Table IX

Reductions of Ethyl Benzoate in Various Solvents

Solvent	Reactants, mmoles			Temp.,[a] °C.	Time, hr.	Hydride used, mmoles	Reduction, %
	Ester	$NaBH_4$	$AlCl_3$				
Tetrahydrofuran	5.00	5.50	1.80	80	3.0	8.5	85
Diethyl ether	5.00	7.50	2.50	40	3.0	3.4	34
Dioxane	5.00	4.00	1.40	100	3.0	Small	Small
Tetrahydrofuran–diglyme (4:1)	5.00	5.00	1.70	80	3.0	9.7	97
Ethyl ether–diglyme (4:1)	5.00	5.00	1.70	40	3.0	10.9	100

[a] Bath temperature.

Other Solvents for Reduction.—The utility of other ether solvents for these reductions was examined by treating ethyl benzoate with sodium borohydride and aluminum chloride in tetrahydrofuran, ethyl ether, dioxane, and in tetrahydrofuran and ethyl ether each containing 20% diglyme. The results are summarized in Table IX.

Other Metal Halides in Reductions.—On mixing titanium tetrachloride with equivalent amounts of sodium borohydride in diglyme, no precipitation or gas evolution was observed immediately. However, the solution changed color and eventually a gray precipitate separated.

In the case of gallium chloride and zinc chloride mixing, the reagents resulted in the formation of a white precipitate. Stannic chloride produced a vigorous evolution of gas and a gray precipitate separated out. In this process nearly 50% of the initial hydride was utilized.

The precise nature of these reactions is under investigation. In the present study these reaction mixtures were mixed with ethyl benzoate under a set of standard reaction conditions and the extent of reduction estimated from the utilization of hydride by the ester.

The results are summarized in Table X.

The results indicate that both gallium chloride and titanium tetrachloride are effective in bringing about the reduction of ethyl benzoate by sodium borohydride. The reagents formed by these two metal halides appear to be considerably less active than that formed by aluminum chloride. The cost of gallium chloride precludes its application in organic synthesis. Consequently, titanium tetrachloride appears to be particularly promising in producing a reagent with an intermediate activity.

Table X

Reaction of Ethyl Benzoate with Sodium Borohydride—Metal Halide Mixtures in Diglyme

Reactants, mmoles			Temp., °C.	Time, hr.	Hydride used, mmoles	Reduction, %
Ester	$NaBH_4$[a]	Halide				
5.0	5.0	1.7 $GaCl_3$	25	1.0	0.6	6
5.0	5.0	1.7 $GaCl_3$	75	1.0	8.8	88
5.0	5.0	1.7 $GaCl_3$	75	1.0	9.2	92
8.0	5.0	1.7 $GaCl_3$	75	1.0	12.8	80
8.0	5.0	1.7 $GaCl_3$	75	1.0	14.5	90
5.0	5.0	1.25 $TiCl_4$	25	3.0	2.3	23
5.0	5.0	1.25 $TiCl_4$	75	1.0	8.2	82
5.0	5.0	1.25 $TiCl_4$	75	2.0	9.9	99
5.0	5.0[b]	1.25 $SnCl_4$	25	1.0	2.9	29
5.0	5.0[b]	1.25 $SnCl_4$	75	1.0	5.0	50
5.0	5.0	2.5 $ZnCl_2$	25	1.0	0.3	
5.0	5.0	2.5 $ZnCl_2$	75	1.0	0.1	

[a] Solution 1.0 *M* in sodium borohydride. [b] Initial concentration of sodium borohydride. Blanks indicate loss of over 50% of available hydride due to reaction with stannic chloride.

Lafayette, Indiana

[Contribution from the B. F. Goodrich Research Center]

Vinylidene Cyanide. VIII. Reaction with Enolized 1,3-Dicarbonyl Compounds

By J. C. Westfahl and T. L. Gresham

Received December 7, 1955

When vinylidene cyanide and enolized 1,3-dicarbonyl compounds of the type $ACOCH_2COB$, where A is alkyl or aryl and B is alkyl, aryl or alkoxy, are heated, compounds of the type $ACOCH(CH_2CH(CN)_2)COB$ are formed. The preparation, properties and the results of structural studies of some of these compounds are given.

As a continuation of the study of the reactions of vinylidene cyanide (I),[1] the reaction of I with 1,3-dicarbonyl compounds was studied. This paper reports the preparation and properties of several monosubstituted malononitriles of the type $ACOCH(CH_2CH(CN)_2)COB$, where A is alkyl or aryl and B is alkyl, aryl or alkoxy.

Contrary to the behavior of I with enolized ketones reported by Ardis, *et al.*,[2] it was found that polymer-free I and an equivalent amount of ethyl acetoacetate could be mixed at room temperature without immediate polymerization. No polymer was evident after five hours, but after 21 hours the reaction mixture was a clear, firm gel. A small amount of $CH_3COCH(CH_2CH(CN)_2)COOC_2H_5$ (II) was isolated from the polymer gel. It was found that using an excess of ethyl acetoacetate and heating the solution caused the rate of addition of ethyl acetoacetate to I to increase faster than the rate of polymerization of I. The compounds in Table I were prepared in this manner.

The structures of the products were shown to be $ACOCH(CH_2CH(CN)_2)COB$ by hydrolysis with aqueous hydrochloric acid and isolation of the acids formed as shown in Chart I. With dibenzoylmethane and I a mixture of products was obtained. In addition to the product in Table I, a product derived from one molecule of dibenzoylmethane and two molecules of I was also formed. The structure of the bis-compound is not the expected open chain compound, $(C_6H_5CO)_2C(CH_2CH(CN)_2)_2$. The structure of the bis-compound will be reported later.

No products were isolated when the reaction of I with ethyl cyanoacetate and with nitromethane was

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[1] For paper VII in this series, This Journal, **78**, 1669 (1956).

[2] A. E. Ardis, *et al.*, *ibid.*, **72**, 1306 (1950).

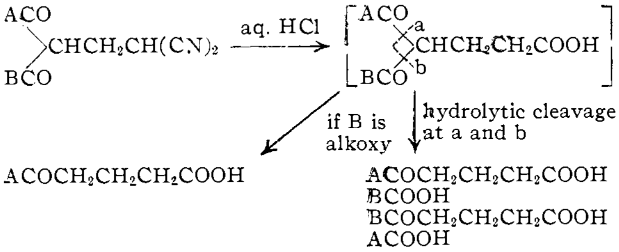
TABLE I

$ACOCH(CH_2CH(CN)_2)COB$

Compound	A	B	R[a]	Solvent	Yield, % (m.p., °C.)	M.p., °C. (pure)	Analysis, % Calculated C	H	N	Found C	H	N
II	CH_3	OC_2H_5	4	None	70.0[b]	....	57.68	5.81	13.46	57.39	5.70	13.40
III	CH_3	CH_3	4	None	63.7 (Crude)	[c]	60.66	5.66	15.72	60.58	5.71	15.72
IV	C_6H_5	C_6H_5	0.5[d]	$CHCl_3$	46.3 (113–114.5)	114.5–115.5	75.48	4.67	9.27	75.39	4.60	9.30
V	C_6H_5	CH_3	1	$CHCl_3$	45.8 (95.5–97.5)	96.7–97.7	69.98	5.04	11.66	69.80	4.95	11.71
VI	C_6H_5	OC_2H_5	2	None	44.6 (77–78)	77–78	66.65	5.22	10.37	66.50	5.12	10.30

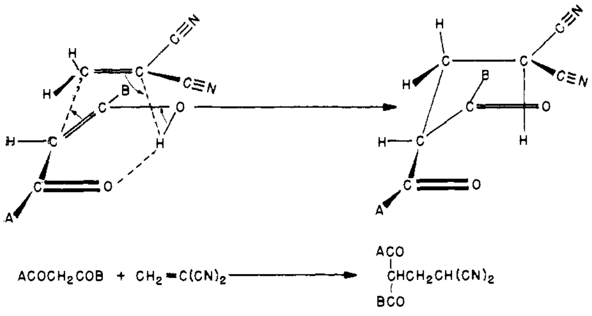
[a] Moles of $ACOCH_2COB$ per mole of I. [b] Product was a liquid, b.p. 117–124° (0.2 mm.), $n^{23.7}D$ 1.4601, d^{20}_4 1.133. [c] M.p. of analytical sample was 84–90°. After recrystallizing crude product from ethanol and then from benzene–hexane the m.p. was 56.2–82°. A further recrystallization from ethanol containing a trace of acetic acid gave crystals of m.p. 79.5–86.5 (capillary), m.p. (Dennis bar)[3] 112°. Decomposition during melting was not evident. [d] The reaction mixture consisted of $(C_6H_5CO)_2CHCH_2CH(CN)_2$ and a product of m.p. 175.5–177° dec. resulting from two molecules of I and one molecule of $C_6H_5COCH_2COC_6H_5$. The formation of bis-product could not be prevented by using an excess of $C_6H_5COCH_2COC_6H_5$.

CHART I



carried out. Addition of phosphorus pentoxide to the reaction mixtures of Table I did not inhibit the reaction. This suggested that the reaction was not catalyzed by traces of water or other bases. The reaction of I with malononitrile to give 1,1,3,3-tetracyanopropane is reported by Ardis, *et al.*,[2] to be prevented by traces of phosphorus pentoxide or sulfur dioxide. The above considerations suggest that an enolized 1,3-dicarbonyl group is necessary for reaction to occur. A plausible mechanism[4] is shown in Chart II.

CHART II



Acknowledgments.—The authors are indebted to J. R. Kubik and A. K. Kuder for the analysis.

Experimental[5]

Since the preparations of the compounds of Table I are similar, only two examples will be given.

α-Cyano-γ-carbethoxy-δ-oxocapronitrile (II).—A solution of 12.6 ml. (13.0 g., 0.10 mole) of ethyl acetoacetate (Eastman Kodak Co., redistilled) and 8.4 ml. (7.9 g., 0.10 mole) of polymer-free, 94% I was added with stirring over a 20-minute interval to 37.9 ml. (39.0 g., 0.30 mole) of ethyl acetoacetate maintained at 105–110° (oil-bath). The resulting solution was stirred and heated at 105–110° for two hours at which time compound I apparently was absent (odor). After a further 30 minutes of heating, the dark yellow, hazy mixture was distilled at 4.5 mm. and an oil-bath temperature of 135°. The recovered ethyl acetoacetate, b.p. 50–60° (4.5 mm.), weighed 37.44 g. (91.2% of excess). The residue containing the product (19.01 g.) distilled at 110–116° (0.01 mm.) to give 14.57 g. (70%) of pale yellow II. A trace of polyvinylidene cyanide was present in the distillate due to depolymerization in the pot and polymerization in the receiver. Redistillation gave colorless II of b.p. 117–124° (0.2 mm.).

α-Cyano-γ-benzoyl-δ-oxocapronitrile (V).—A solution containing 0.3 g. of phosphorus pentoxide and consisting of 8.11 g. (0.05 mole) of benzoylacetone (Eastman Kodak Co.), 15 ml. of chloroform (dried by distillation) and 4.4 ml. (3.9 g., 0.05 mole) of polymer-free, 90% I was refluxed while protected from atmospheric moisture. After five hours of refluxing, the solution was slightly hazy and after 21 hours the reaction mixture was brown in color and hazy due to suspended polymer; compound I was still present (odor). Removal of the chloroform and unreacted I *in vacuo* left 10.90 g. of brown solid. After boiling the solid with ethyl acetate and filtering the hot mixture with suction (filter-aid), the yellow filtrate was diluted with two volumes of hot hexane and cooled to room temperature. The light tan solid which separated was filtered and dried to give 5.51 g. (45.8%) of V, m.p. 95.9–97.5°. Further recrystallization from ethanol (decolorizing carbon) gave colorless crystals, m.p. 96.7–97.7°.

Hydrolysis of II.—A mixture of 10.00 g. (0.048 mole) of II, 20 ml. (0.24 mole) of concd. hydrochloric acid and 15 ml. of distilled water was refluxed for 5 hours. The pale yellow solution was extracted with six portions of ether and the combined ether extract was dried with magnesium sulfate. After filtering, the ether was removed *in vacuo* to leave 4.83 g. (77.4%) of crude, liquid γ-acetylbutyric acid. When this acid was cooled it solidified and when warmed to room temperature it melted. The hydrate of γ-acetylbutyric acid is reported to melt at 35–36°[6]; semicarbazone m.p. 173° dec., reported m.p. 173–174° dec.[7]; oxime m.p. 103–104.5°, reported m.p. 104–105°.[7]

Hydrolysis of V.—Refluxing 3.00 g. (0.013 mole) of V with 20 ml. (0.23 mole) of concd. hydrochloric acid and 10 ml. of water for 18 hours gave a mixture having two liquid phases when hot. When cooled, the water-insoluble liquid solidified. Extraction with chloroform gave a chloroform solution from which the acids were removed by shaking with aqueous sodium bicarbonate solution. Acidification of the sodium bicarbonate solution precipitated a mixture of water-insoluble, chloroform-soluble, solid acids. The filtered, washed and dried solid acid weighed 1.55 g. and had m.p.

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[3] L. M. Dennis and R. S. Shelton, THIS JOURNAL, **52**, 3128 (1930).

[4] This mechanism is based on a suggestion by R. W. Strassburg.

[5] All melting points and boiling points are uncorrected.

[6] L. Wolff, *Ann.*, **216**, 129 (1883).

[7] W. H. Bentley and W. H. Perkin, Jr., *J. Chem. Soc.*, **69**, 1510 (1896).

91–117°, mixture A. The aqueous filtrate from which A separated was combined with the aqueous part of the original hydrolysis mixture. This solution contained the water-soluble acids, mixture B.

Mixture A was separated by steam distillation. Benzoic acid, 0.04 g., m.p. 122–123°, was isolated from the distillate. The m.p. of a mixture with authentic benzoic acid was not depressed. γ-Benzoylbutyric acid, 0.80 g., m.p. 124.5–127.5°, was isolated from the distilland. After one recrystallization from water, the acid had m.p. 127.5–128.5°. The m.p. of a mixture with authentic γ-benzoylbutyric acid of m.p. 128.5–129.5° was not depressed; reported melting points of γ-benzoylbutyric acid are 127.5°[8] and 132°.[9] The semicarbazone had m.p. 211.5–212° dec. after one recrystallization from water, reported m.p. 213° dec.[9]

Mixture B was separated by steam distillation. Acetic acid (0.2 g. by titration) was identified in the distillate by preparing its *p*-bromophenacyl ester, m.p. 83–84.5°; the reported m.p. of *p*-bromophenacyl acetate is 85°.[10] Extraction of the distilland with ether gave, after drying and removing the ether, 0.39 g. of crude γ-acetylbutyric acid. The semicarbazone had m.p. 173–173.5° dec. The reported m.p. of γ-acetylbutyric acid semicarbazone is 173–174° dec.[7]; the m.p. of a mixture with authentic semicarbazone was not depressed.

Hydrolysis of III.—When III was refluxed with aqueous hydrochloric acid a 68% yield of crude γ-acetylbutyric acid containing acetic acid (odor) was obtained. The semicarbazone melted at 173.5° dec.; reported m.p. of γ-acetylbutyric acid semicarbazone is 173–174° dec.[7] The melting point of a mixture with authentic γ-acetylbutyric acid semicarbazone was not depressed.

Hydrolysis of IV.—Refluxing IV with aqueous hydrochloric acid gave a mixture of benzoic acid, m.p. 122–123°, and γ-benzoylbutyric acid, m.p. 128.5–129.5°; reported melting points of γ-benzoylbutyric acid are 127.5°[8] and 132°.[9] The melting point of a mixture of the benzoic acid from the hydrolysis of IV and authentic benzoic acid was not depressed. The semicarbazone of the γ-benzoylbutyric acid had m.p. 210–210.5° dec. The reported m.p. of γ-benzoylbutyric acid semicarbazone is 213° dec.[9]

Hydrolysis of VI.—Refluxing VI with aqueous hydrochloric acid gave a 94.3% yield of crude γ-benzoylbutyric acid. One recrystallization from water gave a 68.6% yield of γ-benzoylbutyric acid, m.p. 128.5–129.5°; reported melting points 127.5°[8] and 132°.[9] The melting point of a mixture with authentic γ-benzoylbutyric acid was not depressed.

BRECKSVILLE, OHIO

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(8) J. Wislicenus and C. K. Kuhn, *Ann.*, **302**, 219 (1898).

(9) A. Ali, *et al.*, *J. Chem. Soc.*, 1013 (1937).

(10) "The Systematic Identification of Organic Compounds," R. L. Shriner and R. C. Fuson, 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 222.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, DOMINION TAR & CHEMICAL CO.]

Studies in Chlorination of Diarylethanes. New Synthesis of DDT Analogs

BY HENRY BADER,[1] W. A. EDMISTON AND H. H. ROSEN

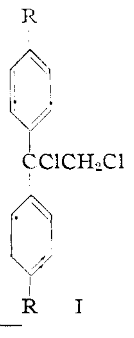
RECEIVED NOVEMBER 25, 1955

Direct chlorination of 1,1-diarylethanes led to analogs of DDT, all having chlorine substituted in the 1-position of the ethylidene group. Sulfuryl chloride in presence of benzoyl peroxide gave the 1,2-dichloro-1,1-diarylethanes (I, R = Cl and Me). Chlorine in presence of peroxides yielded 1,2,2-trichloro-1,1-ditolylethane and 1,2,2,2-tetrachloro-1,1-di-(*p*-chlorophenyl)-ethane. Good yields of highly ring-chlorinated diarylethanes were obtained with chlorine in the presence of ferric chloride or iron dust.

Though a very large number of analogs of DDT have been prepared, the main emphasis was on substitution in the aromatic rings or on variation in the number of chlorine atoms in the aliphatic side-chain and their replacement by isosteric groups. No compounds seem to have been evaluated bearing a chlorine atom in the position 1 of the aliphatic chain, with the exception of the *p,p'*-substituted 1,2,2,2-tetrachloro-1,1-diphenylethanes,[2] prepared by chlorination of the corresponding 2,2,2-trichloroethanes or of the 2,2-dichloroethylenes. A recent review by Gunther and Blinn[3] demonstrates as well the usefulness of DDT-type compounds in organic synthesis. An additional point of interest in the 1-chloro derivatives is that they could be expected to form by direct chlorination of the corresponding unsymmetrical diarylethanes.

Some controversial data have been reported on the side-chain chlorination of diphenylethane. According to Sheibley and Prutton[4] 2,2-dichloro-1,1-diphenylethylene is the main product of direct chlorination at 100–150° in the presence of sunlight. Li,[5] on the other hand, reported the successive formation of a monochloro derivative at 10°, of 1,2,2-trichloro-1,1-diphenylethane between 10–160° and of 1,2,2,2-tetrachloro-1,1-diphenylethane between 160–180°. Some ring chlorination also occurred yielding 1,2,2-trichloro-1,1-phenyl-(*x*-chlorophenyl)-ethane and 2,2-dichloro-1,1-phenyl-(*x*-chlorophenyl)-ethylene. Finally a Japanese patent[6] claimed to prepare a mixture of 1,2,2,2-tetrachloro-1,1-diphenylethane and 1,2,2-trichloro-1,1-diphenylethane by passing chlorine into diphenylethane in sunlight. No chlorination of diaryl ethanes other than diphenylethane seems to have been reported in the literature.

The aim of the present work was to apply the direct chlorination of diarylethanes to the prepara-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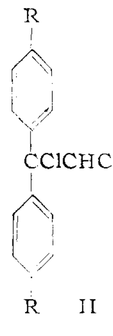
II

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[1] Ortho Research Foundation, Raritan, N. J.

[2] I. E. Balaban, British Patent 632,639 (1949).

[3] F. A. Gunther and R. C. Blinn, *J. Chem. Education*, **27**, 654 (1950).

[4] F. E. Sheibley and C. F. Prutton, THIS JOURNAL, **62**, 840 (1940).

[5] H. Y. Li, *J. Chem. Soc. Japan*, **64**, 1399 (1943); *C. A.*, **41**, 3779 (1947).

[6] S. Kubota and A. Nkamur, Japanese Patent 175,484 (1948); *C. A.*, **44**, 8046 (1950).