solvents, and hot water. They were not hydrolyzed in hydrochloric acid, and unchanged after a 2-hr. exposure in air at 45–50° to ultraviolet light from a 100-w. Hanovia mercury arc lamp (Model 608A36) at a distance of 4 in.

Homopolymerization of the complexes with boron trifluoride etherate gave a dark brown oligomer; copolymerizations with styrene and ethyl acrylate using a free-radical catalyst were sluggish, and gave gray copolymers which turned black by heat or light.

Acknowledgment.—The authors thank Dr. N. L. Zutty for helpful discussions, Messrs. C. H. Carder and H. J. Paxton for assistance in the experimental work, and Mr. E. R. Santee, Jr., for the n.m.r. data.

The Photochemical Conversion of Fumaronitrile and Acetone to Oxetanes

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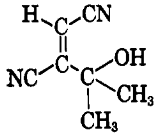
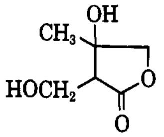
The light-catalyzed reaction of fumaronitrile and acetone provides a mixture of *cis*- and *trans*-oxetanedinitriles. The structures of the oxetanes are established and some of their acidic hydrolysis products described.

The light-catalyzed reaction of carbonyl compounds with olefins to form oxetanes[1] was ignored until Büchi's[2] investigation of the reaction 10 years ago. Since then a considerable effort has been expended in studying the scope and mechanism of the reaction.[3] Recently some older literature work came to our attention that suggested it contained one of the earliest examples of oxetane formation, although this had not been recognized.

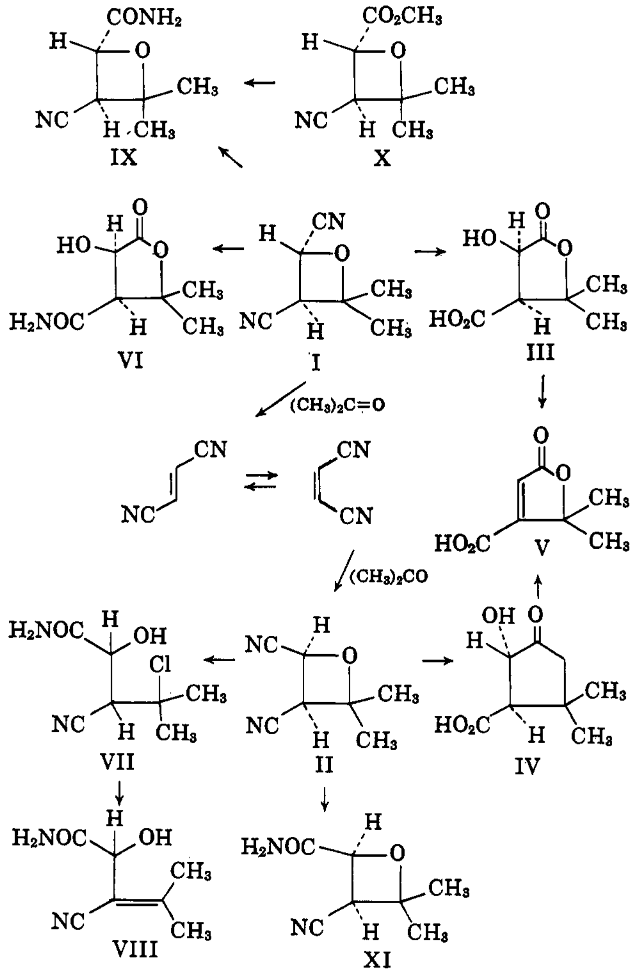
Stoermer[4] had observed that fumaronitrile in ethanol isomerized under ultraviolet radiation to give a low yield of maleonitrile. In addition, a considerable amount of ethoxysuccinic acid was formed. In an attempt to improve the yield of the isomerization, Jennen[5] used acetone as the solvent.[6] While he did obtain some isomerization to maleonitrile, the principal product of the reaction was a material, $C_7H_8N_2O$, to which he assigned structure A,[7] since acid hydrolysis yielded a lactone acid which he regarded as oxyisoterebinic acid lactone (B).


A


B

Since these structures appeared unlikely, we have repeated the reaction and followed the course of product formation by means of gas–liquid chromatography (g.l.c.). The first product observed was maleonitrile closely followed by the oxetane I (Scheme I). Finally oxetane II was noticed. After most of the starting material had been converted, the oxetanes were isolated and purified. The infrared spectra of both oxetanes showed a nitrile band but no hydroxyl or olefin absorption. The n.m.r. spectrum of I showed singlets for two methyl groups and a coupling of 6 c.p.s. for the remaining two protons. The corresponding coupling constant for the isomer II appeared to be 8.5 c.p.s. while the presence of the methyl groups was again indicated by two singlets.

SCHEME I



The reaction of acetone and fumaronitrile with ultraviolet light filtered out by Pyrex below 290 mμ led to the same product mixture but at a considerably slower reaction rate. Maleonitrile and acetone are converted to a mixture of the same compounds but with a higher proportion of II. However, in methanol, fumaronitrile is not isomerized to maleonitrile by ultraviolet light above 290 mμ. Apparently at this wave length

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(1) E. Paterno and G. Chieffi, *Gazz. chim. ital.*, **39**, 341 (1909).

(2) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

(3) (a) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); (b) P. DeMayo, *Advan. Org. Chem.*, **2**, 367 (1960); (c) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, **No. 22**, 1425 (1964); (d) L. A. Singer and P. D. Bartlett, *ibid.*, **No. 28**, 1887 (1964).

(4) R. Stoermer, *Ber.*, **44**, 660 (1911); **46**, 276 (1913).

(5) J. Jennen, *Bull. soc. chim. Belges*, **46**, 258 (1937).

(6) The only other work involving irradiation of fumaronitrile is the recent photodimerization to tetracyanocyclobutane: G. W. Griffin, J. E. Basinski, and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 1012 (1962).

(7) Griffin[6] incorrectly quotes this structure as the dihydro compound.

the initially formed acetone triplet catalyzes the isomerization of the unsaturated nitriles.[8] It would appear that only one isomeric oxetane arises from each of the initially formed diradicals since g.l.c. fails to show any of the *cis* isomer II until an appreciable concentration of maleonitrile has been built up.

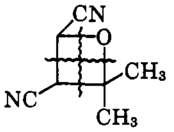
Hydrolysis of each of the oxetanes with concentrated hydrochloric acid as reported by Jennen yielded the isomeric lactones, III and IV. Both products contained hydroxyl, lactone, and carboxylic acid groups, according to their respective infrared spectra. The n.m.r. data were consistent with the presence of a *gem*-dimethyl group attached to a tertiary carbon bearing an oxygen atom. While the signals for the two downfield protons of the *cis*-lactone acid III[9] showed an apparent coupling constant of 7.5 c.p.s., the value for the *trans*-lactone acid IV was 11 c.p.s. N.m.r. analysis and thin layer chromatography of each total crude hydrolysis product failed to show the presence of the other isomer.

Pyrolysis of both the *trans*- and *cis*-lactone acids III and IV yielded terebilenic acid (V). Its structure was reconfirmed by analysis and infrared and n.m.r. spectra.

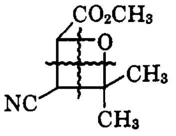
The stereospecific conversion of the oxetanes I and II to the lactones III and IV, respectively, appeared of interest. In an effort to isolate some of the intermediate hydrolysis products, the *trans*-oxetane I was shaken for 3 min. with concentrated hydrochloric acid. During this brief period, the oxetane ring was opened, both nitrile groups were hydrolyzed, and a lactone was formed. Analysis and infrared and n.m.r. spectra allowed the assignment of the *cis*-lactone amide structure VI to the product. Under essentially the same conditions, the *cis*-oxetane II provided a different hydrolysis product.[10] Analysis indicated an empirical formula of $C_7H_{11}ClN_2O_2$ and the infrared spectra showed hydroxyl, nitrile, and amide absorption bands. The n.m.r. spectrum showed signals for a *gem*-dimethyl group and two downfield protons on adjacent carbon atoms, and confirmed the presence of hydroxyl and amide groups. The chemical shift of the *gem*-dimethyls (1.71 p.p.m.) was interpreted to indicate that a chlorine rather than an oxygen atom was attached to the same carbon.[11] On this basis, structure VII was assigned to the hydrolysis product. Supporting evidence was obtained by treatment of the hydrolysis product (VII) with sodium ethoxide in alcohol which removed the chlorine to give a crude product showing hydroxyl, unsaturated nitrile, and amide absorption bands in its infrared spectrum. The n.m.r. spectrum supported structure VIII.

All of the hydrolysis products described above could arise from the oxetanes I and II by opening of the oxetane ring with subsequent hydrolysis of the nitrile groups. The following results would indicate that this route is not necessarily the correct one. For example, hydrolysis of the *trans*-oxetane I in more dilute hydrochloric acid at room temperature for 10 min. led to the formation of the oxetaneamide IX. In methanolic hydrochloric acid, I was hydrolyzed to the oxetane methyl ester X. Finally, the *cis*-oxetane II in methanolic hydrochloric acid yielded the *cis*-oxetaneamide XI.

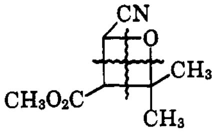
While the analytical values and infrared and n.m.r. spectra all supported the structural assignments made for the hydrolysis products with oxetane rings, it seemed desirable to have additional supporting evidence for these structures. This was obtained from the mass spectra of the volatile methyl ester X and its parent compound I. Both compounds failed to show any molecular ion or M − 1 peak. This is not too surprising since even simple aliphatic nitriles show only very weak peaks in the molecular-ion region.[12] In both spectra, the largest mass peak is a weak M − 15 peak that is probably the result of the loss of a methyl radical from the molecule.[12] Most of the remaining peaks in the spectra of I can be accounted for by a cleavage of the molecule along the lines indicated in Ia, and subsequent ionization and further cleavages. In a similar manner, the spectra of X can be accounted for as shown in Xa. Analogy to the other hydrolysis products makes the alternate structure XII less attractive. Although XII cannot be ruled out completely by the mass spectra because many of the peaks can be accounted for by either Xa or XII, the presence of strong *m/e* 82 and 81 which are also in the spectrum of Ia provides additional support for structure X.



Ia

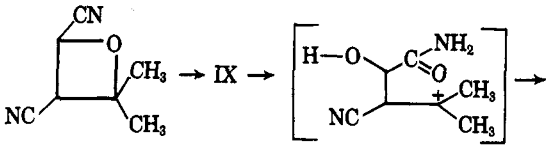


Xa



XII

Finally the structure of the amide IX was verified by conversion of X to IX. Considering all these hydrolysis products, one can postulate the sequence of reactions as being a hydrolysis of the nitrile adjacent to the oxygen to give the amide IX followed by protonization of the oxetane oxygen and ring opening to give the stabilized carbonium ion XIII. This can be



XIII

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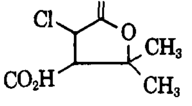
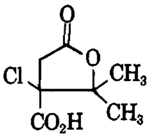
[8] J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

[9] A lactone acid with the structure of III or IV has been reported incorrectly by Beilstein as being the sodium carbonate hydrolysis product of α-chloroterebenic acid. The original literature shows that Roser [*Ann.*, **220**, 263 (1883)] actually assigned structure ii to α-chloroterebinic acid and the corresponding hydroxyl structure to the carbonate hydrolysis product. Beilstein incorrectly reports structure i for α- and ii for β-chloroterebinic acid.



i



ii

i is β-chloroterebinic acid which was later shown [R. Fittig and B. Frost, *Ann.*, **226**, 370 (1884)] to give terebilenic acid (V) on hydrolysis.

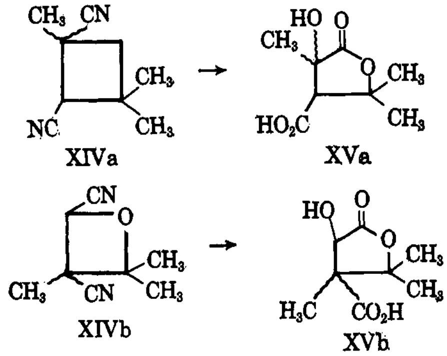
[10] In these hydrolysis experiments, only the principal and most easily isolated product was studied and no effort was made to investigate minor by-products.

[11] For example, in the same solvent the chemical shift of the *gem*-dimethyl group of isopropyl alcohol is 1.05 p.p.m. while with isopropyl chloride the value is 1.48 p.p.m.

[12] R. Beugelmans, D. A. Williams, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 1386 (1964).

attacked by the amide oxygen to give eventually the lactone III, or by chloride ion to form VII.

The reaction of mesocononitrile in acetone in the presence of ultraviolet light also has been described.[13] Although the product was not isolated in pure form, it was hydrolyzed in hydrochloric acid to give a material whose analysis does agree with XVa or XVb. It thus appears probable that the compounds obtained were XIVa or b and XVa or b in analogy to the results reported here.



XIVa XVa

XIVb XVb

Experimental

Melting points and boiling points are uncorrected. The n.m.r. spectra were obtained on the Varian A-60 instrument with chemical shifts reported in parts per million from tetramethylsilane. The solvents used are indicated (DMSO = dimethyl sulfoxide). The nature of the peaks are shown by singlet (s), doublet (d), and broad complex (b).

Irradiation of Fumaronitrile and Acetone.—A solution of 90 g. of fumaronitrile in 1350 ml. of acetone was irradiated with a Hanovia mercury arc lamp (450 w.) with water cooling and nitrogen gas stream agitation. The course of the reaction was followed by g.l.c. assay at regular intervals. After 56 hr. the disappearance of fumaronitrile had slowed sufficiently so the irradiation was stopped. Removal of the acetone gave an oil that assayed as follows by g.l.c.: fumaronitrile, 14%; maleonitrile, 12%; I, 64%; and II, 22.5%. The oil was distilled through a 36-in. spinning-band column at a reflux ratio of 5:1.

Fraction 1, b.p. 83–86° (4 mm.), 26.7 g., consisted largely of fumaronitrile and maleonitrile by g.l.c. assay.

Fraction 2, b.p. 88–91° (1 mm.), was crystallized from an ether–hexane mixture to give 45 g. of the *trans*-oxetane I: m.p. 41–42.3°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 4.56 μ; δ^{DMSO} = 1.53 (3H, s), 1.57 (3H, s), 4.53 (1H, d, J = 6.5 c.p.s.), and 5.65 (1H, d, J = 6.5 c.p.s.) p.p.m.

Anal. Calcd. for $C_7H_8N_2O$: C, 61.75; H, 5.92; N, 20.58. Found: C, 62.00; H, 5.83; N, 20.77.

Mass spectrometry showed the following peaks in descending order of intensity: *m/e* 43, 41, 81, 39, 58, 27, 28, 54, 29, 38, 51, 52, 42, 66, 121, 53, 37, 40, 44, 78, 80, and 82.

Fraction 3, b.p. 117-118° (1 mm.), was crystallized from ether to give 19.7 g. of *cis*-oxetane II: m.p. 59.5–60.2°; $\lambda_{\max}^{\mathrm{CHCl}}$ 4.56 μ; δ^{DMSO} = 1.50 (3H, s), 1.61 (3H, s), 4.42 (1H, d, J = 8.5 c.p.s.), and 5.60 (1H, d, J = 8.5 c.p.s.) p.p.m.

Anal. Calcd. for $C_7H_8N_2O$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.75; H, 5.80; N, 20.46.

When the irradiation described above was repeated with the ultraviolet light filtered out below 290 mμ by a Pyrex filter, the same product mixture was obtained but required 120 hr. of irradiation. Irradiation of maleonitrile in acetone under the conditions of the above experiment led to a similar mixture but with a higher per cent of II.

Hydrolysis of the *trans*-Oxetane I.—A mixture of 1 g. of I and 30 ml. of concentrated HCl was stirred and refluxed for 2 hr. Evaporation *in vacuo* gave a white powder that was extracted with ether in a Soxhlet apparatus for 2 days. The ether solution was concentrated, diluted with hexane, and left at 0° to provide 840 mg. of product, m.p. 157–166°. Concentration of the filtrate gave an additional 237 mg. of material. Recrystallization from ethyl acetate yielded pure III: m.p. 165–167° dec.; $\lambda_{\max}^{\mathrm{KBr}}$ 2.93, 5.68, and 5.85 μ; $\delta^{\mathrm{D_2O}}$ = 1.97 (6H, s), 3.93 (1H, d, J = 7.5 c.p.s.), and 5.60 (1H, d, J = 7.5 c.p.s.) p.p.m.

Anal. Calcd. for $C_7H_{10}O_5$: C, 48.27; H, 5.79. Found: C, 47.98; H, 5.73.

Hydrolysis of the *cis*-Oxetane II.—Repetition of the above experiment with 1 g. of II provided 684 mg. of material, m.p. 155–157°, by crystallization from ether–hexane and 450 mg. of less pure material. Recrystallization from ethyl acetate gave pure IV: m.p. 159.5–161° dec.; $\lambda_{\max}^{\mathrm{KBr}}$ 2.93, 5.72, and 5.82 μ; $\delta^{\mathrm{D_2O}}$ = 1.86 (3H, s), 2.12 (3H, s), 3.79 (1H, d, J = 11 c.p.s.), and 5.55 (1H, d, J = 11 c.p.s.) p.p.m.

Anal. Calcd. for $C_7H_{10}O_5$: C, 48.27; H, 5.79. Found: C, 48.30; H, 5.89.

Pyrolysis of the *trans*-Lactone Acid III.—III (1 g.) was heated at 190–220° for 2 hr. The residue was distributed between ethyl acetate and 5% sodium bicarbonate. Acidification of the bicarbonate layer followed by three ethyl acetate extractions gave 725 mg. of an oil after removal of the solvent. The oil was dissolved in carbon tetrachloride, filtered, concentrated, and allowed to crystallize at 0° to give 160 mg. of crude product, m.p. 135–137°.

Recrystallization from ether–carbon tetrachloride gave pure V: m.p. 166–168° (lit.[9] m.p. 168°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.97, 5.80 (broad), and 6.15 μ; $\delta^{\mathrm{CDCl_3}}$ 1.64 (6H, s), 6.74 (1H, s), and 10.34 (1H, s) p.p.m.

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.16. Found: C, 54.03; H, 5.23.

Pyrolysis of the *cis*-Lactone Acid IV.—Repetition of the above experiment with IV yielded V, m.p. 164–166°, which was identical with the sample of V above by mixture melting point determination and comparison of the infrared spectra.

Brief Hydrolysis of the *trans*-Oxetane I.—I (1 g.) was dissolved in 5 ml. of concentrated hydrochloric acid by shaking for 1 min. (solution temperature 58°). After an additional 2 min. the solution was evaporated *in vacuo* as rapidly as possible. The resulting white glass was taken up in 10 ml. of hot methanol to provide 639 mg. of crude product, m.p. 205–208°. Two recrystallizations from methanol–ethyl acetate gave a pure sample of *trans*-lactone amide VI: m.p. 217–219°; $\lambda_{\max}^{\mathrm{KBr}}$ 2.94, 5.64, and 6.01 μ; $\delta^{\mathrm{D_2O}}$ = 1.96 (6H, s), 3.88 (1H, *d*, J = 7.5 c.p.s.), 5.57 (1H, d, J = 7.5 c.p.s.) p.p.m. (In F_3CCO_2H the n.m.r. spectrum also showed a broad amide proton peak centered at 7.59 p.p.m.)

Anal. Calcd. for $C_7H_{11}NO_4$: C, 48.55; H, 6.40; N, 8.09. Found: C, 48.63; H, 6.28; N, 8.08.

Brief Hydrolysis of the *cis*-Oxetane II.—A mixture of 2 g. of II and 10 ml. of concentrated hydrochloric acid was shaken for 4 min. and then evaporated *in vacuo* as rapidly as possible. The residue was triturated with 10 ml. of water and filtered to give 760 mg. of product, m.p. 130–136°. Recrystallization from ethyl acetate–ether yielded 420 mg. of VII: m.p. 154–155°; $\lambda_{\max}^{\mathrm{KBr}}$ 2.79, 2.99, 4.44, and 5.99 μ; δ^{DMSO} = 1.77 (6H, s), 3.70 (1H, d, J = 2 c.p.s.), 3.73 (1H, s), 4.38 (1H, d, J = 2 c.p.s.), and 7.59 (2H, b) p.p.m.

Anal. Calcd. for $C_7H_{11}ClN_2O_2$: C, 44.09; H, 5.82; Cl, 18.60; N, 14.70. Found: C, 44.43; H, 5.72; Cl, 18.43; N, 14.93.

Basic Degradation of VII.—To a solution of 100 mg. of sodium in 10 ml. of ethanol was added 170 mg. of VII. After standing at 25° for 1 hr. the solution was diluted with 10 ml. of water and acidified. Ether extraction provided 90 mg. of oily VIII: $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.92, 4.52, and 5.97 μ; $\delta^{\mathrm{F_3CCO_2H}}$ = 2.17 (3H, s), 2.28 (3H, s), 5.47 (1H, s), and 7.9 (2H, b) p.p.m.[14]

Hydrolysis of the *trans*-Oxetane I in Dilute Hydrochloric Acid.—A solution of 5 ml. of concentrated hydrochloric acid and 5 ml. of water was added to I (2 g.) that had been previously melted and cooled to 25°. The suspension was shaken for 10 min. during which a clear solution formed which was rapidly evaporated to dryness *in vacuo*. The residue was distributed between 10 ml. of ethyl acetate and 10 ml. of water and the pH of the water layer was adjusted to 7.0 with a few drops of 5% sodium hydroxide. The mixture was subjected to a nine-tube countercurrent distribution by moving the water layers forward. Each tube was evaporated to dryness *in vacuo*. Tubes 0 and 1 contained 643 mg. of material that was largely *trans*-oxetane (infrared spectra). Tubes 8 and 9 contained 312 mg. of material that was a mixture of several components (thin layer chromatography) and was not

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(13) G. Duez, *Bull. classe sci., Acad. roy. Belg.*, **25**, 646 (1939).

(14) In F_3CCO_2H the chemical shifts of the methyl groups of β,β-dimethylacrylonitrile appear at 1.99 and 2.13 p.p.m.

investigated further. Tubes 3–7 (538 mg.) yielded a homogeneous single-spot crystalline material (thin layer chromatography). Recrystallization from methanol provided 356 mg. of IX: m.p. 160°; $\lambda_{\max}^{\mathrm{KBr}}$ 2.97, 4.43, and 5.95 μ; $\delta^{\mathrm{DMSO}} = 1.46$ (3H, s), 1.56 (3H, s), 3.89 (1H, d, $J = 7$ c.p.s.), 4.88 (1H, d, $J = 7$ c.p.s.), and 7.57 (2H, b) p.p.m.

Anal. Calcd. for $C_7H_{10}N_2O_2$: C, 54.53; H, 6.59; N, 18.17. Found: C, 54.40; H, 6.59; N, 18.26.

Hydrolysis of the *trans*-Oxetane in Methanolic Hydrogen Chloride.—A solution of 2 g. of I in 20 ml. of 1 *N* HCl in methanol was left at 25° for 20 min. and then evaporated to dryness *in vacuo*. The residue was taken up in 20 ml. of hot water. Crystallization gave 1.8 g. of X; m.p. 59–61°. A sample was recrystallized from ether for analysis: m.p. 64°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.88, 4.56, and 5.70 μ; $\delta^{\mathrm{DMSO}} = 1.46$ (3H, s), 1.57 (3H, s), 3.46 (3H, s), 4.17 (1H, d, $J = 7.5$ c.p.s.), and 5.17 (1H, d, $J = 7.5$ c.p.s.) p.p.m.

Anal. Calcd. for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28. Found: C, 56.65; H, 6.51; N, 8.22.

Mass spectra of X showed the following peaks in descending order of intensity: *m/e* 43, 29, 82, 58, 41, 81, 29, 27, 28, 55, 52, 54, 59, 80, 31, 53, 83, 40, 44, 66, 45, 38, 33, 154, 60, 37, 110, 112, 64, 67, 65, and 56.

From the aqueous mother liquors of the crystallization above, there was obtained 200 mg. of a mixture (m.p. 152–195°) that was taken up in ethyl acetate and extracted several times with 5% sodium bicarbonate. Evaporation of the ethyl acetate provided 18 mg. of VI (mixture melting point and infrared spectra). Acidification and ethyl acetate extraction of the combined water layers gave 109 mg. of a mixture that contained III and VI (infrared spectra and thin layer chromatography.)

Conversion of X to IX.—To 60 mg. of X was added 1 ml. of methanol and 1 ml. of concentrated ammonium hydroxide. After standing at 25° for 2 hr., the solution was evaporated to dryness *in vacuo* and the residue was crystallized from ethyl acetate giving 18 mg. of IX (mixture melting point and infrared spectra), m.p. 152–154°.

Hydrolysis of the *cis*-Oxetane with Methanolic HCl.—A solution of II (1 g.) and 20 ml. of *N* HCl in methanol was left at 25° for 20 min. and then evaporated to dryness *in vacuo*. The residue was crystallized from 10 ml. of water to give 610 mg. of XI, m.p. 185–190°. Recrystallization from ethyl acetate gave a pure material: m.p. 207–208°; $\lambda_{\max}^{\mathrm{KBr}}$ 2.92, 3.15, 4.44, and 5.97 μ; $\delta^{\mathrm{DMSO}} = 1.53$ (6H, s), 4.22 (1H, d, $J = 9.5$ c.p.s.), 4.96 (1H, d, = 9.5 c.p.s.), and 7.59 (2H, b) p.p.m.

Anal. Calcd. for $C_7H_{10}N_2O_2$: C, 54.53; H, 6.59; N, 18.17. Found: C, 54.65; H, 6.36; N, 17.92.

Acknowledgment.—We are indebted to Professor G. Büchi for the mass spectra reported herein. We also thank Mr. L. Lackey for technical assistance.

Solvent Effects in the Reaction of Grignard Reagent with 1-Alkynes[1]

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Received July 30, 1964

The kinetics of the reaction between ethylmagnesium bromide and 1-alkynes in diethyl ether, *n*-dibutyl ether, diethylene glycol diethyl ether, and tetrahydrofuran have been studied in detail in the range of from 0–40° by measuring the rate of evolved ethane gas. It has been found that the reaction is second order in diethyl ether and in *n*-dibutyl ether, third order in tetrahydrofuran, and about 2.5 order in diethylene glycol diethyl ether. ΔE^* and ΔS^* for the reaction in each solvent were obtained. Possible mechanisms of the reaction are presented.

The constitution of the Grignard reagent has been reinvestigated with chemical and physical techniques by several groups of workers in recent years. Dessy and co-workers[2,3] demonstrated that an equimolar mixture of diethylmagnesium and magnesium bromide in diethyl ether yields the same species as that from ethylmagnesium bromide in diethyl ether, that is, the Grignard reagent prepared in the usual manner. This conclusion seems to have been confirmed by infrared spectral studies[4] and by n.m.r. studies[5] by other workers. From the experimental results that there was only a low percentage of magnesium exchange between diethylmagnesium and radioactive magnesium bromide in diethyl ether solvent, Dessy, *et al.*,[6] concluded that in diethyl ether the predominant species in the Grignard reagent was $R_2Mg{\cdot}MgX_2$ and that the Grignard reagent is best represented by the equilibrium shown in eq. 1. Recently the above Mg^{28} exchange reaction

$$R_2Mg{\cdot}MgX_2 \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

was reinvestigated and both no exchange results and statistical exchange results have been found in two systems which differed only in magnesium sources.[7] The cause of this dichotomy is unknown at present. Ashby and Becker[8] proposed by the fractional crystallization method and by ebullioscopic measurements that in tetrahydrofuran (THF) monomeric species RMgX predominates in simple alkyl Grignard reagents in contrast to dimeric species existing in diethyl ether. Recently, Salinger and Mosher[4] concluded by infrared spectral studies that in THF the Grignard reagents can be interpreted in terms of the equilibrium of eq. 2.

$$R_2Mg + MgX_2 \rightleftharpoons 2RMgX \qquad (2)$$

Stucky and Rundle[9] showed by X-ray analysis that crystals of phenylmagnesium bromide contain C_6H_5-$MgBr{\cdot}2Et_2O$ units. These diverse and partially conflicting observations suggest that the nature or equilibria of the Grignard reagents may vary depending upon the variety of solvents as well as of organic radicals or halides. Therefore, it appeared of interest to investigate the solvent effects on the kinetics of a Grignard reaction in order to give an information concerning the precise nature of the Grignard reagents.

Lewis and Wright[10] studied solvent effects in the reaction between ethylmagnesium bromide and benzophenone and assumed that the difference of the yields of products was attributed to the difference of basicity

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(1) A portion of this work was presented at the 17th Meeting of the Chemical Society of Japan, Tokyo, Japan, April 1964; Abstracts of Papers, p. 156.

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