from the azonitrile decomposition, m.p. 101–103°, was not depressed; mixed m.p. 100–102.5°. The ultraviolet, infrared, and n.m.r. spectra of the two products were identical.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.81; H, 8.62; N, 14.63.

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[13] W. Hückel and H. Kindler, *Chem. Ber.*, **80**, 202 (1947).

[14] A. M. Gaddis and L. W. Butz, *J. Am. Chem. Soc.*, **69**, 1203 (1947).