DL-Methylphenyltrifluoromethylcarbinol[20,21] (5.7 g), bp 95–100° (20 mm), prepared in 89% yield by the action of phenylmagnesium bromide on methyl trifluoromethyl ketone and in 90% yield by the action of methylmagnesium iodide on phenyl trifluoromethyl ketone) was treated in ether solution (30 ml) with sodium hydride (4.0 g, 50% mineral oil dispersion) followed by refluxing (1 hr) with dimethyl sulfate (4 g) to give the methyl ether **3** (6.1 g). This product showed no unreacted carbinol by vpc analysis (UCON LB 1715, 5 ft × 0.25 in., 150°, helium flow rate 30 ml/min, retention time 4 min): nmr (CDCl$_3$) δ 1.78 (q, 3 H, J = 0.8 Hz, long range CF$_3$ coupling), 3.22 (s, 3 H), 7.2 ppm (broad, 5 H, aromatic).

Anal. Calcd for C$_{10}$H$_{11}$F$_3$O: C, 58.81; H, 5.43. Found: C, 58.98; H, 5.51.

This material was used as a calibration standard for vpc and thin layer chromatography (tlc) studies in connection with the following sulfur tetrafluoride reactions.

Reactions of Sulfur Tetrafluoride with DL-*O*-**Methylatrolactic Acid 2.**—A stainless steel hydrogenation-type autoclave, 150-ml capacity, was charged with *O*-methylatrolactic acid[22] (2.0 g) and

cooled to −60°. Sulfur tetrafluoride (25 g) was condensed in the autoclave followed by hydrogen fluoride (29 g) and the mixture was shaken at 20–25° for 24 hr. The reaction mixture was processed as indicated previously.[23] No starting material was recovered but no methylphenyltrifluoromethylcarbinyl methyl ether could be detected by tlc. Essentially the same procedure was conducted at 50° for 22 hr and at 90° for 3 days. In these runs a spot was observed on tlc with the same R_f value as the desired ether, but preparative silica gel chromatography failed to isolate any of the desired ether. Further experiments in which SF$_4$ was added to the acid sample **2** in water to generate the HF *in situ* were likewise unsuccessful, leading in some cases to block residues and in others to mixtures like the above which contained no starting acid but in which the ether could not be detected.

Registry No.—3, 26315-60-6; **6** (R = H), 26315-61-7; **6** 2,4-DNP, 26315-62-8; **10,** 26315-63-9; **11,** 26315-64-0; **14,** 26164-19-2.

(20) G. V. Kazennikova, T. V. Talalaeva, A. V. Zimin, A. P. Simonov, and K. A. Kocheskov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* 1066 (1961); *Chem. Abstr.,* **55,** 271546 (1961).

(21) D. L. Dull, Ph.D. Thesis, Stanford University, 1967, p 110.

(22) D. J. Cram and K. R. Kopecky, *J. Amer. Chem. Soc.,* **81,** 2748 (1959).

(23) H. M. Peters, D. M. Feigl, and H. S. Mosher, *J. Org. Chem.,* **33,** 4245 (1968).

The Peroxide-Initiated Decarbonylation of 9-Carbazolylacetaldehyde. A Possible Free-Radical Displacement[1a]

BRUNO M. VITTIMBERGA AND MATTHEW L. HERZ[1b]

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881

The peroxide initiated decarbonylation of 9-carbazolylacetaldehyde was studied in *o*-dichlorobenzene at 140 and 170° in an effort to observe a free radical N → C migration. No migration was detected. A reaction did occur, however, with the formation of 9-methylcarbazole, 1,2-dicarbazol-9-ylethene, and dicarbazol-9-ylmethane. Evidence is presented to support the structures of these compounds and the mechanism of their formation.

As part of a study on free-radical migration reactions,[2,3] we were prompted to investigate the peroxide-initiated decarbonylation of 9-carbazolylacetaldehyde (1). It was hoped that the stabilizing forces in this molecule would contribute to the first example of a nitrogen to carbon free-radical migration.[4]

This system was chosen because of its similarity to 9-phenyl-9-fluorenylacetaldehyde (2) which on decarbonylation was found to give a smooth conversion to

$$Cb{-}CH_2{-}\overset{\overset{\textstyle O}{\|}}{C}{-}H$$

1

2

$$\left(Cb = \text{[carbazol-9-yl]} \right)$$

9-phenylphenanthrene.[5] Similar rearrangement in **1** would reduce ring strain with the simultaneous formation of the strongly stabilized free radical of the type R—CH$_2$—Ṅ—Ar.

The desired rearrangement would be expected to occur irreversibly[6] and most probably lead to the formation of the stable aromatic compound, phenanthridine, in a manner similar to the reaction of **2**. Radical stabilization and relief of ring strain, which are not necessary for carbon-to-carbon migration,[7] could provide the necessary driving force for nitrogen-to-carbon homolytic phenyl migration.

The aldehyde, **1**, was synthesized by an alkaline permanganate oxidation of 9-allylcarbazole[8] to yield 1-carbazol-9-yl-2,3-dihydroxypropane. This glycol was further oxidized with periodic acid to yield **1** the structure of which was verified by infrared, nmr and elemental analyses.

The di-*t*-butyl peroxide (DTBP) initiated decarbonylation was carried out both in the presence of oxygen and in deoxygenated systems. The results appear in Table I. When the decarbonylation was carried out in the presence of excess oxygen under the various conditions described in Table I (runs 1, 2, and 3), the only product
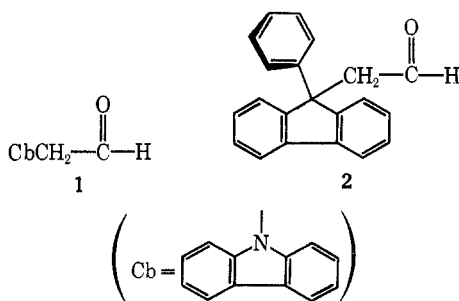
(1) (a) Based on the Ph.D. Thesis of M. L. Herz, University of Rhode Island, 1969. U.S. Army Natick Laboratory, Natick, Mass. (b) American Hoeshst Fellow, 1967–1968.

(2) For a review, see C. Walling, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 409 ff.

(3) (a) J. W. Wilt and M. Stumpf, *J. Org. Chem.,* **30,** 1256 (1965); (b) J. W. Wilt and O. Koluve, *J. Amer. Chem. Soc.,* **87,** 2071 (1965); (c) J. W. Wilt, O. Koluve, and J. F. Kraemer, *ibid.,* **91,** 2624 (1969).

(4) A possible 1,3-N → C migration has recently been described by R. W. Binkley, *Tetrahedron Lett.,* 1893 (1969).

(5) B. M. Vittimberga, *ibid.,* 2383 (1965).

(6) W. Rickatson and T. S. Stevens, *J. Chem. Soc.,* 3960 (1963).

(7) (a) W. H. Urry and N. Nicholaides, *J. Amer. Chem. Soc.,* **74,** 5163 (1952). (b) F. H. Seubold, *ibid.,* **75,** 2532 (1953); (c) L. H. Slaugh, *ibid.,* **81,** 2262 (1959).

(8) This compound was prepared using a modification of the procedure of B. Levy, *Monatsh. Chem.,* **33,** 182 (1912).

TABLE I

DECARBONYLATION OF CARBAZOLYLACETALDEHYDE

Run	Concn,[a] M	% CO[b]	% Cb–CH₃[c]	% Cb₂CH₂[c]	% Cb—CH= CH–Cb[c]
1[d,e]	Neat	35			12.8
2[e]	6				2.4
3[d,f]	6				0.8
4	1	58	8.6	4.3	
5	3	60[h]	9.3	4.7	
6	6	58	6.5	7.2	
7	6[i]	40	7.2	3.7	
8[g]	6	50	30.6	0.4[j]	

[a] The solvent used was o-dichlorobenzene. Unless otherwise noted the reaction temperature was 140° using two 20 mol % portions of DTBP added 2 hr apart. [b] Carbon monoxide was based on the theoretical amount of gas that would be produced in a complete reaction and was detected by vpc; however, the per cent of gas evolved is uncorrected for other possible volatile products making these values approximations. [c] Based on the total amount of recovered solids. [d] DTBP (90 mol %) was employed at 170°. [e] Oxygen was present in the reaction system. [f] Solution saturated with oxygen. [g] Thiophenol (35 mol %) was present. [h] DTBP (one 40 mol % portion) was used. [i] Not degassed, but in a closed system with very limited oxygen. [j] Recovered 0.500 g of the disulfide.

that could be isolated from the reaction mixture was 1,2-dicarbazol-9-ylethene (4). The structure of 4 was

$$Cb—CH{=}CH—Cb$$
4
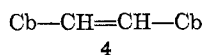
assigned on the basis of its elemental, infrared, and mass spectrographic analysis and by its synthesis from 1,2-dicarbazol-9-ylethane (*vide infra*).

The yields of 4 were low and varied. In the case where none of this olefin was formed, the products were the same as those formed in deoxygenated systems (*vide infra*) The presence of oxygen in sufficient amounts appeared necessary for the formation of this product. This was evident from the fact that only those reactions in which a large amount of oxygen was present in the system (runs 1, 2, and 3) gave 4. Presumably, when oxygen was present in limited quantities it could be flushed from the reaction mixture by the volatile products formed in the reaction.
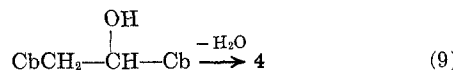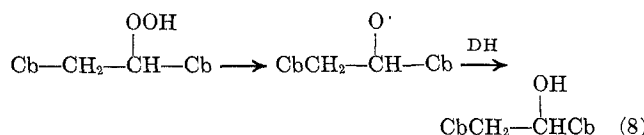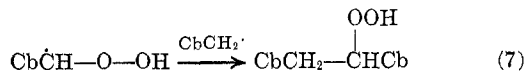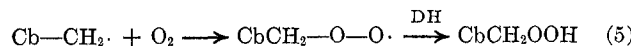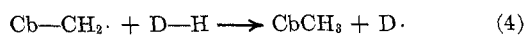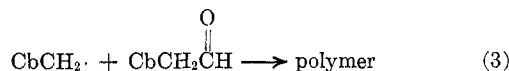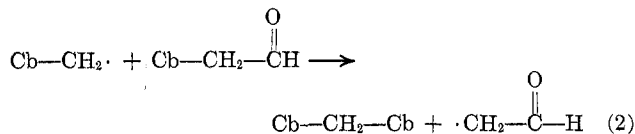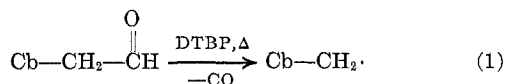
When the solutions were deoxygenated prior to reaction, two different products were isolated along with polymeric material and unreacted aldehyde. The compounds were identified as 9-methylcarbazole (5) and the novel dicarbazol-9-ylmethane (6), the structure of which was assigned on the basis of its elemental, ir, nmr and mass spectrographic analyses [m/e (rel intensity) 346 (16, M⁺), 180 (100)]. Further support for structure 6 was obtained by treating this compound with 47% hydriodic acid which produced carbazole in 83% yield. The decarbonylation data indicate that the 9-carbazolylmethyl radical is rather stable and does not propagate the reaction.

Contrary to results found in other systems (*i.e.*, the neophyl radical[9]), dilution did not change the nature of the products formed. This indicates that if any rearrangement were possible, it would occur at a much slower rate than the other processes which consume the radical, such as coupling, hydrogen abstraction, etc.

At first it was felt that dicarbazolylethene 4 was formed by coupling of the unrearranged radical followed by oxidation. To test this hypothesis the cou-

(9) S. Winstein and F. H. Seubold, *J. Amer. Chem. Soc.*, **69**, 2916 (1947).

pling product, 1,2-dicarbazole-9-ylethane (7) was synthesized by a carbazole anion displacement on the ditosylate of ethylene glycol. Surprisingly, this compound was found to be very stable at temperatures up to 170° even in the presence of oxygen and was recovered unchanged when added to decarbonylation reactions of 1. It could, however, be dehydrogenated at 170°, in the presence of both oxygen and large amounts of DTBP, to the olefin 4 and amorphous material. The conversion of 7 to 4 most likely occurs by way of the hydroperoxide which then reacts according to eq 8 in the scheme below.

The following mechanism is proposed to explain the observations.

$$Cb—CH_2—\overset{\overset{O}{\|}}{C}H \xrightarrow[-CO]{DTBP,\Delta} Cb—CH_2\cdot \qquad (1)$$

$$Cb—CH_2\cdot + Cb—CH_2—\overset{\overset{O}{\|}}{C}H \longrightarrow$$
$$Cb—CH_2—Cb + \cdot CH_2—\overset{\overset{O}{\|}}{C}—H \qquad (2)$$

$$CbCH_2\cdot + CbCH_2\overset{\overset{O}{\|}}{C}H \longrightarrow polymer \qquad (3)$$

$$Cb—CH_2\cdot + D—H \longrightarrow CbCH_3 + D\cdot \qquad (4)$$

$$Cb—CH_2\cdot + O_2 \longrightarrow CbCH_2—O—O\cdot \xrightarrow{DH} CbCH_2OOH \qquad (5)$$

$$Cb—CH_2OOH \xrightarrow{+O\cdot} Cb\dot{C}H—O—O—H \qquad (6)$$

$$Cb\dot{C}H—O—OH \xrightarrow{CbCH_2\cdot} CbCH_2—\overset{\overset{OOH}{|}}{C}HCb \qquad (7)$$

$$Cb—CH_2—\overset{\overset{OOH}{|}}{C}H—Cb \longrightarrow CbCH_2—\overset{\overset{O\cdot}{|}}{C}H—Cb \xrightarrow{DH} CbCH_2—\overset{\overset{OH}{|}}{C}HCb \qquad (8)$$

$$CbCH_2—\overset{\overset{OH}{|}}{C}H—Cb \xrightarrow{-H_2O} 4 \qquad (9)$$

When oxygen is present in the reaction of 1 it acts to prevent the formation of 5 and 6 and reaction 5 becomes the major path for the production of monomeric products. The 9-carbazolylmethyl radical is trapped by oxygen and consequently is prevented from undergoing reactions 2, 3, and 4, thereby allowing the formation of 4. Although it is probable that dicarbazolylethane 7 once formed would be converted to the olefin, the absence of this compound among the products of any of these reactions, particularly those carried out in the absence of oxygen, makes it highly doubtful that coupling is a reaction of any importance in this system. Moreover, at temperatures above 100° it would be expected that formation and decomposition of hydroperoxides would become increasingly competitive especially at the higher temperatures.[10] Besides the normal peroxide induced reactions, oxidation of the starting material, intermediates, and products can occur thereby reducing the amount of monomeric material obtained.

In deoxygenated solutions the carbazolylmethyl radical is sufficiently reactive to undergo reactions 2-4. Although this radical is present in large concentrations

(10) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 710.

in these solutions, it does not undergo coupling to any observable extent with thiyl, *t*-butoxy, or methyl radicals (the latter produced by the decomposition of the *t*-butoxy radicals). For the most part it undergoes nonchain reactions with the starting aldehyde, **1**, such as attack on the carbonyl group or aromatic substitution on the very active carbazole nucleus.[11] These reactions are the most likely source of the polymeric material which makes up the remainder of the reaction products.

The 9-carbazolylmethyl radicals which are not consumed by polymer formation react by two possible routes to form discrete products. They can either abstract hydrogen to form 9-methylcarbazole (reaction 4) or undergo a reaction with **1** that appears to be a free radical displacement (reaction 2). Acetaldehyde radicals which would also form through this mechanism would be expected to undergo decomposition under the conditions of the reaction.[12]

In order to test the possibility that dicarbazolylmethane might arise from the coupling of 9-carbozolyl and 9-methylcarbazolyl radicals, the decarbonylation was carried out in the presence of thiophenol as a radical trap. No detectable carbazole, which is stable under the conditions used, was formed in the reaction thus precluding this coupling mechanism as a possibility.

The polymeric material which was obtained was not examined extensively since it could not be purified by chromatography, sublimation, or recrystallization. Infrared and nmr analysis of this material show it to be an amorphous, polymeric substance very similar to that obtained by the acid catalyzed condensation of **1**.[13]

It is very doubtful that any rearrangement occurred, since phenanthridine was found to be stable to the reaction conditions. The results obtained with the addition of a hydrogen donor show the 9-carbazolylmethyl radical to be the major radical produced by the decarbonylation which has its origin in **1**. The failure of this radical to undergo rearrangement could be due, in part, to a stabilizing influence of the nitrogen atom as well as the possible delocalization over the π system of carbazole. Its poor hydrogen abstracting ability and simple HMO calculations carried out on this system support such possibilities.[14] The large bond order associated with the 9,10 bond would further increase the activation energy to prevent the rearrangement.

(11) W. A. Waters and J. E. White, *J. Chem. Soc. C*, 740 (1968).

(12) The two most likely products to be formed from reactions of the acetaldehyde radical, · CH₂C(═O)H, are ketene and acetaldehyde. Under the conditions of the reaction the latter would undergo decarbonylation to yield carbon monoxide and methyl radical. R. K. Brinton and D. H. Volmen [*J. Chem. Phys.*, **20**, 1053 (1952)] found that in the gas phase DTBP did, in fact, cause this decarbonylation at temperatures of 124 to 156°. For another example of a free-radical displacement, see H. M. Frey and R. Walsh, *Chem. Commun.*, 159 (1969).

(13) M. L. Herz and B. M. Vittimberga, Abstracts, First Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 1969, No. 226. The ir spectrum of the product obtained from the acid-catalyzed condensation of **1** had bands at 3410, 2990, 2940, 1750, 1205, 1120, 720, and 745 cm⁻¹. The intractable material from the decarbonylation reaction showed similar absorption except for the fact that its bands were broadened and differed in intensity at 1740 (C═O) and 3410 cm⁻¹ (OH). The nmr (acetone-*d₆*) spectrum showed typical, intense but undefined carbazole resonance (δ 8.3–6.8) and broad unresolved peaks of varying (between samples) intensities between δ 5.9 and 1.1.

(14) For a discussion of the possible stabilizing effect of nitrogen, see R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1967). Bond orders and free-valence indices were determined for this system on an IBM 360 Model 50 computer using a coulomb integral of 1.5 and a resonance integral of 1.0: see A. Streitwieser, Jr., "Molecular Orbital Theory," Wiley,

Further efforts are being made to obtain information which might allow greater insight into the mechanism of this and other related reactions.

Experimental Section

All melting points are corrected and were determined on a Thomas–Hoover melting point apparatus. The nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer at 60 MHz using tetramethylsilane as an internal standard. Infrared spectra were determined in potassium bromide on either a Beckman IR-8 or a Perkin-Elmer Model 521 spectrophotometer. All the ultraviolet spectra were measured on a Cary Model 15 spectrophotometer in absolute ethanol. The microanalyses were performed by Micro-Analysis, Inc., Wilmington, Del.

Preparation of 9-Allylcarbazole.—The potassium salt of carbazole, prepared from the fusion at 260° of 100 g (0.582 mol) of carbazole and 34.0 g (0.606 mol) of potassium hydroxide, was mixed with 50.0 ml (70.0 g, 0.538 mol) of allyl bromide, 80 ml of dry benzene, and 0.2 g of potassium iodide in a 500 ml erlenmeyer flask carrying a condenser capped with a drying tube. After 30 min of very moderate reaction, the flask was placed in an ice bath and 5 ml of dry DMF was added to produce a highly exothermic reaction. When the reaction had subsided, a further portion of 15 ml (21.0 g, 0.162 mol) of allyl bromide was added, the ice bath was removed, and the reaction was stirred overnight using a magnetic stirrer. The resulting slurry was filtered, the inorganic salts washed with acetone and the filtrate evaporated. The product (red crystals) was recrystallized from denatured ethanol (89.7 g, 0.434 mol, 74.5%): mp 55–56° (lit.⁸ mp 56°); ir 3060, 2990, 2945, 1625, 1420, 997, and 933 cm⁻¹; nmr (CDCl₃) δ 7.9–6.8 (m, 8), 5.73 (m, 1, -CH═), 4.90 (m, 2, CH₂═), and 4.60 (m, 2, CH₂).

1-Carbazol-9-yl-2,3-dihydroxypropane.—A solution of 100 g (0.483 mol) of 9-allylcarbazole, 2.0 g (0.356 mol) of potassium hydroxide, and 700 ml of acetone was cooled, with stirring, to ~10°. A solution of 80 g (0.595 mol) of potassium permanganate dissolved in 61% aqueous acetone was then added with vigorous stirring over a period of 1.5 hr at such a rate that the solution temperature remained constant. The mixture produced was stirred with 3 g of activated charcoal for 6 hr and the manganese dioxide was removed by suction filtration to give a light red solution. After evaporation of the acetone a solid remained which was purified by recrystallization, first from 50% aqueous methanol and then from denatured ethanol, to yield the desired product (76.7 g, 0.318 mol, 65.8%): mp 134.5–136°; ir 3240 (O–H), 1030, and 1050 cm⁻¹ (C–O); nmr (acetone-*d₆*) δ 7.5 (m, aromatic), 4.41 (m, CH₂-Cb), 4.11 (s, 2, O–H), 3.82 (m, CH-OH), and 3.62 (m, CH₂-OH).

*Anal.* Calcd for C₁₅H₁₅NO₂ (241.3): C, 74.67; H, 6.27; N, 5.81. Found: C, 74.72; H, 6.34; N, 5.90.

9-Carbazolylacetaldehyde (1).—To a solution of 20.0 g (0.083 mol) of the diol and 850 ml of 76% aqueous methanol was added with stirring 20.0 g (0.088 mol) of periodic acid in 250 ml of water. This produced a gold colored solution which immediately gave a white precipitate. After 1.5 hr, 600 ml of water was added and the precipitate was collected on a filter, washed well with water, and dried over anhydrous calcium chloride. Crystallization of this product from carbon tetrachloride gave the pure aldehyde (16.2 g, 0.078 mol, 93.5%): mp 140.5–141.5°; ir 2850 (aldehyde C–H), and 1730 cm⁻¹ (C═O); nmr (CDCl₃) δ 9.63 (t, 1, *J* = 4.0 Hz), 7.5 (m, 8), 4.76 (d, 2, *J* = 4.0 Hz).

Anal. Calcd for C₁₄H₁₁NO (209.25): C, 80.36; H, 5.30; N, 6.70. Found: C, 80.46; H, 5.23; N, 6.66.

The 2,4-dinitrophenylhydrazone of **1** melted 125–126°.

Materials and Equipment Used in the Free-Radical Decarbonylations.—Matheson, Coleman, and Bell 1,2-dichlorobenzene was purified by shaking successively with (1) small portions of concentrated sulfuric acid until the acid layer remained *colorless*,

New York, N. Y., 1961, p 123. These values are shown below in the usual manner.
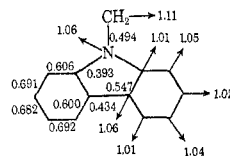
(2) water, (3) 10% aqueous sodium carbonate until carbon dioxide evolution ceased, (4) water, and then dried over calcium chloride and distilled (bp 178.5–179.0°). The di-*t*-butyl peroxide (DTBP) was distilled under vacuum [bp 55–56° (120 mm)]. Matheson, Coleman, and Bell benzenethiol [bp 53–54° (10 mm)] was used without further purification.

The vpc analysis of the gases produced by the decarbonylation was carried out using a Perkin-Elmer Model 154 vapor fractometer equipped with a 20 × 0.25 in. column containing molecular sieve 5A. The analysis was carried out at room temperature with a helium carrier gas flow rate of 3 cc/min in order to confirm the evolution of carbon monoxide as a reaction product.

Thermal Stability of 1.—The 9-carbazolylacetaldehyde (0.50 g, 0.24 mmol) and 2.5 ml of *o*-dichlorobenzene were placed in a 18 × 150 mm test tube. After the tube was flushed with nitrogen gas, which was bubbled through the solvent for 30 min, it was sealed with a rubber stopper, equipped with a rubber policemen which had been slit to act as a gas bleed, and then heated at 140° for 8 hr. At the end of this time the light tan solution was cooled yielding crystals of 1 with a brownish tint (mp 138–140°).

Thermal Stability of 1 in the Presence of Thiophenol.—The thermal stability experiment described above was repeated using 0.50 g (0.24 mmol) of aldehyde, 0.25 ml (0.209 g, 0.244 mmol) of thiophenol and 2.5 ml of *o*-dichlorobenzene. A temperature of 140–145° was used for a period of 7 hr. The solvent was removed on a rotary evaporator (90°) and the crystalline residue was recrystallized from carbon tetrachloride. The recovered material melted at 141–142° (0.46 g, 92%) and had an infrared spectrum which was superimposable on that of the starting aldehyde.

Carbazole Stability under the Reaction Conditions.—Carbazole 0.50 (2.00 mmol), was placed in a 50 ml three-necked flask equipped with a gas inlet tube, condenser, and serum cap. To this was added 5 ml of *o*-dichlorobenzene and the temperature raised to 144–145°. Nitrogen was bubbled into the mixture as the temperature was raised and throughout the entire reaction period. After 1 hr at this temperature 0.175 g (0.22 ml, 1.20 mmol, 40 mol %) of DTBP was injected through the serum cap causing the solution to darken slightly. Heating was continued for 4 hr at this temperature. Then on cooling, a crystalline mass formed, wt 0.66 g. The solid was recrystallized from ethanol giving white crystalline plates melting at 243.5–244.5°. This was shown to be carbazole by infrared spectroscopy and mixture melting point determination, wt 0.47 g (95%).

Phenanthridine Stability under the Reaction Conditions.—The experiment described above for carbazole was repeated with phenanthridine. The quantities used were 0.50 g (2.79 mmol) of phenanthridine, 0.162 g (0.204 ml, 1.11 mmol) of DTBP and 5 ml of *o*-dichlorobenzene. At the end of the 4 hr reaction time the solvent was removed under vacuum giving 0.58 g of white solid as a residue. Recrystallization from ethanol gave 0.46 g (92%) of white crystals which melted at 106–107° and which had an infrared spectrum identical with that of a known sample of phenanthridine. Mixture melting point determination with the starting material showed no depression.

Preparation of 9-Methylcarbazole.—Carbazole (15 g, 0.090 mol), methyl sulfate (15.0 ml, 20.0 g, 0.159 mol) and 75 ml of acetone were stirred with a magnetic stirrer for 10 min. To this rapidly stirred mixture was added 15.0 g (0.376 mol) of sodium hydroxide in 10 ml of water. After 15 min the carbazole had gone into solution with the formation of precipitate of sodium sulfate. The mixture was then poured into 600 ml of water containing 25 ml of concentrated ammonium hydroxide to precipitate the desired product. The reaction gave an almost quantitative yield of 9-methylcarbazole which was recrystallized from 95% ethanol: mp 86–89° (lit.[16] 88°); ir 3045, 2920, 1462, and 1350 cm⁻¹; nmr (CDCl₃) δ 8.2–2.0 (m, 8, aromatic), 3.66 (s, 3).

Preparation of the Ditosylate of Ethylene Glycol.—To a cooled solution of 10.0 g (9 ml, 0.161 mol) of ethylene glycol and 150 ml of pyridine in a 250 ml erylenmeyer flask was added 120 g (0.630 mol) of tosyl chloride with vigorous stirring. After a solution had formed the flask was left in the refrigerator for 8 hr. The crystalline mass which formed was poured into 600 ml of cold water and the mixture stirred for 15 min. The product was separated by filtration and dried in a vacuum desiccator (57.0 g, 0.154 mol, 96%), mp 117–119° (lit.[16] 126–127°).

Preparation of 1,2-Dicarbazol-9-ylethane.—The ditosylate of ethylene glycol (30.0 g, 0.081 mol) was placed in a 500 ml round-

bottomed flask. A solution of 16.0 g (0.097 mol) of carbazole, 20 g (0.50 mol) of sodium hydroxide, 13 ml of water, and 150 ml of acetone was added to the flask and the mixture stirred for 30 min. The solution was then heated at reflux on a steam bath for 6 hr. The resulting solution was evaporated to one-half volume and poured with stirring into 350 ml of water to produce a brown precipitate which was isolated on a filter and washed with water to give a pasty mass. After drying in a vacuum desiccator over calcium chloride the crude product was extracted with hot ligroin (bp 60–90°). The residue was recrystallized from benzene to give the desired product, **7** (2.1 g, 5.85 mmol, 7.2%): mp 304–305°; ir 3050, 2950, and 2890 cm⁻¹ (C–H).

Anal. Calcd for $C_{26}H_{20}N_2$ (360.5): C, 86.63; H, 5.59; N, 7.77. Found: C, 86.72; H, 5.57; N, 7.65.

Stability of 1,2-Dicarbazol-9-ylethane. A. At 140°.—In a 25 ml flask equipped with a condenser 0.50 g (1.39 mmol) of **7** was dissolved in 5 ml of *o*-dichlorobenzene at 140°. To this solution was added 0.26 ml (0.206 g, 1.41 mmol) of DTBP and the reaction vessel was shaken for 4 hr while open to the atmosphere. The contents of the flask, allowed to cool, formed a crystalline mass (0.424 g), which was found to be starting material by ir and melting point, and tars which were not examined extensively. Infrared spectra showed that no conversion to dicarbazolylethene (4) had been effected.

Similarly, 0.20 g (0.555 mmol) of **7** was heated at 140 with 2 ml of *o*-dichlorobenzene and 0.050 ml (0.054 g, 0.488 mmol, 88 mol %) of thiophenol for 5 hr. All the starting material in this case was recovered unchanged.

B. At 170°.—In a 18 × 150 mm test tube 200 mg of **7** was heated at 170° for 17 hr while oxygen was bubbled through the solution. Upon cooling 0.194 g of the starting material (identified by mp and infrared spectrum) was recovered unchanged.

In a 10 ml pear-shaped flask equipped with a gas-inlet tube and a condenser, 0.200 g of **7** in 1 ml of *o*-dichlorobenzene was flushed for 1 hr with nitrogen at 170° (bath temperature). Then over a period of 2 hr 0.0804 g (0.666 g, 4.56 mmol, 800 mol %) of DTBP was added. Heating was continued with nitrogen flushing for 15 hr after which, upon cooling, 0.184 g of slightly impure starting material was recovered (mp 289–293°). The filtrate contained ~60 mg of a red amorphous material which contained no olefin (4) as determined by ir spectral analysis, but some small amount of carbazole substituted material that could not be isolated in amounts large enough to identify.

Using similar apparatus 0.200 g of **7**, 1.22 ml (1.23 g, 1.12 mmol) of thiophenol, and 1 ml of *o*-dichlorobenzene was heated at 167° (bath temperature) for 16 hr with an oxygen flow. The solution was then poured into 10 ml of 95% ethanol to precipitate unchange **7**, 0.180 g (mp 301–303°; ir identical with that of an authentic sample). Further manipulation resulted in the isolation of 0.430 g of phenyl disulfide [mp 59–60 (lit.[17] 61°) which did not depress the melting point of an authentic sample upon admixture and which had an ir spectrum identical with that of a standard spectrum (*vide ante*)].

A mixture of 1.00 g (2.78 mmol) of 1,2-dicarbazol-9-ylethane, 2.0 ml (1.59 g, 10.9 mmol) of DTBP, and 4 ml of *o*-dichlorobenzene was heated in an 18 × 150 mm test tube open to the atmosphere at 165–170° (bath temperature) for eight hr. At the end of this time a second 2 ml portion of DTBP was added and the heating continued for a total of 20 hr to produce a deeply colored solution from which crystals (0.220 g) were separated. The remainder of the material was separated on 50 g of Woelm neutral alumina (activity grade I) in an 18 × 300 mm column. The elution of this material with hexane, hexane-benzene (3:1), and hexane-benzene (2:1) produced a clear oil (0.068 g) which appeared by ir and nmr spectroscopy to be predominantly aliphatic material and was evidently produced by the peroxide decomposition.[18] Further elution with hexane-benzene (1:1), hexane-benzene (1:2), and benzene gave 0.063 g of crystalline material. Finally, elution with polar solvents produced amorphous materials which contained small amounts of carbazole (~0.050 g estimated by ir spectra). The crystalline material was composed of a mixture of the 1,2-dicarbazol-9-ylethene and lesser amounts of starting material. Comparison

(15) T. S. Stevens and S. H. Tucker, *J. Chem. Soc.*, **123**, 2140 (1923).
(16) W. F. Edgell and L. Parts, *J. Amer. Chem. Soc.*, **77**, 4899 (1955).

(17) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1934, p 653.
(18) The ir spectrum shows weak absorption at 3045, 750, and 720 cm⁻¹ characteristic of the carbazole ring system. The nmr spectrum had extremely weak bands at about δ 7.5 with broad complex bands at δ 4.0–0.8. On this basis it was assumed that this fraction is principally aliphatic in nature and was probably derived from reactions of the initiator.

of the ir spectrum of the mixture with the spectra of prepared mixtures of the authentic materials provides an estimated 70%, 1,2-dicarbazol-9-ylethene (*vide infra*). Careful recrystallizations of the material from benzene gave 0.135 g: mp 333–336°; ir spectrum and mixture melting point determination further confirmed the identity of the compound. Thus the dehydrogenation produced 0.202 g (0.566 mmol, 20.4%) of 4 and large quantities of intractable decomposition product leaving 0.086 g (9%) of recoverable starting material.

Decarbonylation of 9-Carbazolylacetaldehyde. A. In the Presence of Oxygen with 90 mol % of Peroxide at 170° (Table I, Run 1).—In a 50 ml flask maintained at 170 ± 5° and equipped with an addition funnel and a condenser, followed by an inverted graduated cylinder to collect gases, was placed 7.0 g (0.033 mol) of 1. DTBP (4.40 g, 0.030 mol, 90 mol %) was then added over a period of 3.5 hr and the mixture was heated for another 15.5 hr during which time ~260 ml (35% of the theoretical amount) of gases was evolved. The solution which resulted was placed in acetone to separate a refractory crystalline material and a soluble amorphous material. The crystalline material upon recrystallization from benzene gave 0.71 g (2.03 mmol, 12%) of 1,2-dicarbazol-9-ylethene (4): mp 340–342° dec; ir 3080, 3045, 930, 915, and 890 cm^{-1}; mass spectrum (70 eV at 240°) m/e (rel intensity) 359 (37), 358 (100, M$^+$), 192 (16), 191 (18), 190 (6), 180 (10), 179 (26), 178 (16), 176 (10, M^{2+}), 167 (7), 166 (6), 165 (9), 152 (5), 140 (5).

Anal. Calcd for C$_{26}$H$_{18}$N$_2$ (385.4): C, 87.12; H, 5.06; N, 7.82. Found: C, 86.93; H, 4.67; N, 7.88; mol wt (by mass spectroscopy), 358.

The remainder of the material could be separated into two portions both with a reddish brown color; one was an ether soluble glass and the other an ether insoluble amorphous solid. These materials had identical spectra, which were very similar to that of other amorphous solids obtained in the condensations and other decarbonylation experiments (*vide infra*) and which proved to be intractable.[13]

B. In the Presence of Oxygen with 60 mol % Peroxide at 140° (Run 2).—In a flask maintained at 140 ± 1° connected to a shaker apparatus and open to the atmosphere was placed 5.0 g (2.39 mmol) of 1 and 5.0 ml of o-dichlorobenzene forming a light yellow solution. To this, 2.10 g (1.43 mmol, 60 mol %), of DTBP was added in three portions over a period of 6.5 hr. The oil with a reddish-brown color produced by the reacton was dissolved in a minimum of carbon tetrachloride and this concentrated solution placed on a 22 × 350 mm column of 60 g of Mallinckrodt silicic acid (100 mesh). Elution with hexane gave only o-dichlorobenzene (~4.5 ml) and with hexane–benzene (1:1) gave 0.10 g of a crystalline material which was identified by ir spectrum and mp as 4. Further elution with this solvent mixture followed by hexane–benzene (1:3) gave a red tar, from which starting material could be separated by crystallization from carbon tetrachloride, and an amorphous solid. Further elution with ether and acetone gave a second band of the amorphous solid. Finally, methanol was used to strip the column of any remaining organic matter. It was estimated from the characteristic carbonyl absorption (1730 cm^{-1}) that ~1.6 g of the aldehyde (32%) was still present in a mixture with the amorphous solids. These solids (~3.1 g) gave infrared spectra like that obtained for the amorphous materials in the preceding experiment.

C. In Deoxygenated Solutions with 40 mol % Peroxide at 140° (Runs 4–7).—In a flask maintained at 140 ± 1° connected to a shaker apparatus and to an inverted gas buret was placed 2.50 g (0.012 mol) of 1 and 2.0 ml of o-dichlorobenzene (6 M). To the solution which formed after 5 min, 0.584 g (0.0048 mol, 40 mol %) of DTBP was added over a period of 4 hr. The reaction solution was allowed to cool and was then chromatogrammed on a 22 × 350 mm column of Mallinckrodt silicic acid (100 mesh). Elution with solvent mixtures of increasing polarity yielded 1, 5, and carbazole mixed with colored amorphous material.

Since 6 is insoluble in ether and acetone, it could be separated easily by washing with ether or ether–acetone mixtures in which 5 or carbazole are soluble. The identification of these components of the reaction mixture was made by comparison of their melting points and ir spectra with those of authentic samples.

Decarbonylations were carried out employing this procedure for product separation of 1 M (run 4) and 3 M (run 5) concentrations of aldehyde. With these low concentrations of 1 it was necessary to remove most of the o-dichlorobenzene by flash

evaporation at 90° before chromatography. The various reaction conditions and results are listed in Table I.

D. With Mercaptan Using 40 mol % Peroxide at 140° (Run 8).—To a deoxygenated solution of 5.0 g (2.39 × 10^{-2} mol) of 1, 0.845 ml (0.911 g, 34.6 mol %) of thiophenol, and 4.0 ml of o-dichlorobenzene (6 M)—in a flask connected to a shaker apparatus and an inverted gas buret, and maintained at 140 ± 1°—was injected 1.76 ml (1.40 g, 40 mol %) of DTBP over a period of 4 hr. The solvent was removed by flash evaporation at 90° and replaced with carbon tetrachloride (~25 ml). From the solution crystallized 0.537 g of 1 (mp 140–142°) which was isolated on a filter. The remaining material which was dissolved in a minimum amount of carbon tetrachloride was separated as usual by column chromatography on silicic acid to yield, in order of elution from the column, phenyl disulfide,[19] 5, a mixture of 5, 6, and carbazole,[20] and mixtures of colored glasses.

The product yields are given in Table I (run 8).

The 9-methylcarbazole was identified by comparison of ir and nmr spectra and mp (87–89°) with those of an authentic sample (*vide ante*). In addition its structure was confirmed by its mass spectrum (70 eV) m/e (rel intensity) 181 (57, M$^+$), 166 (100, M$^+$ − CH$_3$), 165 (43), 152 (13, M$^+$ − :N–CH$_3$), 140 (10), 139 (34).

The structure of 6 was based upon the following data: mp 307° dec; ir 3045, 2960, 2920 (C–H), and 1060 cm^{-1}; nmr (CDCl$_3$)[21] δ 8.2–7.1 (m, 8) and 6.7 (s, 1); mass spectrum (70 eV) m/e (rel intensity) 347 (4.2), 346 (16, M$^+$), 181 (22), 180 (100), 167 (14), 152 (14), 140 (10).

Anal. Calcd for C$_{25}$H$_{18}$N$_2$ (346.4): C, 86.88; H, 5.24; N, 8.09. Found: C, 86.45; H, 5.51; N, 8.26; mol wt (by mass spectroscopy), 346.

E. In the Presence of 1,2-Dicarbazol-9-ylethane Using 40 mol % Peroxide at 140°.—In a 30 × 150 mm test tube were placed 0.625 g (2.99 mmol) of 9-carbazolylacetaldehyde, 0.625 g (1.74 mmol) of 1,2-dicarbazol-9-ylethane, and 6 ml of o-dichlorobenzene and the mixture heated to 140° in an oil bath. The solution which formed was degassed by bubbling in nitrogen gas for 15 min after which the tube was connected to a gas measuring system and the entire system flushed with nitrogen for an additional 15 min. Then 0.146 g (0.184 ml, 0.0012 mol, 40 mol % relative to aldehyde) of DTBP was injected and the gas evolution was measured for a period of 4 hr. When the red reaction mixture was cooled, crystals formed which were separated by filtration and recrystallized from benzene (0.263 g, mp 300–302°). This material was shown to be dicarbazolylethane by infrared and mixture melting point determination. The combined filtrates were then subjected to chromatographic separation on silicic acid. The total amount of solid isolated from the reaction was 1.195 g composed of 74.3 mg (6.7%) of 9-methylcarbazole, 13.4 mg (1.1%) of 1,2-dicarbazol-9-ylethene, 552.2 mg (46.3%) of 1,2-dicarbazol-9-ylathane, 33.0 mg (2.8%) of aldehyde (1), and 521.6 mg (43.6%) of amorphous solid. Identifications were made by melting point and infrared spectroscopy. Approximately 90% of the added dicarbazolylethane was recovered in this reaction.

Degradative Reactions of 6. A. Oxidation.—Using the method of Rieveschl and Ray,[22] 1.0 g (3.2 mmol) of dicarbazol-9-ylmethane was dissolved in 25 ml of glacial acetic acid and treated with 5.0 g (17 mmol) of sodium dichromate and 2.15 ml (2.37 g, 22.7 mmol) of acetic anhydride to give 0.1 g of carbazole (mp 242–247° and ir spectrum identical with that of an authentic sample) and water soluble oils which were not examined.

B. Reduction with Hydriodic Acid.—A mixture of 0.174 g (0.502 mmol) of 6 and 5.0 ml (2.85 g, 18.4 mmol) of 47% hydriodic acid in an 18 × 150 mm test tube was frozen at liquid

(19) The phenyl disulfide recovered from the column (0.230 g) was recrystallized once from 95% ethanol: mp 59–60° (lit.[17] 60–61°); ir 3090, 1590, 1480, 1440, 740, and 690 cm^{-1}; nmr (CDCl$_3$) δ 7.6–7.0 (m).

(20) The infrared spectrum of the material separated from 6 by extraction with ether indicates a very small band which could be attributed to the N–H stretching of carbazole. An estimate of the maximum quantity of carbazole present using the low intensity peak at 3420 cm^{-1} gives a value of 10 mg. If this band were carbazole, this amount is certainly much too small to lead to the large amount of dicarbazol-9-ylmethane obtained by this reaction without hydrogen donor present.

(21) This nmr spectrum was measured on a Varian HA-100 spectrometer using tetramethylsilane as an internal standard.

(22) G. Rieveschl, Jr., and F. E. Ray, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 420.

nitrogen temperature and the tube sealed. After heating the tube at 150° for 58 hr the contents were poured into water and the brown precipitate that was produced was isolated by filtration and dried. Recrystallization from 95% ethanol gave carbazole (0.140 g, 0.837 mmol, 83%) which was identified by its melting point and infrared characteristics.

Registry No.—**1**, 25557-77-1; 2,4-dinitrophenyl-hydrazone of **1**, 25557-78-2; **4**, 25557-80-6; **6**, 6510-

63-0; **7**, 25557-82-8; 1-carbazol-9-yl-2,3-dihydroxypropane, 25557-79-3.

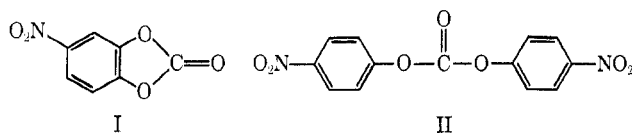# The Hydrolysis of Bis(4-Nitrophenyl) Carbonate and the General Base Catalyzed Hydrolysis of o-(4-Nitrophenylene) Carbonate

Thomas H. Fife* and Diane M. McMahon

Department of Biochemistry, University of Southern California, Los Angeles, California 90033

The rates of hydrolysis of o-(4-nitrophenylene) carbonate have been measured in H_2O at 30°. The values of k_{obsd} for spontaneous hydrolysis are independent of pH from pH 1 to pH 7. In this pH region a water-catalyzed reaction is occurring with a D_2O solvent isotope effect (k_{H_2O}/k_{D_2O}) of 2.35. As acid concentration is increased from 1.0 M to 5.29 M, the rate of hydrolysis decreases. This behavior is similar to that observed previously for bis(4-nitrophenyl) carbonate. Hydrolysis is catalyzed by a series of general base catalysts. A linear plot of log k_B vs. the pK_a of the catalyzing base is obtained with a slope of 0.30. The point for imidazole fits well on this line with catalysts of much lower basicity including H_2O. The value of $k_{Im}^{H_2O}/k_{Im}^{D_2O}$ is 3.49, indicating proton transfer in the transition state. In contrast, nucleophilic catalysis takes place in the imidazole-catalyzed hydrolysis of bis(4-nitrophenyl) carbonate. Formation and decomposition of an intermediate could be observed in that reaction. Reasons for the mechanism change with the cyclic ester are discussed.

The imidazole-catalyzed hydrolysis of esters having a leaving group of low basicity, such as p-nitrophenyl acetate, has been shown to take place with nucleophilic attack by imidazole at the carbonyl of the ester.[1,2] It was thought that it would be of considerable interest to determine the effect on rate and mechanism of constraining an ester with a good leaving group in a cyclic cis configuration since constraint of this type could take place in an enzymatic reaction, and indeed has been suggested for α-chymotrypsin.[3] As part of a general investigation of steric effects on the mechanisms of hydrolysis of esters and amides, both enzymatic and nonenzymatic,[4] we have therefore studied the hydrolysis of the cyclic ester o-(4-nitrophenylene) carbonate (I) and, for comparison purposes, the analogous noncyclic bis(4-nitrophenyl) carbonate (II). The hydrolysis of

I   II

bis(4-nitrophenyl) carbonate in various acid solutions where the reaction involves water catalysis has been studied,[5] but kinetic studies of carbonate ester hydrolysis in buffer solutions have not been previously reported.

Experimental Section

Materials.—o-(4-Nitrophenylene) carbonate was prepared from 4-nitrocatechol and phosgene by the same procedure previously

utilized for the preparation of bis(4-nitrophenyl) carbonate.[5] The pale yellow crystals melted at 99–100°. *Anal.* Calcd for $C_7H_3NO_5$: C, 46.42; H, 1.67; N, 7.72. Found: C, 46.47; H, 1.71; N, 7.67. The infrared spectrum was consistent with structure I. There was no absorption band present due to phenolic OH. Complete hydrolysis in HCl or in buffered solutions gave 1 equiv of 4-nitrocatechol per equiv of ester, as determined spectrophotometrically.

N-(p-Nitrophenoxycarbonyl)imidazole was prepared by adding dropwise 5.0 g (0.025 mol) of p-nitrophenyl chloroformate in dry benzene to 3.4 g (0.05 mol) of imidazole in refluxing dry benzene. The mixture was stirred for 2 hr, cooled, and filtered. Upon evaporation of the benzene a solid residue was obtained which was recrystallized from benzene. The material melted at 128–129°. *Anal.* Calcd for $C_{10}H_7N_3O_4$: C, 51.51; H, 3.03; N, 18.02. Found: C, 51.62; H, 3.01; N, 17.94.

p-Nitrophenyl chloroformate was obtained from K and K Laboratories. Acetonitrile was Eastman Kodak Spectrograde and was further purified by distillation from P_2O_5 and K_2CO_3. Deuterium oxide (99.8%) was obtained from Bio-Rad Laboratories. Hydrochloric acid was Baker Reagent grade. The concentration of HCl solutions was determined by titration of standard base. Imidazole was obtained from Eastman Kodak and was recrystallized from benzene. All other chemicals were reagent grade.

Kinetic Measurements.—The rates of hydrolysis of o-(4-nitrophenylene) carbonate at 30° in H_2O were followed by measuring the appearance of 4-nitrocatechol at 335 mμ or the monoanion at 410 mμ with a Gilford 2000 recording spectrophotometer. The hydrolysis of bis(4-nitrophenyl) carbonate was followed by measuring the appearance of p-nitrophenol at 330 mμ or p-nitrophenoxide ion at 400 mμ. The spectrum of the solution upon completion of the reaction was identical with that of p-nitrophenol or 4-nitrocatechol in the appropriate buffer solution.

In spectrophotometric determinations the ester was dissolved in acetonitrile and 50 μl of this solution was added with a Hamilton syringe to 3 ml of solution in the cuvette with stirring. The reactions were followed to completion, and infinity points were stable. Constant temperature (±0.1°) was maintained by circulating water from a Precision Scientific Lo-Temptrol 154 circulating water bath around the cell compartment. The temperature inside the cell compartment was determined with a probe supplied with the Gilford instrument. Pseudo-first-

* Author to whom correspondence should be addressed.

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