change are compared. For deuteration, P_0 and P represent starting pressure and pressure at time t, respectively; for exchange p_0/P is equal to P_{0D_2}/P_{D_2}, wherein P_{0D_2} and P_{D_2} are initial pressure and pressure at time t, respectively, of the D_2 species. Since the analytical method takes no cognizance of species, it was necessary to consider two extreme cases for evaluating the pressure of D_2 at time t: (1) that all the measured exchange is due to the conversion of D_2 to H_2, and (2) that the measured exchange represents only the conversion of D_2 to HD. Consideration of these cases gives two possible extremes for the disappearance of D_2 with time, as indicated by the two broken lines of Fig. 4. The upper one coincides with the experimental points for deuteration. Since the utilization of D_2 to form HD is preponderant in the early stages of the exchange, it is quite likely that the disappearance of D_2 is represented more nearly by the upper one, so that consumption of D_2 in deuteration proceeds at about the same rate as the consumption of D_2 in exchange with pure acetic acid. Therefore, if the two reactions were competing for deuterium in the ordinary kinetic sense, one should have had no difficulty in detecting the exchange process.

The fact that the deuterium pressure falls off during the reduction reaction does not mean that the measured exchange, expressed as atomic per cent. hydrogen, would be correspondingly diminished. On the contrary, if both reactions were occurring at the same rate, the atomic per cent. hydrogen should not change at all, since this quantity is independent of the pressure. This statement follows directly from the data of Fig. 1. Since the exchange reaction is somewhat slower than the deuteration reaction, the atomic per cent. hydrogen might diminish somewhat, but should certainly be detected if the two reactions were competing.

In the presence of nitroethane, the exchange of deuterium with acetic acid proceeds unhindered, since the acetic acid in this case can become chemisorbed on the catalyst surface and exchange with the deuterium.

While the hydrogenation of nitrobenzene appears to be better explained by a mechanism of the Rideal–Eley type, the mechanism of the hydrogenation of nitroethane is not apparent from the exchange studies. It does appear that hydrogenation and exchange in this case are taking place independently of each other, inasmuch as hydrogenation is independent of the gas pressure, while deuterium exchange is proportional to the first power of that pressure. This might appear to constitute an anomaly, since in the hydrogenation reaction the hydrogen may be presumed to be strongly adsorbed on the catalyst surface, while in the exchange reaction it is presumably weakly adsorbed. However, this may indicate that the reactions occur on different catalyst sites, or may be a consequence of the fact that acetic acid is much more strongly adsorbed than hydrogen while the hydrogen, in turn, is more strongly adsorbed than the nitroethane.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XXVI. The Preparation and Properties of Some ω-Cyanoalkylketene Acetals

BY S. M. MCELVAIN AND RICHARD D. MULLINEAUX[1]

De-alcoholation of the ω-cyano-orthoesters III, IV and V with aluminum methoxide yields the corresponding ω-cyanoketene acetals VI, VII and VIII, exclusively. The alternative cyclic structures of the type of IX were eliminated as possible de-alcoholation products by hydrolysis of VII and VIII to the respective normal esters and by the conversion of VI to carbomethoxycyanomethylketene acetal (X) with chloroformic ester; this reagent converts other ketene acetals smoothly to the corresponding carbalkoxyketene acetals (XIII). Sodium methoxide is shown to be a catalyst for the de-alcoholation of methyl δ-cyano-orthovalerate (V) to the ketene acetal VIII. Further reaction of VIII with this base yields initially 1-methoxy-2-cyanocyclopentene-1 (XVII), which then suffers cleavage to 2-cyanocyclopentanone (XVIII) and dimethyl ether. The relationships between the boiling points of these ω-cyanoketene acetals and the corresponding normal and orthoesters are pointed out.

The facile pyrolysis of methyl orthocyanoacetate to methanol and cyanoketene dimethylacetal was reported[2] in Paper XX of this series. In contrast to the behavior of this orthoester, the homologous methyl ortho-β-cyanopropionate (III) when subjected to pyrolysis lost methanol quite slowly and was converted to a tar.[3] It seemed of interest to investigate the de-alcoholation of the latter orthoester, as well as the homologous compounds IV and V, with the aluminum alkoxides, which recently have been found[4] to be efficient catalysts for the conversion of orthoesters to ketene acetals. Aside from a further extension of this method of de-alcoholation, there was the possibility that the hydrogen in the α-position to the cyano group might be involved in the de-alcoholation with the production of an alicyclic ketal such as IX instead of a ketene acetal.

Each of the ω-cyano-orthoesters III, IV and V, which was readily prepared from the corresponding dinitrile I *via* the iminoester hydrochloride (II), was readily de-alcoholated at 250° with 30 mole per cent. of aluminum methoxide to the ketene

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[1] E. I. du Pont de Nemours and Company Research Assistant 1951.

[2] S. M. McElvain and J. P. Schroeder, THIS JOURNAL, **71**, 47 (1949).

[3] *Ibid.*, **71**, 40 (1949); J. P. Schroeder, Ph.D. Thesis, University of Wisconsin, 1948.

[4] S. M. McElvain and (a) J. T. Venerable, THIS JOURNAL, **72**, 1661 (1950); (b) W. R. Davie, *ibid.*, **73**, 1400 (1951).

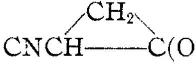
acetals VI, VII and VIII in yields of 72–86%. Aluminum *t*-butoxide also catalyzed these de-alcoholations, but the resulting ketene acetals, which were obtained in somewhat lower yields, were contaminated after distillation from the catalyst with volatile aluminum *t*-butoxy compounds.[4b]

$$\underset{\text{I}}{\mathrm{CN(CH_2)_nCH_2CN}} \xrightarrow[\mathrm{HCl}]{\mathrm{CH_3OH}} \underset{\text{II}}{\mathrm{CN(CH_2)_nCH_2C(OCH_3){=}NH_2Cl}} \xrightarrow{\mathrm{CH_3OH}}$$

$$\mathrm{CN(CH_2)_nCH_2C(OCH_3)_3} \xrightarrow[250^\circ]{\mathrm{Al(OCH_3)_3}} \mathrm{CN(CH_2)_nCH{=}C(OCH_3)_2 + CH_3OH}$$

III, n is 1
IV, n is 2
V, n is 3

VI, n is 1
VII, n is 2
VIII, n is 3

The structures of the ketene acetals VII and VIII were readily shown by hydrolysis to the corresponding normal esters, methyl γ-cyanobutyrate and methyl δ-cyanovalerate. It seemed, however, that the structure of VI could not be unequivocally established by this simple reaction because the possible alternative de-alcoholation product  (IX) IX could conceivably undergo hydrolysis to yield the same normal ester, methyl β-cyanopropionate, as would VI. The structure of VI was definitely established by reaction with methyl chloroformate. It was expected that VI would react with this acyl halide to yield the malonic ester XI, while a similar reaction of this halide with the cyclopropane structure IX would yield a succinic ester derivative. However, the reaction of methyl chloroformate with VI did not yield XI directly, but instead gave methyl chloride, methyl β-cyanopropionate and the disubstituted ketene acetal X. The latter compound was readily converted by hydrolysis to XI, which proved to be identical with an authentic sample prepared from dimethyl malonate and chloroacetonitrile.

$$\mathrm{2VI + ClCOOCH_3 \longrightarrow CH_3Cl +}$$
$$\mathrm{CNCH_2CH_2COOCH_3 +} \underset{\text{X}}{\mathrm{CNCH_2C(COOCH_3){=}C(OCH_3)_2}}$$

$$\mathrm{X} \xrightarrow{\mathrm{H_3O^+}} \underset{\text{XI}}{\mathrm{CNCH_2CH(COOCH_3)_2}} + \mathrm{CH_3OH}$$

This unexpected reaction of VI with methyl chloroformate to yield the carbomethoxyketene acetal X prompted an investigation of the behavior of some other ketene acetals with this acyl halide. Ketene dimethylacetal and methylketene diethylacetal reacted with chloroformic ester in the same manner as VI to yield the carbalkoxyketene acetals (XIII), which were converted by hydrolysis to the corresponding malonic esters (XIV). In contrast to this behavior, neither the carbalkoxyketene acetals (XIII) nor phenylketene dimethylacetal, $\mathrm{C_6H_5CH{=}C(OCH_3)_2}$, gave any reaction when heated with a chloroformic ester. It appears, therefore, that a substituent, such as phenyl and carbalkoxy, which carries an unsaturated center in conjugation with the double bond of the ketene acetal, is capable of reducing the electron density of the α-carbon of ketene acetal sufficiently to prevent its initial facile reaction with the chloroformic ester to form the intermediate carbonium ion XII. When XII is formed, the extraction of a proton from it by the second molecule of the ketene acetal produces the reaction product XIII.

The formation of the ketene acetals VI, VII and VIII rather than cyclic ketals in the de-alcoholation of the orthoesters III, IV and V with aluminum alkoxides furnishes additional support for the earlier suggestion[4] that the alkoxide functions by coördination of the aluminum with an oxygen of the orthoester followed by a concerted breakdown of this complex into the reaction products, alcohol and the ketene acetal.

$$\mathrm{RCH{=}C(OR')_2} \xrightarrow{\mathrm{ClCOOR'}}$$
$$\underset{\text{XII}}{\left[\mathrm{RCH(COOR')\overset{\oplus}{C}(OR')_2}\right]} \xrightarrow{\mathrm{RCH{=}C(OR')_2}}$$
$$\mathrm{R'Cl + RCH_2COOR' +} \underset{\text{XIII}}{\mathrm{RC(COOR'){=}C(OR')_2}} \xrightarrow{\mathrm{H_3O^+}}$$
$$\underset{\text{XIV}}{\mathrm{RCH(COOR')_2}}$$

Sodium methoxide was found to be a catalyst for the de-alcoholation of methyl ortho-δ-cyanovalerate V to the ketene acetal VIII. This unexpected reaction was discovered when an attempt was made to cyclize V to 2-cyanocyclopentanone dimethylketal in the presence of 5 mole per cent. of this base. It was expected that the carbanion XV would cyclize with the elimination of a methoxyl anion. Instead, methanol was evolved as the reaction mixture approached 250°, and if the reaction were stopped after one equivalent of the alcohol had been collected, a 50% yield of the ketene acetal VIII together with a small amount of 1-methoxy-2-cyanocyclopentene-1 (XVII) were obtained. It appears that the carbanion XV, which would seem to be the most likely initial product of the reaction of sodium methoxide with V, caused a de-alcoholation of its orthoester function, in a manner similar to that previously postulated for the dealcoholation of pentaethoxyethane,[5] to yield VIII (probably *via* the anion XVI) and regenerate the basic catalyst.

$$\mathrm{V + \overset{\ominus}{O}CH_3 \longrightarrow CH_3OH +} \underset{\text{XV}}{\mathrm{CN\overset{\ominus}{C}H(CH_2)_3C(OCH_3)_3}} \rightleftarrows$$
$$\underset{\text{XVI}}{\mathrm{CN(CH_2)_3\overset{\ominus}{C}HC(OCH_3)_3}} \longrightarrow \mathrm{VIII + \overset{\ominus}{O}CH_3}$$

If the heating of V with 5 mole per cent. of sodium methoxide were continued to the point where the evolution of methanol ceased, two equivalents of the alcohol were obtained. The other reaction products were XVII (15%) and a useless tar. It appeared, therefore, that the ketene acetal (VIII) was the precursor of both XVII and the tar. This supposition was substantiated when it was found that VIII with 5 mole per cent. of the

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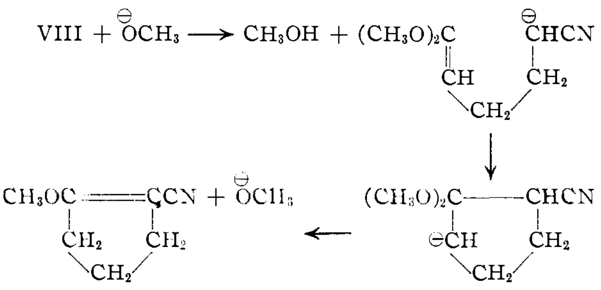
[5] S. M. McElvain and R. L. Clarke, This Journal, **69**, 2661 (1947).

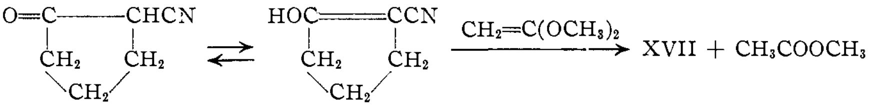
base at 250° gave practically the same yields of these products as were obtained from the orthoester V when the reaction was run to the completed evolution of methanol.

The cyclization of VIII to XVII in the presence of sodium methoxide, which is analogous to the base-catalyzed condensation of acetoacetic and malonic esters with ketene diethylacetal,[6] may be illustrated as



XVII

The structure of XVII was confirmed by comparison with an authentic sample prepared by the reaction of 2-cyanocyclopentanone (XVIII) with ketene dimethylacetal:



XVIII

If the cyclization of VIII to XVII followed the course shown above, it seemed that the yield of cyclized product might be increased and the tar formation decreased if a higher ratio of the basic condensing agent were used in the reaction. The use of 100 mole per cent. of the base was impracticable because it produced a solid reaction mass that charred when heated, but when VIII was heated with 75 mole per cent. of sodium methoxide a smooth reaction occurred. Dimethyl ether (50%) and methanol (90%) were evolved and 42% of VIII was recovered; acidification of the residue gave a 51% yield of 2-cyanocyclopentanone (XVIII). The sodium enolate of this latter product and the dimethyl ether doubtless were produced in this reaction by the cleavage of the initially formed 1-methoxy-2-cyanocyclopentene-1 (XVII) by sodium methoxide, as a pure sample of XVII was readily converted to these products when heated with the base.

Attempts to effect similar cyclizations of the ketene acetals VI and VII with sodium methoxide produced only irresolvable tars.

In addition to the chemical properties outlined above, it is of interest to note the relationship of the boiling points of the various ω-cyanoketene acetals to those of the corresponding normal esters and orthoesters. These are listed in Table I along with similar values for a typical alkyl substituted compound, *n*-propylketene dimethylacetal. The boiling point of the latter compound, as well as those of most of the other ketene acetals, generally lie between the boiling points of the normal ester and the orthoester.[7] The boiling point of the first member of the cyano series, cyanoketene dimethylacetal,[2] in which the unsaturation of the cyano group is conjugated with the double bond of the ketene acetal, is considerably higher than that of either of the corresponding esters; a similar relationship exists when a carbalkoxy or phenyl substituent is attached to the α-carbon of the ketene acetal.[7] However, when the cyano group is moved out of this position of conjugation, as it is in the homologous cyanoalkyl substituents of VI, VII and VIII, the boiling point of the ketene acetal is progressively lowered below that of either of the related esters. Such abnormally low relative boiling points, which hitherto have been observed only in the case of tetraethoxyethylene,[5] would seem to indicate an intramolecular interaction of the functional groups of the ω-cyanoalkylketene acetals.

TABLE I

BOILING POINTS OF SOME KETENE ACETALS, NORMAL ESTERS AND ORTHOESTERS

R	B.p., °C. (mm.)		
	$RCH{=}C(OCH_3)_2$	RCH_2COOCH_3	$RCH_2C(OCH_3)_3$
CN	126 (11)	92 (11)	102 (13)
$CNCH_2$	96 (9)	96.5 (9)	102 (9)
$CN(CH_2)_2$	96.5 (8)	99 (8)	110 (8)
$CN(CH_2)_3$	110 (9)	117 (9)	128 (9)
$CH_3(CH_2)_3$	144 (750)	127 (750)	166 (750)

Experimental

ω-Cyano Iminoester Hydrochlorides (II) (a) Methyl Imino-β-cyanopropionate Hydrochloride.—This compound was prepared by the procedure of McElvain and Schroeder.[2] Distillation of commercial succinonitrile (American Cyanamid Co.) from phosphorus pentoxide gave pure starting material, m.p. 54–55°. Varying the size of the run from one to three moles did not materially change the yield of methyl imino-β-cyanopropionate hydrochloride.

(b) Methyl Imino-γ-cyanobutyrate Hydrochloride.—Using the same procedure as above, a solution of 98 g. (1.05 moles) of glutaronitrile[8] ($n^{25}D$ 1.4343) and 33.5 g. (1.04 mole) of absolute methanol in 600 ml. of dry ether and 50 ml. of dioxane was treated with 45 g. (1.25 moles) of anhydrous hydrogen chloride. After 15 days the yield of **methyl imino-γ-cyanobutyrate hydrochloride** was 107 g. (63.5%). A second run using the filtrate from this preparation gave an 85% yield of this compound in ten days.

Anal. Calcd. for $C_6H_{11}ClN_2O$: Cl, 21.84. Found: Cl, 21.92.

(c) Methyl Imino-δ-cyanovalerate Hydrochloride.—Pure adiponitrile, m.p. 1.0–1.5°, $n^{25}D$ 1.4368,[9,10] was obtained by distilling commercial adiponitrile (Mathieson Co.) from phosphorus pentoxide. The same procedure was used as for the preparation of methyl imino-β-cyanopropionate hydrochloride except that no dioxane was necessary to obtain a homogeneous solution. The yield of **methyl imino-δ-cyanovalerate hydrochloride** on the first run was 75%. The yield of product was improved in subsequent runs by using the filtrate from a previous run as solvent. In this way yields as high as 98% were obtained and the average yield for a series of runs was 90%.

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[6] S. M. McElvain, *et al.*, THIS JOURNAL, **62**, 1281 (1940); **64**, 1831 (1942).

[7] S. M. McElvain, *Chem. Revs.*, **45**, 453 (1949).

[8] C. S. Marvel and E. M. McColm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 536.

[9] The refractive index, nD 1.4597 (*Chem. Zentr.*, **72**, II, 807 (1901)), originally reported by Henry is the only one given in the standard reference books.

[10] Korshak and Pakhomov (*C. A.*, **36**, 3488 (1942)) have recently reported $n^{20}D$ 1.4380 for adiponitrile.

Anal. Calcd. for $C_7H_{13}ClN_2O$: Cl, 20.07. Found: Cl, 20.03.

ω-Cyano-orthoesters.—The previously reported[2] procedure was modified for these preparations. A mixture of the iminoester hydrochloride and methanol was shaken until solution, accompanied by marked cooling, was complete. As soon as the iminoester hydrochloride was in solution the reaction mixture began to warm due to the heat of reaction. The reaction mixture was kept cool by placing in the refrigerator for one hour. After eight hours, at which time the reaction was complete, ether (3 ml. per ml. of methanol) was added to complete the precipitation of ammonium chloride and the latter was filtered from the solution. The solution was then made basic to litmus with methanolic sodium methoxide and any precipitated sodium chloride was filtered. After the solvent had been removed by distillation, the product was distilled rapidly under diminished pressure. Refractionation of this product through a 40-cm. McMahon packed column gave pure orthoester. It was necessary to distil the product rapidly from the original reaction residues because the small amount of sodium methoxide present caused considerable decomposition during the time necessary for a fractionation. Runs larger than 1 mole gave lower yields than those reported.

(a) **Trimethyl Ortho-β-cyanopropionate** (IV).—A mixture of 75 g. (0.5 mole) of methyl imino-β-cyanopropionate hydrochloride in 500 ml. of methanol gave 54 g. (67%) of IV, b.p. 104–105° (10 mm.), n^{25}_{D} 1.4267 (reported[2] b.p. 73–74° (0.5 mm.), n^{25}_{D} 1.4269). This product was purified by treating overnight with aqueous ammonia to remove any normal ester *via* amide formation.

(b) **Trimethyl Ortho-γ-cyanobutyrate** (III).—The reaction of 63.0 g. (0.374 mole) of methyl imino-γ-cyanobutyrate hydrochloride with 250 ml. of absolute methanol gave 17.5 g. (88%) of ammonium chloride and 47 g. (67%) of IV, b.p. 108.5–109° (8 mm.), n^{25}_{D} 1.4292, d^{25}_4 1.035.

Anal. Calcd. for $C_8H_{15}NO_3$: C, 55.87; H, 8.73; CH_3O, 53.6. Found: C, 55.47; H, 8.67; CH_3O, 51.5.

IV reacted with dilute hydrochloric acid to give **methyl γ-cyanobutyrate** in 85% yield, b.p. 98–99° (8 mm.), n^{25}_{D} 1.4253.

Anal. Calcd. for $C_6H_9NO_2$: CH_3O, 24.4. Found: CH_3O, 23.8.

(c) **Trimethyl Ortho-δ-cyanovalerate** (V).—A 144 g. (0.815 mole) sample of methyl imino-δ-cyanovalerate hydrochloride reacted in 500 ml. of absolute methanol to give 39.2 g. (91.5%) of ammonium chloride and 115 g. (75%) of V, b.p. 128–129° (9 mm.), n^{25}_{D} 1.4344, d^{25}_4 1.0197.

Anal. Calcd. for $C_9H_{17}NO_3$: C, 57.72; H, 9.15; CH_3O, 49.6. Found: C, 57.72; H, 9.14; CH_3O, 48.3.

V reacted with dilute hydrochloric acid to give a 94% yield of **methyl δ-cyanovalerate**, b.p. 116–117° (9 mm.), n^{25}_{D} 1.4307, d^{25}_4 1.0201 (reported[11] b.p. 93° (3 mm.)).

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.59; H, 7.80; CH_3O, 22.0. Found: C, 59.60; H, 7.74; CH_3O, 21.0.

ω-Cyanoketene Acetals (a) **Cyanomethylketene Dimethylacetal** (VI) (i) From III **and Aluminum Methoxide.**—A suspension of 3.5 g. (0.029 mole) of aluminum methoxide,[4a] in 17 g. (0.107 mole) of III was placed in a 50-ml. flask connected to a 20-cm. Vigreux column and stillhead. The suspension was heated to a bath temperature of 260° for one hour, during which time 3.2 g. (94%) of methanol was collected. The reaction mixture was allowed to cool and then the product was distilled under diminished pressure; after a small forerun, a uniform main fraction of 11.8 g. (86%) of **cyanomethylketene dimethylacetal** (VI), b.p. 95–96° (9 mm.), n^{25}_{D} 1.4420, d^{25}_4 1.034, was obtained. It was found particularly important (a) to use orthoester completely free of normal ester, (b) to stop the reaction at the point when the evolution of methanol ceased, because the normal ester, orthoester and ketene acetal all boil so close together that good separation could not be obtained.

Anal. Calcd. for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.00. Found: C, 56.88; H, 6.98; N, 10.75.

(ii) **From III and Aluminum *t*-Butoxide.**—A solution of 15.0 g. (0.058 mole) of aluminum *t*-butoxide[4b] and 18.4 g. (0.115 mole) of III in a 50-ml. flask fitted with a 40-cm. Vigreux column and stillhead, was heated at 185° for two hours, during which time a distillate of 8.06 g. (95%) of *t*-butyl alcohol was collected. The product was then distilled under reduced pressure to give 10.2 g. (69%) of crude material, b.p. 94–96° (9 mm.), n^{25}_{D} 1.4410. Redistillation gave 9.5 g. (63%) of pure VI, b.p. 94.8–95° (9 mm.), n^{25}_{D} 1.4417. A small amount of colloidal material, which was very hard to separate, was usually suspended in the product. Davie[4b] has reported this material to be aluminum monomethoxy di-*t*-butoxide which, unlike the aluminum *t*-butoxide, is volatile and contaminates the higher boiling ketene acetals.

(b) **β-Cyanoethylketene Dimethylacetal** (VII).—A suspension of 4.4 g. (0.037 mole) of aluminum methoxide in 21.5 g. (0.124 mole) of trimethyl ortho-γ-cyanobutyrate (IV), n^{25}_{D} 1.4292, in a 50-ml. flask fitted with a 15-cm. Vigreux column and a stillhead, was heated to 260° for 50 minutes. At this time methanol had ceased to be evolved; 3.57 g. (90%) was collected. All of the volatile material, 15.7 g. (90%), n^{25}_{D} 1.4430, was removed by heating under reduced pressure. Redistillation of this product gave 13.8 g. (79%) of VII, b.p. 95–95.5° (8 mm.), n^{25}_{D} 1.4446, d^{25}_4 1.008.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.86; CH_3O, 43.7. Found: C, 59.52; H, 7.90; CH_3O, 42.3.

The reaction of 1.5 g. of VII with 5 ml. of distilled water containing 1 drop of concentrated hydrochloric acid gave 1.1 g. (81%) of methyl γ-cyanobutyrate, b.p. 101–102° (9 mm.), n^{25}_{D} 1.4252.

(c) **γ-Cyanopropylketene Dimethylacetal** (VIII) (i) **From V with Aluminum Methoxide.**—A suspension of 3.65 g. (0.03 mole) of aluminum methoxide in 20 g. (0.107 mole) of V, n^{25}_{D} 1.4344, was placed in a 50-ml. flask and attached to a short Vigreux column and stillhead. The mixture was heated to 250° for 20 minutes, during which time 3.38 g. (99%) of methanol was collected. After cooling, the pressure in the system was lowered and all of the volatile material was quickly removed from the catalyst by reheating. A total of 14.8 g. (89%) of distillate, n^{25}_{D} 1.4492, was thus obtained. This crude product was treated with 0.2 g. of sodium hydroxide at room temperature for 15 minutes to remove any normal ester, and then distilled to give 12.5 g. (75%) of pure VIII, b.p. 108–109° (8 mm.), n^{25}_{D} 1.4488, d^{25}_4 0.9894.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.92; H, 8.44. Found: C, 61.88; H, 8.54.

(ii) **From V with Aluminum *t*-Butoxide.**—A solution of 11.0 g. (0.0425 mole) of aluminum *t*-butoxide in 15.5 g. (0.083 mole) of trimethyl ortho-δ-cyanovalerate (V), n^{25}_{D} 1.4347, reacted at 175° to give 4.2 g. (70%) of *t*-butyl alcohol and 7.0 g. (57%) of crude VIII. Treatment of this product with 0.5 g. of sodium hydride to remove the normal ester gave 6.3 g. (50%) of VIII, b.p. 109–110° (9 mm.), n^{25}_{D} 1.4486.

(iii) **From Pyrolysis of V.**—Pyrolysis of 18.8 g. (0.1 mole) of trimethyl ortho-δ-cyanovalerate (V), n^{25}_{D} 1.4344, at 260° for five hours gave 3.2 g. (100%) of methanol. Only 3.5 g. (22%) of γ-cyanopropylketene dimethylacetal (VIII) and 5.0 g. (35%) of impure methyl δ-cyanovalerate were isolated from the reaction mixture, the remainder of the product being tar. Total hydrolysis of a portion of the initial reaction mixture with concentrated sulfuric acid gave a 90% yield of adipic acid, m.p. 149–151°, but no steam-volatile ketone.

The addition of one drop of dilute hydrochloric acid to a suspension of 1 g. of VIII, n^{25}_{D} 1.4418, in 5 ml. of distilled water gave 0.8 g. (88%) of methyl δ-cyanovalerate, b.p. 116–117° (9 mm.), n^{25}_{D} 1.4306.

(iv) **From V with Sodium Methoxide.**—A suspension of 0.5 g. (5 mole %) of sodium methoxide in 34.7 g. (0.185 mole) of V, n^{25}_{D} 1.4344, in a 125-ml. flask fitted with a short Vigreux column and stillhead, was heated to 260°. In 25 minutes 6.6 g. (120% of one equivalent) of methanol had been collected and the reaction was discontinued. Fractionation of the product gave the following fractions: (1) 2.39 g., b.p. 91–105° (9 mm.), n^{25}_{D} 1.4775; (2) 11.8 g., b.p. 107–110° (9 mm.), n^{25}_{D} 1.4470; (3) 2.5 g., b.p. 111–117° (9 mm.), n^{25}_{D} 1.4371; (4) 3.11 g., b.p. 120–128° (9 mm.), n^{25}_{D} 1.4350. Fraction 1 contained approximately 1.7 g. (8%) of 1-methoxy-2-cyanocyclopentene-1 (XVII) on the basis of refractive index; refractionation of fraction 2 gave 10 g. (41%) of γ-cyanopropylketene dimethylacetal (VIII), b.p. 109–110° (9 mm.), n^{25}_{D} 1.4486; a methoxyl determina-

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(11) British Patent 568,941 (1945); *C. A.*, **41**, 4511 (1947).

tion of fraction 3 indicated that it contained some normal ester; 2.6 g. of unchanged orthoester (V), b.p. 128–129° (9 mm.), n^{25}_{D} 1.4350 was obtained from fraction 4.

Reactions of Ketene Acetals with Chloroformic Esters (a) Ketene Dimethylacetal.—A mixture of 25 g. (0.284 mole) of the ketene acetal, n^{25}_{D} 1.4052, and 13.4 g. (0.142 mole) of methyl chloroformate was placed in a 50-ml. flask fitted with a thermometer extending into the solution and a reflux condenser, which was connected at the top to a Dry Ice–acetone cold trap. The mixture was heated slowly to 57°, at which point the reaction temperature rose higher than the bath temperature. The bath temperature was held at 60° while the reaction temperature rose to 65° where it remained for 30 minutes. During this time 5.0 g. (35%) of methyl chloride collected in the cold trap. Fractionation of the product gave 17.2 g. of low boiling material and 12.1 g. (30%) of a product, b.p. 104–110° (8 mm.), which solidified on standing. The low boiling material was shown by refractionation to consist of methyl acetate (37%), b.p. 56–61°, and unchanged methyl chloroformate and ketene acetal. Recrystallization of the solid fraction from 60–68° petroleum ether gave platelets of pure **carbomethoxyketene dimethylacetal**, m.p. 57–58°.

Anal. Calcd. for $C_6H_{10}O_3$: C, 49.31; H, 6.90; CH_3O, 63.5. Found: C, 49.67; H, 6.97; CH_3O, 61.2.

A mixture of 1 g. of this ketene acetal and 5 ml. of distilled water, when treated with 1 drop of concentrated hydrochloric acid, gave a noticeable evolution of heat. The solution was shaken for five minutes and then was saturated with sodium chloride, extracted with ether, and the ether layer dried over anhydrous sodium sulfate. After evaporation of the ether, distillation of the product gave 0.7 g. of dimethyl malonate, b.p. 175–178° (740 mm.), n^{25}_{D} 1.4102, which, after standing overnight with concentrated ammonia, yielded malonamide, m.p. 167–169°.

(b) **Methylketene Diethylacetal.**—A solution of 9.41 g. (0.087 mole) of ethyl chloroformate in 11.28 g. (0.087 mole) of methylketene diethylacetal, n^{25}_{D} 1.4120, was heated to 110° in the same apparatus described in (a). After 30 minutes, in which time 2.5 g. (45%) of ethyl chloride was collected, the product was fractionated to give 8.4 g. of low boiling material and 7.9 g. of a product, b.p. 104–108° (10 mm.), n^{25}_{D} 1.4382. Refractionation of the latter material gave **methylcarbethoxyketene diethylacetal**, b.p. 99–100° (8 mm.), n^{25}_{D} 1.4385.

Anal. Calcd. for $C_{10}H_{18}O_4$: C_2H_5O, 68.8. Found: C_2H_5O, 66.5.

Hydrolysis converted this ketene acetal to diethyl methylmalonate, b.p. 192–195° (740 mm.), n^{25}_{D} 1.4097, which gave methylmalonamide, m.p. 207–210°, with concentrated ammonia.

(c) **Cyanomethylketene Dimethylacetal** (VI).—In the manner described in (a), 11.84 g. (0.093 mole) of VI, n^{25}_{D} 1.4414, and 4.42 g. (0.088 mole) of methyl chloroformate were heated to 70° at which time the reaction temperature exceeded the bath temperature. The bath temperature was held at 76° for two hours while the reaction temperature rose to 80° and then returned to 75°; during this time 1.5 g. (33%) of methyl chloride was collected. Fractionation of the product through a 40-cm. Vigreux column gave 1.6 g. of unchanged methyl chloroformate, 4.2 g. (38%) of methyl β-cyanopropionate, and 5.8 g. (31%) of **carbomethoxycyanomethylketene dimethylacetal** (X), b.p. 110–111° (1.0 mm.), n^{25}_{D} 1.4770, d^{25}_{4} 1.184. This product solidified in the refrigerator, m.p. 18–20°.

Anal. Calcd. for $C_8H_{11}NO_4$: C, 51.89; H, 5.99; N, 7.54. Found: C, 51.83; H, 6.18; N, 7.52.

Hydrolysis of X, n^{25}_{D} 1.4770, as above gave **dimethyl cyanomethylmalonate** (XI), b.p. 132–134° (8 mm.), n^{25}_{D} 1.4380. Three recrystallizations of the ammonolysis product of XI gave **cyanomethylmalonamide**, m.p. 246–248° (dec.) with softening and browning at 230°. The mixed melting point of this product and the cyanomethylmalonamine, prepared in the following procedure, was 246–248° (dec.) with softening and browning at 230–235°.

To a solution of sodium methoxide, prepared by the reaction of 5.75 g. (0.25 mole) of sodium with 125 ml. of absolute methanol, was added 39.5 g. (0.29 mole) of dimethyl malonate and the solution was warmed until it became clear. Then 18.9 g. (0.25 mole) of chloroacetonitrile was added slowly and the mixture was heated to reflux for two hours. The alcohol was removed by distillation, water was added to dissolve the sodium chloride and the solution was extracted with ether. After evaporation of the ether, the product was distilled and the following fractions were obtained: 8.1 g. at 78° (11 mm.), n^{25}_{D} 1.4127, 4.3 g. at 140–142° (11 mm.), n^{25}_{D} 1.4382, and a residue of 8.5 g. of tar. The second fraction was refractionated to give 3.1 g. (10%) of **dimethyl cyanomethylmalonate** (XI), b.p. 137–138° (10 mm.), n^{25}_{D} 1.4387, d^{25}_{4} 1.019.

Anal. Calcd. for $C_7H_9NO_4$: C, 49.12; H, 5.30; N, 8.16. Found: C, 49.07; H, 5.37; N, 8.14.

XI was allowed to stand with concentrated ammonia overnight. White platelets formed in the solution which were filtered and dried. Three recrystallizations from 50% ethanol–water gave pure cyanomethylmalonamide, m.p. 247–248° (dec.) with softening and browning at 230–235°.

Anal. Calcd. for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.8. Found: C, 42.58; H, 4.90; N, 29.6.

Reaction of γ-Cyanopropylketene Dimethylacetal (VIII) **with (i) 5 Mole % Sodium Methoxide.**—A suspension of 0.2 g. (5 mole %) of sodium methoxide in 11.1 g. (0.0715 mole) of VIII, n^{25}_{D} 1.4488, in a 25-ml. flask fitted with a 10-cm. Vigreux column and stillhead, was heated to 255°, at which time methanol began to be evolved slowly. After heating at this temperature for 1.5 hours, 2.1 g. (91% of one equivalent) of methanol had been collected. Distillation of the reaction mixture gave two fractions containing 3 components: (1) 1.6 g. (18%) of impure 1-methoxy-2-cyanocyclopentene-1 (XVII), b. p. 95–105° (10 mm.), n^{25}_{D} 1.4805; (2) 2.4 g. of a mixture of γ-cyanopropylketene dimethylacetal and methyl δ-cyanovalerate, b.p. 105–120° (10 mm.).

When the same reaction was run except that only 1.3 g. (55% of one equivalent) of methanol was collected, 1.1 g. (12%) of XVII and 5.0 g. (45%) of unchanged VIII were isolated from the reaction mixture.

The materials boiling below 105° (10 mm.) from a number of such runs were combined and treated with methanol and a trace of anhydrous hydrogen chloride in order to convert any γ-cyanopropylketene dimethylacetal present to the corresponding orthoester and facilitate fractionation. The reaction mixture was neutralized with sodium methoxide and fractionated to give a total of 8 g. of nearly pure **1-methoxy-2-cyanocyclopentene-1** (XVII), b.p. 111–112° (23 mm.), n^{25}_{D} 1.4874.

XVII was prepared by the reaction of 9.9 g. (0.091 mole) of 2-cyanocyclopentanone[12] (XVIII), n^{25}_{D} 1.4665, with 11.0 g. (0.125 mole) of ketene dimethylacetal. The reaction mixture immediately became quite warm. After the reaction had abated, the mixture was heated to 100° for one hour and then distilled to give 7.2 g. (65%) of material, b.p. 75–95° (9 mm.). Fractionation of this product gave 6.1 g. (55%) of XVII, b.p. 84–85° (9 mm.), n^{25}_{D} 1.4880. The best fraction in this range had the following properties: b.p. 84.5° (9 mm.), n^{25}_{D} 1.4892. A mixture of 5 g. of XVII prepared in this way and 5 g. of XVII obtained from the reaction of sodium methoxide with γ-cyanopropylketene dimethylacetal (VIII) was refractionated. A total of 8.0 g. (80%) of **1-methoxy-2-cyanocyclopentene-1** was recovered with properties identical to the best previously obtained, b.p. 84.5–85° (9 mm.), n^{25}_{D} 1.4890.

Anal. Calcd. for C_7H_9NO: C, 67.72; H, 7.31; CH_3O, 25.5; N, 11.53. Found: C, 67.43; H, 7.65; CH_3O, 26.0; N, 11.48.

A suspension of 3.0 g. (0.055 mole) of sodium methoxide in 7.07 g. (0.0575 mole) of XVII, n^{25}_{D} 1.4890, was heated to 250° for one hour. Within 15 minutes it was no longer possible to stir the reaction mixture but the heating was continued for an additional 45 minutes, during which time 0.5 g. (28%) of methanol and 0.8 g. (31%) of dimethyl ether were collected. Extraction of the solid reaction mixture with ether gave 1 g. (14%) of unchanged XVII; neutralization and extraction of the basic residue gave 1.2 g. (20%) of impure 2-cyanocyclopentanone, b.p. 125–130° (9 mm.), n^{25}_{D} 1.4635. This product reacted with semicarbazide hydrochloride to give 1.3 g. (75%) of α-cyanocyclopentanone semicarbazone, m.p. 192–195°.

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[12] Prepared by the procedure of Ziegler, *et al.*, (*Ann.*, **504**, 94 (1933)) from reaction of lithium diethylamide with adiponitrile; it had the following properties: b.p. 135–136° (15 mm.), n^{25}_{D} 1.4670; m.p. of semicarbazone 195–195.5° (*cf.* S. R. Best and J. F. Thorpe, *J. Chem. Soc.*, **95**, 685 (1909)).

(ii) **With 75 Mole % Sodium Methoxide.**—A suspension of 13.05 g. (0.242 mole) of sodium methoxide in 50 g. (0.322 mole) of VIII was placed in a 200-ml. centrifuge bottle connected to a stillhead and arranged for stirring. The stillhead was connected to a Dry Ice–acetone cold trap so that any distillate would pass a water condenser and then into the cold trap. The stirrer was started and the reaction mixture was heated to 255–260° for one and three-quarter hours. At this time 7.11 g. (92%) of methanol had collected at the water condenser and 7.0 g. of material had collected in the cold trap. Distillation of this latter material to a second cold trap gave 6.5 g. (50%) of dimethyl ether, identified as its boron trifluoride complex.[13] The reaction mixture was cooled, 50 ml. of dry ether was added and the suspension was centrifuged. After the solid had been extracted with a total of 200 ml. of ether, the ether was evaporated and the residue distilled to give 21.0 g. (42%) of unchanged γ-cyanopropylketene dimethylacetal (VIII), b.p. 109–110° (9 mm.), n^{25}D 1.4488. The residue from the ether extraction was suspended in 100 ml. of ether and 14.5 g. (0.242 mole) of glacial acetic acid was added slowly with stirring. The resulting suspension was centrifuged and the sodium acetate was triturated with ether and centrifuged three times. Evaporation of the ether and distillation of the product gave 13.60 g. (61.4%) of 2-cyanocyclopentanone (XVIII), b.p. 135–136° (15 mm.), n^{25}D 1.4658. Redistillation of this product gave 12.3 g. of pure XVIII, b.p. 123–124° (8 mm.), n^{25}D 1.4672.

In the same apparatus used above a suspension of 11 g. (0.204 mole) of sodium methoxide in 42 g. (0.33 mole) of cyanomethylketene dimethylacetal (VI) was heated to 200° at which time a vigorous, exothermic reaction commenced. The reaction maintained itself for 10 minutes, during which time 7 g. (100%) of methanol had been collected. The reaction was then stopped by placing the flask in cold water. The reaction mixture had solidified and expanded to fill the centrifuge bottle. The cooled product was a hard black solid from which only 1 g. of methyl δ-cyanopropionate was extracted after acidification with acetic acid.

A suspension of 4.0 g. (0.075 mole) of sodium methoxide in 14.1 g. (0.10 mole) of β-cyanoethylketene dimethylacetal (VII) was heated to 240° as described above. After 40 minutes, during which time 2.1 g. (88%) of methanol and 1.6 g. (46%) of dimethyl ether were collected, the reaction was stopped. The reaction mixture was worked up in the usual way, except that ethyl acetate rather than ether was used for the extraction, to give a recovery of 4.05 g. (28.5%) of VII, b.p. 95–96° (8 mm.), n^{25}D 1.4446. The basic residue was neutralized with 4.45 g. (0.075 mole) of glacial acetic acid, but only a small amount of tar was obtained by extraction. More tar was obtained by dissolving the solid residues in 50 ml. of water acidified with 2 ml. of concentrated sulfuric acid.

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[13] A. W. Laubengayer and G. R. Findlay, This Journal, **65**, 884 (1943).

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

Ketene Acetals. XXVII. The Bromination of Various Ketene Acetals

By S. M. McElvain and William R. Davie[1]

Monosubstituted ketene acetals (II, III and IV), when added to a solution of bromine, yield the corresponding bromoesters and alkyl halides (reaction 1). A reverse order of mixing of the reactants causes II and III to follow reaction 2 to a large extent; the resulting γ-bromo-β,β-dialkoxyesters (X and XI) are readily converted by pyrolysis to the tetronic acid enol ethers (XII and XIII). Under certain conditions dimethyl α,α'-diphenylsuccinate (XIV) may be formed during the bromination of the phenylketene acetal (III); possible reactions (4 and 5) to account for the formation of XIV are discussed. The cyanoketene acetal (IV) follows a different bromination course to yield a bromocyanoketene acetal (XVII) *via* reaction 6. The dimethylketene acetal (XVIII), which yields only methyl α-bromoisobutyrate regardless of the method of bromination, is converted in part to the corresponding bromo-orthoester XXII when brominated in the presence of an orthoester. A mechanism for this unusual reaction is shown in reactions 7 and 7a. Bromination of the unsubstituted ketene diethylacetal (XXIV) is complicated by the ease of polymerization of this compound; the only pure products that could be isolated were the mono- and dibromoesters XXV and XXVII. The structures and properties of the two products resulting from the action of diazomethane on 3,5-diphenyltetronic acid (XXIX) have been determined (reaction 10).

In the third paper[2] of this series the bromination of bromoketene diethylacetal (I) was described. At 0–5° this ketene acetal absorbed only 0.7 of an equivalent of bromine. This apparently incomplete absorption of bromine was shown to be the result of two concurrent reactions, in one of which the bromine added to an equivalent of the ketene acetal to give ethyl dibromoacetate (V) and ethyl bromide (reaction 1) while in the other (reaction 2) bromine reacted with two equivalents of the ketene acetal to yield the ketal of a tribromoacetoacetic ester (IX) and ethyl bromide.

The present paper reports the results of a study of the reaction of bromine with methylketene diethylacetal (II), phenylketene dimethylacetal (III), cyanoketene dimethylacetal (IV), dimethylketene dimethylacetal (XVIII) and ketene diethylacetal (XXIV).

With the exception of the unsubstituted ketene acetal XXIV, each of these acetals consumed practically the theoretical amount of bromine, when it was added to a solution of bromine in carbon tetrachloride at 0–5°, and yielded the corresponding bromoester VI, VII or VIII *via* reaction 1. The disubstituted ketene acetal XVIII gave similar results when the order of addition was reversed so that a high initial excess of the ketene acetal was present. However, under these latter reaction conditions, the monosubstituted ketene acetals II, III and IV showed significantly different behaviors.

When bromine was added to methylketene acetal (II) at 0–5° only 58% of the theoretical amount was absorbed; similar results were obtained when the bromination was conducted at −78°. The only reaction products were the bromoester VI (20%) and the bromoketal X (77%) (reaction 2). This latter product could be distilled at 0.5 mm., but at higher pressures, *e.g.*, 15 mm., distillation converted X to the tetronic acid enol ether XII with the elimination of alcohol and ethyl bromide (reaction 3).

The phenylketene acetal IV absorbed 92% of the theoretical amount of bromine at 0–5° when a

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[1] Wisconsin Alumni Research Foundation Research Assistant, 1950–1951.

[2] A. Magnani and S. M. McElvain, This Journal, **60**, 2210 (1938).