the spectrum of benzoyl chloride (C=O, 5.60). The decomposition products of II were analyzed and characterized as were those of I.

Registry No.—I, 5704-66-5; II, 25726-04-9.

Acknowledgments.—The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

The Alumina-Catalyzed Condensation of 9-Carbazolylacetaldehyde[1]

Bruno M. Vittimberga* and Matthew L. Herz[2]

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

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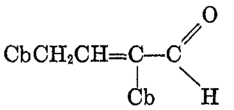
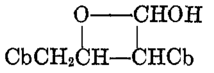
The literature contains few examples of the condensation of aldehydes or ketones catalyzed by alumina.[3] During a study of the decarbonylation of 9-carbazolylacetaldehyde[4] (I), we found that, when this aldehyde is passed through a chromatographic column prepared with neutral alumina (activity grade I), it undergoes facile conversion to 2,4-dicarbazol-9-yl-2-butenal (II) (20%) and to an alcohol III (7%), which was assigned the novel structure III, along with considerable polymeric solid.



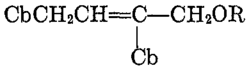
II



III

(Cb = 9-carbazolyl)

Structure II was assigned on the basis of information obtained from its mass, infrared, and nmr spectra and by conversion to derivatives which were characterized by similar techniques (see Table I). Reduction of II with sodium borohydride in 80% aqueous dioxane gave an alcohol IV (76%) which when treated with pyridine–acetic anhydride gave the monoacetate V (76%).

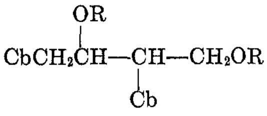


$$\mathrm{CbCH_2CH{=}\underset{\displaystyle Cb}{C}{-}CH_2OR}$$

IV, R = H
V, R = Ac

The elucidation of the structure of III was difficult owing to its very low solubility in conventional solvents. Its structure is based in part on spectroscopic data and the properties of its derivatives given in Table I. Purified III gave one spot by tlc, a correct analysis for $C_{28}H_{22}N_2O_2$, and an ir spectrum which is consistent with the proposed structure. In addition, mass spectroscopy gave a molecular weight of 418 and a fragmentation pattern similar to that of the dehydrated form II. The reaction of III with base yielded, on neutralization, carbazole (27%), a small amount of II, and considerable amorphous solid. The isolation of II from these hydrolyses confirms the conclusions reached from the mass spectral data and establishes the presence of the carbon skeleton of II as part of structure III. Evidently, the reaction of III with base causes the oxetane ring to open with the simultaneous formation of an aldehyde group which activates the carbazole bearing 2 position toward nucleophilic attack.

This possibility was supported when the hydrolysis of III was carried out under reducing conditions with sodium borohydride. Under these conditions the aldehyde group was reduced as it formed yielding the diol VI (90%) which gave a negative periodic acid test as expected. The diacetate VII was prepared as usual with pyridine and acetic anhydride.



$$\mathrm{CbCH_2\overset{\displaystyle OR}{C}H{-}\underset{\displaystyle Cb}{C}H{-}CH_2OR}$$

VI, R = H
VII, R = Ac

The amorphous solid obtained in the column reaction could not be separated into components by either chromatography, sublimation, or attempted recrystallization. Its infrared spectrum was identical with that of the polymeric material obtained by the acid-catalyzed condensation of I.

When III was acetylated, an acetate (VIII) formed (67%) which had a saponification equivalent consistent with the monoacetate of III and showed a single acetate carbonyl peak in the ir spectrum and one acetate peak in the nmr spectrum. The saponification yielded the same products as did the treatment of III with base.

The mass spectrum of VIII had a fragmentation pattern very similar to that of III except for the parent peak of III at *m/e* 418 and a peak at *m/e* 669 (8.1%). We have not yet identified the latter peak but it seems reasonable to assume that it is due to some decomposition product which could have formed at the near decomposition temperature (about 300°) required to vaporize this sample.[5]

In an effort to obtain further confirmation of the molecular weight of III, cryoscopic and ebullioscopic molecular weight determinations were attempted. Unfortunately, these attempts were not successful due to the low solubility of III and its low stability. In hot solvent (about 90°) nmr showed extensive decomposition in a matter of minutes; at room temperature under dry nitrogen, degradation became apparent by elemental analysis after a few weeks.

The mechanism of this reaction appears to be an acid-catalyzed aldol condensation which must occur in this system because of high attraction of the carbazole nucleus for the activated alumina surface[6] and the increased stability of the enol form of the aldehyde due to its conjugation with the heteroaromatic ring system. In strongly acidic solutions the condensation proceeds rapidly to produce an insoluble material even at temper-

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* To whom correspondence should be addressed.

[1] Presented in part at the Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 14, 1968.

[2] American Hoechst Fellow, 1967–1968.

[3] For room temperature reactions, see A. M. Kuliev, A. M. Levshina, and A. G. Zul'fugarova, *Azerb. Khim. Zh.*, No. 5, 29 (1959); *Chem. Abstr.*, **59**, 2638*a* (1963); also, K. Tanabe and Y. Morisowa, *Chem. Pharm. Bull.* **11**, 536 (1963).

[4] Synthesis reported in B. M. Vittimberga and M. L. Herz, *J. Org. Chem.*, **35**, 3694 (1970).

[5] We had also considered the dimer of structure III as a possibility for III, but this seems unlikely because of the absence of a complicated fragmentation pattern above *m/e* 400.

[6] E. Funakubo, T. Nagai, and J. Moritani, *Kogyo Kaguku Zasshi*, **65**, 782 (1962); *Chem. Abstr.*, **59**, 1445*g* (1963). Also, E. Funakubo, T. Nagai, and G. Kon, *Kogyo Kagaku Zasshi*, **66**, 33 (1963); *Chem. Abstr.*, **59**, 12145*f* (1963).

TABLE I

PHYSICAL PROPERTIES[a]

Compd	Formula	Mp, °C	M	Ir, cm^{-1}	Nmr, τ
I	$C_{14}H_{11}NO$	140.5–141.5	209[b]	2850 (ald C—H) 1730 (C—O)	0.37 (t, 1, J = 4.0 Hz), 2.5 (m, 8) 5.24 (d, 2, J = 4.0 Hz) ($CDCl_3$)
II	$C_{28}H_{20}N_2O$	172–174	400[b]	$\left.\begin{matrix}2820\\2730\end{matrix}\right\}$ (ald C—H) 1690 (C=O) 1640 (C=C)	0.42 (s, CH=O), 2.50 (m, Cb protons), 3.10 (t, J = 6.6 Hz, CH=) 5.06 (d, J = 6.6 Hz, CH_2) (acetone-d_6)
III	$C_{28}N_{22}N_2O_2$	221–226	418[b]	3535 (OH) $\left.\begin{matrix}1220\\1150\\1115\end{matrix}\right\}$ (C—O)	2.5 (m, Cb protons), broad unresolved bands between 6.6 and 3.1, 8.0 (s, weak, OH) (nitrobenzene-d_5)
IV	$C_{28}H_{22}N_2O$	164–165		3270 (O—H) 1675 (C=C) 1060 (C—O)	2.5 (m, 16), 3.59 (t, 1, J = 6.0 Hz, CH=), 5.24 (d, 2, J = 6.0 Hz), 5.5 (s, 2), 8.39 (s, 1, OH) ($CDCl_3$)
V	$C_{30}H_{24}N_2O_2$	145.5–146.5	441.5[c]	1745 (C=O) 1665 (C=C) $\left.\begin{matrix}1215\\1025\end{matrix}\right\}$ (C—O)	2.5 (m, 16), 3.59 (t, 1, J = 6.4 Hz), 4.09 (s, 2), 5.31 (d, 2, J = 6.4 Hz), 8.20 (s, 3)($CDCl_3$)
VI	$C_{23}H_{24}N_2O_2$	218–220		3400 (OH) $\left.\begin{matrix}1150\\1110\end{matrix}\right\}$ (C—O)	Complex splitting between 6.6 and 3.0 (6 protons), 2.5 (m, 16), 8.01 (s, 2, OH) ($CDCl_3$)
VII	$C_{32}H_{28}N_2O_4$	192.5–194.5		1745 (d, C=O) $\left.\begin{matrix}1230\\1050\end{matrix}\right\}$ (C—O)	Two regions of complex splitting at 6.65–4.65 (m, 5) and 4.0–1.7 (m, 17), acetate protons at 8.43 (s, 3), 8.30 (s, 3) ($CDCl_3$)
VIII	$C_{30}H_{24}N_2O_3$	295 dec	462[c,d]	1750 (C=O) $\left.\begin{matrix}1225\\1120\end{matrix}\right\}$ (C—O)	2.5 (m, Cb protons), broad unresolved bands between 8.4 and 3.6, 8.73 (s, strong) (pyridine-d_5, 100 Mc)

[a] All spectra were taken in KBr. New compounds gave elemental analyses that were within 0.30% of the theoretical value for C, H, and N except for II and V which after many recrystallizations analyzed correctly for N but were off 0.5% in C and H. [b] By mass spectroscopy. [c] By saponification equivalent. [d] No resolution of parent peak.

atures about 10°. In contrast to this, the aldehyde I was recovered unchanged after 3 days at reflux in alcoholic potassium hydroxide solution. These facts support a mechanism involving acid catalysis.

The column appears to have two functions: (1) it catalyzes the reaction, and (2) it prevents the complete conversion of the aldehyde to polymeric materials. The alumina, in effect, dilutes the aldehyde by allowing reaction to occur only at separated active sites, thereby causing a localized dimerization reaction. The aldol, which could not be isolated, must dehydrate to II or react to form III. Though structure III seems energetically unlikely, it might be the result of distortion in the molecule caused by the steric repulsion of the large carbazolyl groups. A study of the mechanism of this reaction with aromatic systems is in progress and will be reported subsequently.

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 Mc unless otherwise indicated 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. The microanalyses were performed by Micro-Analysis, Inc., Wilmington, Del.

The Reaction of I with Alumina.—The 9-carbazolylacetaldehyde (5.0 g, 0.24 mol) was passed over 60 g of aluminum oxide (Woelm neutral, activity I, pH 7.5) using eluents of increasing polarity from benzene to methanol. The earlier fractions contained II (~20%) and III (~7%) while in the later fractions these were mixed with a red amorphous solid. These compounds were separated by fractional recrystallization from ethanol. The amorphous solid formed in this reaction gave an ir spectrum which is essentially the same as that for the solid formed by acid-catalyzed polymerization (*vide infra*) of 9-carbazolylacetaldehyde. Its nmr spectrum (in acetone-d_6) showed strong carbazole type aromatic proton resonance (τ 2.5) with broad unresolved absorption between τ 4.1 and 7.1, and three weak peaks about τ 8.9. The acetate, VIII, was prepared by heating III (100 mg, 2.4 × 10^{-4} mol) in 5.0 ml of pyridine (dried over sodium hydroxide) and 3.0 ml (3.24 g, 0.032 mol) of acetic anhydride on a steam bath for 1.5 hr to give a precipitate. The mixture was poured over crushed ice and solids were removed by suction filtration, washed with 2% hydrochloric acid, and finally washed thoroughly with water. The acetate was recrystallized from 2-butanone to give white crystals (0.074 g, 1.6 × 10^{-4} mol, 67%). The saponification of this acetate or the treatment of III (100 mg) with base followed by neutralization produced a precipitate in ~100% yields. The precipitate was resolved on a silica column to yield 30 mg of carbazole, 10 mg of II, and amorphous solid.

The Reduction of II by Sodium Borohydride.—To a stirred solution of 0.350 g (8.7 × 10^{-4} mol) of II in 25 ml of 80% aqueous dioxane at 0° was added 0.050 g (1.3 × 10^{-3} mol) of sodium borohydride. This was followed immediately by 6 drops of 20% sodium hydroxide solution and the resulting solution was stirred for 1 hr. Then it was allowed to warm to room temperature at which point it was made slightly acid to litmus with 20% acetic acid and was poured into 200 ml of water. Stirring produced a curdy precipitate which was separated by filtration and washed thoroughly with water. The crude material was recrystallized from carbon tetrachloride to yield 0.265 g of IV (6.6 × 10^{-4} mol, 76%).

The monoacetate V was prepared by the procedure used to produce the acetate of III (76% yield).

Reduction of III by Sodium Borohydride.—The hemiacetal, III, was reduced as was described above for the reduction of II to yield, after repeated recrystallization from ethanol, VI (37%). The diacetate VII was prepared in 95% yield by the procedure described above for the esterification of III.

The Acid-Catalyzed Condensation of I.—The aldehyde (1.0 g, 4.8 × 10^{-3} mol) was dissolved in a stirred, cooled solution of 25 ml of acetic acid and 0.77 ml (1.4 g, 1.4 × 10^{-2} mol) of sulfuric acid. The starting material was completely converted over a period of 24 hr to a highly insoluble grayish precipitate. The product was repeatedly extracted with carbon tetrachloride to give a green material which decomposed at ~375°: ir 3410 (O—H), 1750 (C—O), 1205, 1150, and 1120 cm^{-1} (C—O).

Registry No.—I, 25557-77-1; II, 25894-27-3; III, 25894-28-4; IV, 25894-29-5; V, 25894-30-8; VI, 25894-31-9; VII, 25894-32-0; VIII, 25894-33-1.

Acknowledgments.—We thank Dr. Charles Merritt, Jr., and his group at the U. S. Army Natick Laboratories, Natick, Mass., and Mr. Donald L. Travis of Varian Associates for the mass spectra determinations.

Cyclohexadienyl Cations. II. Evidence for a Protonated Cyclohexadienone during the Dienone–Phenol Rearrangement[1,2]

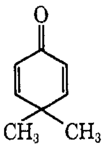
V. P. Vitullo[3]

Department of Chemistry, University of Kansas,
Lawrence, Kansas 66044

Received April 2, 1970

In an earlier paper[1] we suggested that the oxygen-protonated cyclohexadienone formed from 4-dichloromethyl-4-methylcyclohexadienone (2) in concentrated acid could be considered a good model for the first intermediate in the dienone–phenol rearrangement.[4] The structure of this ion as well as its equilibrium acidity dependence in concentrated acid solution was firmly established.[1,5] While this suggestion seemed entirely reasonable, it lacked force because of the demonstrated reluctance of 2 to undergo the dienone–phenol rearrangement. Thus, even at 60° in 80% sulfuric acid, 2 rearranges only slowly (half-life ~ 24 hr) to afford a mixture of two rather unusual products.[6]

In this paper, we would like to report the results of a similar investigation on a closely related system, 4,4-dimethylcyclohexadienone (1). This substrate does undergo the dienone–phenol rearrangement rapidly at 25° in 70% perchloric acid to form a single major product, 3,4-dimethylphenol, in >90% yield. Thus, we reasoned that the detection of a protonated cyclohexadienone during the isomerization of this substrate would not suffer from the deficiencies noted above for 2.



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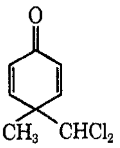

2

Results and Discussion

1 was prepared in a straightforward manner by condensation of the pyrrolidine enamine of isobutyraldehyde with methyl vinyl ketone.[7,8] The resulting 4,4-dimethylcyclohexenone was oxidized to the corresponding dienone using 2,3 dichloro-5,6-dicyanobenzoquinone in refluxing carbon tetrachloride.

The uv spectrum of 1 in water is characteristic of a $\Delta^{2,5}$-cyclohexadienone.[9] However, in concentrated sulfuric or perchloric acid solution the spectrum is completely different and nearly identical with that produced by dissolving 2 in concentrated sulfuric acid. These results are summarized in Table I.

Table I

Ultraviolet Spectral Properties of Neutral and Protonated Cyclohexadienones

Dienone	Solvent	λ_{max} (nm)	Log ϵ
1	H_2O	235	4.17
2^a	H_2O	238	4.15
1	71.0% $HClO_4$	260, 295	4.12, 3.57
2^a	90.5% H_2SO_4	262, 294	4.12, 3.56

^{a} Data from ref 1.

The long wavelength band of the species formed by protonation of 1 can be used to monitor its concentration as a function of acid concentration. The results of such an investigation for solutions of 1 in both sulfuric and perchloric acids are reported in Tables II and III.

Table II

Equilibrium Protonation Data for 1 in $HClO_4$ at 25.3°

Absorbance^a	Wt % of $HClO_4$	$[DH^+]/[D]^b$	$-H_0{}^c$
0.215	41.03	0.157	2.26
0.355	44.35	0.292	2.81
0.573	47.61	0.576	3.18
0.812	50.50	1.076	3.55
1.058	53.55	2.07	4.00
1.200	56.44	3.26	4.47
1.395	59.03	8.08	5.02
1.605	64.16		6.26
1.538	68.83		7.45
1.542	70.95		8.01

^{a} At 295 nm, concentration 4.12×10^{-4} *M*, cell path 1 cm. ^{b} Ratio of concentrations of protonated [DH$^+$] to neutral [D] species. ^{c} H_0 values from K. Yates and H. Wai, *Can. J. Chem.*, **43,** 2131 (1965).

Table III

Equilibrium Protonation Data for 1 in H_2SO_4 at 25.3°

Absorbance^a	Wt % of H_2SO_4	$[DH^+]/[D]^b$	$-H_0{}^c$
0.149	36.28	0.102	2.15
0.276	42.10	0.200	2.57
0.445	46.57	0.383	3.01
0.668	51.75	0.712	3.56
0.842	54.34	1.100	3.84
1.188	60.07	2.83	4.46
1.402	65.02	6.82	5.09
1.633	94.70		9.79
1.583	94.70		9.79

^{a} At 295 nm, concentration 4.12×10^{-4} *M*, cell path 1 cm. ^{b} Ratio of concentrations of protonated [DH$^+$] to neutral [D] species. ^{c} H_0 values from M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85,** 878 (1963).

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[1] Part I: V. P. Vitullo, *J. Org. Chem.*, **34,** 224 (1969).

[2] Presented in part at the 157th National Meeting of the American Chemical Society, April 1969, Minneapolis, Minn., Abstract ORGN 163.

[3] Address all correspondence to Department of Chemistry, University of Maryland, Baltimore, Md. 21228.

[4] For a discussion of possible mechanisms of the dienone–phenol rearrangement, see A. J. Waring, *Advan. Alicycl. Chem.*, **1,** 207 (1966), and references contained therein.

[5] E. C. Friedrich, *J. Org. Chem.*, **33,** 412 (1968).

[6] T. G. Miller, *ibid.*, **27,** 1549 (1962).

[7] E. Benzing, *Angew. Chem.*, **71,** 521 (1959).

[8] G. A. Smith, B. J. L. Hiff, W. H. Powers, III, and D. Caine, *J. Org. Chem.*, **32,** 2851 (1967).

[9] Reference 4, p 188.