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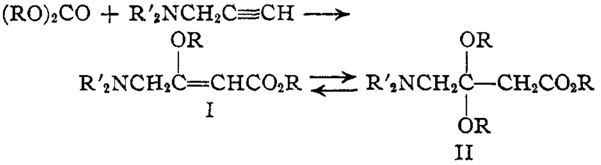
Condensation of Acetylenes with Esters. 3-Dialkylamino-1-propynes with Alkyl Carbonates and Alkyl Benzoates and Phenylacetylene with Methyl Oxalate[1]

BY W. J. CROXALL,[1a] J. O. VAN HOOK AND H. J. SCHNEIDER

This study was conducted to provide additional examples of the condensation of acetylenes with esters. For this purpose the condensation of some 3-dialkylamino-1-propynes with alkyl carbonates and alkyl benzoates has been undertaken. A further extension of this reaction is described for the condensation of phenylacetylene with methyl oxalate. 3-Dialkylamino-1-propynes react with alkyl carbonates to give mixtures of the corresponding alkyl β-alkoxy-γ-dialkylaminocrotonates (I) and alkyl β,β-dialkoxy-γ-dialkylaminobutyrates (II). Two of the dialkylaminopropynes with an alkyl benzoate produced the 1-benzoyl-3-dialkylamino-1-propynes (III). Phenylacetylene in a similar type reaction with methyl oxalate yielded methyl α-oxo-γ-phenyl-γ-methoxy-β-butenoate (IV). Secondary products derived from IV were isolated together with an unidentified red colored compound.

The condensation of acetylene and mono substituted acetylenes with alkyl carbonates[2,3] and alkyl benzoates[1] has been previously reported. The present paper is an extension of this reaction utilizing 3-dialkylamino-1-propynes as the acetylenic reactants. In addition the condensation of phenylacetylene with methyl oxalate is herein recorded.

The condensation of a 3-dialkylamino-1-propyne with an alkyl carbonate in the presence of a basic condensation agent such as benzyltrimethylammonium alkoxide or sodium alkoxide yielded alkyl β-alkoxy-γ-dialkylamino crotonates (I) and alkyl β,β-dialkoxy-γ-dialkylaminobutyrates (II) as indicated in the equations



$$(RO)_2CO + R'_2NCH_2C{\equiv}CH \longrightarrow \underset{\text{I}}{R'_2NCH_2\overset{OR}{\overset{|}{C}}{=}CHCO_2R} \rightleftarrows \underset{\text{II}}{R'_2NCH_2\underset{OR}{\underset{|}{\overset{OR}{\overset{|}{C}}}}{-}CH_2CO_2R}$$

The various 3-dialkylamino-1-propynes used for this study were 3-dimethylamino-1-propyne, 3-diethylamino-1-propyne, 3-morpholino-1-propyne and 3-(N-methyl-N-3,3,5-trimethylhexylamino)-1-propyne. In addition an aminoöctyne, namely, 5,7,7-trimethyl-3-morpholino-1-octyne, was employed. The alkyl carbonates were the methyl, and ethyl esters. Table I summarizes the various experiments. Yield values based on the condensing agents in some of the experiments indicate the reaction to be catalytic.[2]

TABLE I

3-DIALKYLAMINO-1-PROPYNES WITH ALKYL CARBONATES

3-Dialkylamino-1-propyne	Moles	Carbonate	Moles	Catalyst	Moles	Mole ratio II:I isolated[d]	Yield moles %[a] Carbonate	Yield moles %[a] Propyne
Dimethyl	2.5	Methyl	10.0	$BTAOCH_3$[b]	0.24	1:2	45	60
Dimethyl	0.55	Methyl	2.16	$NaOCH_3$	.2	1:1	19	48
Dimethyl	4.15	Ethyl	15.0	$BTAOC_2H_5$	.75	1:3	81	72
Diethyl	0.4	Ethyl	3.0	$BTAOC_2H_5$	.46	1:4	28	55
Morpholino	1.4	Methyl	5.6	$BTAOCH_3$	.14	1:4	48	44
Methyl, nonyl	0.3	Ethyl	2.0	$BTAOC_2H_5$	.29	1:4	26	43
Octyne[c]	0.2	Ethyl	2.0	$BTAOC_2H_5$	.13	1:4	46	70

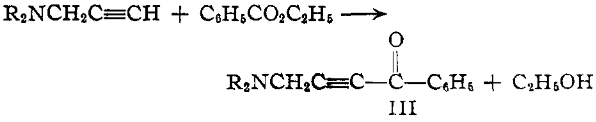
[a] The yields are expressed as mole per cent. of total products based on reactants consumed. [b] BTA is benzyltrimethylammonium. [c] Octyne is 5,7,7-trimethyl-3-(1-morpholino)-1-octyne. [d] Determined by titration with 0.1 N H_2SO_4 using brom phenol blue indicator.

The products (I and II) as isolated in the experiments could not be separated by fractional distillation. However, II was readily converted to I by distillation from a catalytic amount of sodium alkoxide[2] and Table II lists the physical constants of the pure crotonates (I). Conversely it was impossible to convert I exclusively into II by the addition of alcohol to the double bond of I in the presence of sodium alkoxide, all attempts resulting in mixtures of I and II.

Acid hydrolysis of one of the crotonates (I), ethyl β-ethoxy-γ-dimethylaminocrotonate, yielded ethanol, carbon dioxide and an aqueous solution from which the 2,4-dinitrophenylhydrazone of dimethylaminoacetone hydrochloride was obtained. This hydrazone was identical with the corresponding hydrazone hydrochloride obtained from dimethylaminoacetone prepared by hydration of 3-dimethylamino-1-propyne and thus established the structures of the crotonates (I).

Hydrogenation of ethyl β-ethoxy-γ-dimethylaminocrotonate over Raney nickel produced ethyl β-ethoxy-γ-dimethylaminobutyrate.

The condensation of 3-dimethylamino-1-propyne and 3-diethylamino-1-propyne with ethyl benzoate in the presence of benzyltrimethylammonium ethoxide gave instead of the expected alkoxyaminoketones[1] ($R_2NCH_2CH(OR'){=}CHCOC_6H_5$ or $R_2NCH_2C(OR')_2CH_2COC_6H_5$) the corresponding aminoacetylenic ketones, namely, the 1-benzoyl-3-dialkylamino-1-propynes.



$$R_2NCH_2C{\equiv}CH + C_6H_5CO_2C_2H_5 \longrightarrow \underset{\text{III}}{R_2NCH_2C{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5} + C_2H_5OH$$

The yields in this condensation based on the

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[1] For the third paper of this series see W. J. Croxall and J. O. Van Hook, THIS JOURNAL, **71**, 2422 (1949).

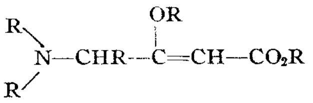
[1a] Summer Chemical Co., Elkhart, Ind.

[2] W. J. Croxall and H. J. Schneider, *ibid.*, **71**, 1257 (1949).

[3] W. J. Croxall and M. Fegley, *ibid.*, **71**, 1261 (1949).

Table II

Physical Constants and Analyses



$R_2N{-}CHR{-}C(OR){=}CH{-}CO_2R$

	B.p., °C.	Mm.	$n^{20}D$	d^{20}_{20}	M_R Calcd.	M_R Found	Formula	Analyses, % Calculated C	H	N	Found C	H	N	Equiv. wt.[a] Calcd.	Found
Ethyl β-ethoxy-γ-dimethylaminocrotonate	76–78	0.5	1.4620	0.984	55.15	56.23	$C_{10}H_{19}NO_3$	59.69	9.49	6.96	59.51	9.48	6.91	201	200
Ethyl β-ethoxy-γ-diethylaminocrotonate	86–93	.3	1.4650	.954	64.39	65.34	$C_{12}H_{23}NO_3$	62.84	10.12	6.11	62.53	10.00	6.11	229	229
Ethyl β-ethoxy-γ-methylnonyl[b] aminocrotonate	117–123	.15	1.4615	.924	92.09	93.22	$C_{18}H_{35}NO_3$	68.96	11.26	4.69	68.92	11.24	4.58		
Ethyl β-ethoxy-γ-morpholinocrotonate	110–112	.3	1.4849	.984	63.83	65.30	$C_{12}H_{21}NO_4$	59.23	8.71	5.75	59.57	8.63	5.91	243	243
Ethyl 3-ethoxy-4-morpholino-6,6,8-trimethyl-2-nonenoate	149–150	.25	1.4800	.983	100.7	102.7	$C_{20}H_{36}NO_4$	67.76	10.24	3.95	67.62	10.54	4.10		
Methyl β-methoxy-γ-morpholinocrotonate	100–110	.3	1.4936	1.118	54.59	55.98	$C_{10}H_{17}NO_4$	55.81	7.96	6.51	56.15	7.85	6.48	215	217
Methyl β-methoxy-γ-dimethylaminocrotonate	60–61	.25	1.4650	1.021	45.91	46.89	$C_8H_{15}NO_3$	55.47	8.73	8.03	55.13	8.81	7.82	173	176

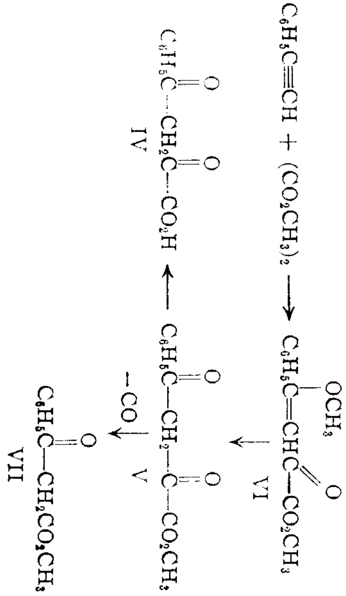
[a] By titration with standard acid to brom phenol blue indicator. [b] Nonyl is 3,3,5-trimethylhexyl.

quaternary alkoxide indicate the reaction to be noncatalytic.[1]

It is interesting to note that in this Laboratory this is the first instance in which acetylenic type compounds have been isolated from the condensation of acetylenes with esters[1,2,3] in the presence of basic condensation agents. Indeed, these results substantiate our previous mechanism[1,2,3] postulating intermediate transitory acetylenic esters[2,3] and acetylenic ketones[1] as the precursors of alkyl β-alkoxyacrylate[2] and β-alkoxychalcone[1] types.

The reaction of phenylacetylene with methyl oxalate in the presence of benzyltrimethylammonium methoxide gave as the principal product methyl α-oxo-γ-phenyl-γ-methoxy-β-butenoate (IV). Secondary products which were derived from the butenoate (IV) were also isolated. Two such compounds were methyl α,γ-dioxo-γ-phenylbutyrate (V) and α,γ-dioxo-γ-phenylbutyric acid (VI). This ester (V) and the corresponding acid (VI) are formed from the butenoate (IV) by hydrolysis since acid conditions were employed for the neutralization of the quaternary ammonium methoxide. There was also isolated, as a crude fraction, an additional material which corresponded to methyl benzoylacetate (VII). The formation of the ester (VII) appears to be the result of decarbonylation of the dioxobutyrate (V).

The over-all sequence of reactions may be represented as



The butenoate (IV) was characterized by conversion to the known dioxobutyrate (V).[4] The yields of the above isolated compounds were low (30–40%). In all the experiments performed there was obtained considerable quantities of nondistillable residues.

When the ratio of phenylacetylene, methyl oxlate and benzyltrimethylammonium methoxide was 1:1:1 only the above products were isolated. However, when a 1.5:1:1 ratio of reactants was used there was obtained, in addition to the above compounds, a red crystalline compound which formed a yellow crystalline derivative with *o*-phenylenediamine. A darker red compound of higher carbon and hydrogen content and higher melting point was obtained when the red compound was crystallized from glacial acetic acid. The characterization of this compound was not carried further. The analytical data on the red compound and its derivatives are given in the **Experimental** section since no further work on this reaction is contemplated.

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(4) W. Wislicenus and W. Stoeber, *Ber.*, **35**, 539 (1902).

Acknowledgment.—We wish to thank Dr. E. L. Stanley and Mr. C. W. Nash under whose directions the analyses were carried out. Miss Marian Fegley and Mr. Raymond Clothier prepared the aminopropynes. Miss R. Lookabaugh prepared the phenylacetylene and Mr. John Erhardt the methyl oxalate.

Experimental

The 3-dialkylamino-1-propynes used in this work were prepared according to the general directions of Reppe.[5] Since 5,7,7-trimethyl-3-(dimethylamino)-1-octyne, obtained from 3,5,5-trimethyl-1-hexanal, dimethylamine and acetylene, has not been previously listed the following constants are reported for this compound: b.p. 105–107° (7 mm.); $n^{20}\text{D}$ 1.4391; neut. equiv., 194 (calcd., 195).

All the ester-substituted acetylene condensations were conducted under anhydrous conditions in an atmosphere of nitrogen. The general procedures were essentially the same as those reported previously[1,3]; specific examples indicating product isolation are summarized.

3-Dimethylamino-1-propyne with Ethyl Carbonate.—A stirred mixture consisting of 1770 g. (15.0 moles) of ethyl carbonate, 149 g. (0.63 mole) of benzyltrimethylammonium ethoxide containing an equivalent of ethanol[3] and 344 g. (4.15 moles) of 3-dimethylamino-1-propyne was warmed to 37° and maintained at 37–41° for 40 hours. The mixture was cooled to 10° and neutralized with an iced aqueous 27% solution of acetic acid, the organic layer separated, dried over anhyd. sodium sulfate and distilled. There was obtained, after removal of 106 g. (1.28 moles) of unreacted propyne and 1403 g. (11.9 moles) of ethyl carbonate, 532 g. of a mixture consisting of 74% ethyl β-ethoxy-γ-dimethylaminocrotonate and 26% ethyl β,β-diethoxy-γ-dimethylaminobutyrate as determined by titration with 0.1 *N* sulfuric acid using brom phenol blue indicator, b.p. 80–100° (2 mm.).

Ethyl β-Ethoxy-γ-dimethylaminocrotonate.—Distillation of 106 g. (0.5 mole) of the above ethyl β-ethoxy-γ-dimethylaminocrotonate and ethyl β,β-diethoxy-γ-dimethylaminobutyrate mixture from 2 g. of sodium ethoxide gave 81 g. (80%) of the pure crotonate.

Attempted Preparation of Ethyl β,β-Diethoxy-γ-dimethylaminobutyrate.—A mixture of one mole of ethyl β-ethoxy-γ-dimethylaminocrotonate and 0.2 mole of sodium dissolved in 200 ml. of anhyd. ethanol was stirred and refluxed in an atmosphere of nitrogen for three hours. The cooled solution was poured into water and the resulting sodium hydroxide neutralized with glacial acetic acid (0.2 mole). The organic layer was separated, dried over anhyd. potassium carbonate and distilled to give 193 g. (89%) of a mixture consisting of 35% ethyl β,β-diethoxy-γ-dimethylaminobutyrate and 65% ethyl β-ethoxy-γ-dimethylaminocrotonate (determined by titration with 0.1 *N* sulfuric acid using brom phenol blue), b.p. 89–97° (2 mm.). A similar experiment employing ethyl β-ethoxy-γ-morpholinocrotonate yielded a mixture composed of 30% ethyl β,β-diethoxy-γ-morpholinobutyrate and 70% ethyl β-ethoxy-γ-morpholinocrotonate.

Ethyl β-Ethoxy-γ-dimethylaminobutyrate.—A solution of 50 g. (0.25 mole) of ethyl β-ethoxy-γ-dimethylaminocrotonate in 100 ml. of ethanol was stirred with 5 g. of Raney nickel at 80° for 15 minutes and filtered. The filtrate was then hydrogenated over 5 g. of Raney nickel at 40–50° and 1000 p.s.i. There was an uptake of 0.25 mole of hydrogen over a period of nine hours. Fractionation through a one-foot packed column gave 35 g. (70%) of the butyrate, b.p. 70° (0.4 mm.); $n^{20}\text{D}$ 1.4269.

Anal. Calcd. for $C_{10}H_{21}O_3N$: N, 6.9. Found: N, 6.6.

Dimethylaminoacetone.—The ketone was obtained in a 69% yield from 3-dimethylamino-1-propyne by the method of Jones and Weedon,[6] b.p. 124–126°; $n^{20}\text{D}$ 1.4114.

The 2,4-dinitrophenylhydrazone hydrochloride of this ketone was obtained from ethyl β-ethoxy-γ-dimethylaminocrotonate in the following manner: A mixture of 20.2 g. (0.1 mole) of the crotonate, 13 ml. of concd. hydrochloric acid and 25 ml. of water was distilled from a Claisen flask. There was obtained one liter of carbon dioxide gas and 11 g. of distillate, b.p. 90–104°. The distillate after saturating and drying with anhyd. potassium carbonate yielded 7 g. (75%) of ethanol. The residue from the original Claisen distillation was poured into a boiling mixture of 15 g. (0.075 mole) of 2,4-dinitrophenylhydrazine dissolved in one liter of anhyd. ethanol. After the addition of 20 ml. of concd. hydrochloric acid, the mixture was refluxed 20 minutes, cooled to room temperature and filtered to give 4 g. of solid, m.p. 210–230°, which was discarded. The filtrate was concentrated to 100 ml., cooled again to room temperature and filtered. There was collected 17 g. (60%) of the crude 2,4-dinitrophenylhydrazone of dimethylaminoacetone hydrochloride. Several recrystallizations from ethanol gave a product of constant m.p. 186–187°.

Anal. Calcd. for $C_{11}H_{16}O_4N_5Cl$: C, 41.57; H, 5.06; N, 22.04. Found: C, 41.70; H, 5.45; N, 21.72.

There was no depression in melting point when this 2,4-dinitrophenylhydrazone was mixed with the corresponding hydrazone obtained from dimethylaminoacetone prepared by the method of Jones and Weedon.[6]

1-Benzoyl-3-dimethylamino-1-propyne.—A mixture of 1.5 moles of benzyltrimethylammonium ethoxide containing an equivalent of ethanol, 900 g. (6.0 moles) of ethyl benzoate and 249 g. (3.0 moles) of 3-dimethylamino-1-propyne (freshly distilled from a small amount of sodium methoxide) was stirred for 20 hours at 35–40°. The reaction mixture was cooled to 5°, neutralized with a solution of 90 g. of acetic acid dissolved in 200 ml. of water, the organic layer separated and dried over anhyd. potassium carbonate. Distillation from a Claisen flask gave, after removal of 50 g. of unreacted propyne and 689 g. of excess ethyl benzoate, 111 g. of crude ketone, b.p. 119–190° (0.1–1.8 mm.) with dec. Redistillation gave 81 g. (49% based on the benzoate consumed) of pure ketone, b.p. 119–123° (0.2 mm.); $n^{20}\text{D}$ 1.626–1.629 (indistinct band).

Anal. Calcd. for $C_{12}H_{13}ON$: C, 76.98; H, 6.99; N, 7.49; mol. wt., 187. Found: C, 77.12; H, 6.83; N, 7.45; mol. wt., 186.

In a similar experiment 1-benzoyl-3-diethylamino-1-propyne was obtained, b.p. 115–125° (0.1 mm.); $n^{20}\text{D}$ 1.605.

Anal. Calcd. for $C_{14}H_{17}ON$: C, 78.10; H, 7.96. Found: C, 77.58; H, 7.68.

Phenylacetylene with Methyl Oxalate.—In a 3-liter, 3-necked flask equipped with a mechanical stirrer there was prepared 240 g. (1.1 moles) of benzyltrimethylammonium methoxide containing an equivalent of methanol.[1] The flask was cooled in an ice-bath to 5° and 118 g. (1 mole) of methyl oxalate, dissolved in 1500 ml. of Grignard ether, was added rapidly. Then with stirring, 153 g. (1.5 moles) of phenylacetylene was added over a ten-minute period. The reaction mixture was allowed to warm to room temperature, stirred overnight and then neutralized with 103 g. of aqueous 36% hydrochloric acid. The aqueous layer which contained suspended solid was separated and diluted with four times its volume of water whereupon additional solid material separated. The brown solid (15 g.) was collected on a filter, suspended in an aqueous 5% sodium bicarbonate solution and extracted with ether. The aqueous layer upon acidification with hydrochloric acid, gave 14 g. of yellow-white crystals of crude α,γ-dioxo-γ-phenylbutyric acid (VI), m.p. 142–145°. The acid was crystallized twice from benzene and dried at 100° *in vacuo*, m.p. 155.5–156°[7]; neut. equiv., 194 (calcd., 192).

The ether extract from above, combined with the original ether extract, was extracted three times with cold aqueous 5% sodium bicarbonate solution. Acidification of the bicarbonate solution with hydrochloric acid gave an additional 30 g. of crude α,γ-dioxo-γ-phenylbutyric acid (VI), m.p. 140–141°; m.p. 155–156° (from benzene).

The combined ether extracts, after removal of ether on the steam-bath at atmospheric pressure, were subjected to high vacuum (1–0.3 mm.) at 40–50° whereupon a dark-red solid was deposited. The residue containing the solid, was treated with 200 ml. of petroleum ether (b.p. 90–100°), warmed to 60° and filtered. The dark-red crystals were washed with 20 ml. of petroleum ether.

The filtrate consisted of two layers. It was distilled to give, after removal of ether and petroleum ether, 31 g. of

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[5] J. W. Reppe and Kastner, U. S. Patent 2,273,141. J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 110.

[6] J. D. Jones and C. L. Weedon, *J. Chem. Soc.*, 782 (1949).

[7] E. Brömme and L. Claisen, *Ber.*, **21**, 1132 (1888).

material, b.p. 45–140° (0.3 mm.) and 35 g. of non-distillable tar. The distillable material was combined with 98 g. of material obtained from other experiments and fractionated to give

Fraction	G.	B.p., °C. (1 mm.)	$n^{20}D$
1	11	49–102	1.5145
2	21	102–109	1.5335
3	12	109–112	1.5378
4	15	112–143	1.5455
5	46	143	1.5696
6	5	143–146	

Methyl Benzoylacetate (VII).—Fraction 3 was found to have a saponification equivalent of 169 (calcd., 178).[8] Treatment of this fraction with 2,4-dinitrophenylhydrazine hydrochloride gave a hydrazone as orange platelets from chloroform, m.p. 169–170°.

Anal. Calcd. for $C_{16}H_{14}N_4O_6$: N, 15.64. Found: N, 15.40.

Methyl α,γ-Dioxo-γ-phenylbutyrate (V).—Fraction 4 partially solidified after standing for three weeks. The crystals were removed on the filter, crystallized from methanol and dried *in vacuo*, m.p. 59.5–61°.[4] Treatment with aqueous copper acetate solution according to the method of Wislicenus and Stoeber[4] gave an olive-colored oil which solidified and was crystallized from methanol, m.p. 240°.

Methyl α-Oxo-γ-phenyl-γ-methoxy-β-butenoate (IV).—Fraction 5 was the pure butenoate (IV). *Anal.* Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45; mol. wt., 220; *MR* 57.05. Found: C, 65.56; H, 5.47; mol. wt., 221; *MR* 57.80.

A 2,4-dinitrophenylhydrazone was prepared and crystallized from chloroform to give orange crystals, m.p. 209–210°. It appears that this derivative is the monohydrazone of the dioxobutyrate (V).

Anal. Calcd. for $C_{17}H_{14}O_7N_4$: N, 14.50. Found: N, 14.30.

Shaking the butenoate (IV) with concentrated hydrochloric acid gave methyl α,γ-dioxo-γ-phenylbutyrate (V), m.p. 59.5° (from methanol) which showed no depression in melting point when mixed with an authentic sample.

Unknown Red Solid.—The red solid material, removed on the filter as described above, was crystallized from an ether-petroleum ether mixture, m.p. 174.5°. Successive recrystallizations from benzene gave material, m.p. 178–178.5°. *Anal.* Found: C, 76.77; H, 5.41; N, 0.0; ash, 0.0; molecular weight (ebulliometric in acetone), 460 ± 10.

Refluxing the red solid in ethanol with *o*-phenylenediamine gave a yellow crystalline compound which on recrystallization from a mixture of benzene and ethanol melted at 224°. *Anal.* Found: C, 79.22; H, 5.68; N, 5.05.

The red compound on heating with glacial acetic acid dissolved and on cooling deposited a darker red compound which when recrystallized from benzene melted at 237–238°. *Anal.* Found: C, 79.51; H, 4.42.

PHILADELPHIA, PENNA. RECEIVED DECEMBER 5, 1950

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[8] K. v. Auwers, *Ann.*, **415**, 230 (1918), reports $n^{24.7}D$ 1.537.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Preparation of Stereoisomeric Alkenyl Lithium Compounds

BY DAVID Y. CURTIN AND ELBERT E. HARRIS

When *cis*-2-*p*-chlorophenyl-1,2-diphenyl-1-bromoethylene is allowed to undergo a lithium–halogen exchange reaction at −20° and the reaction mixture treated with carbon dioxide, only *cis*-2-*p*-chlorophenyl-1,2-diphenyl-1-carboxyethylene is obtained. Treatment of the lithium reagent prepared in this way with methanol gives only *cis*-1-*p*-chlorophenyl-1,2-diphenylethylene. *trans*-2-*p*-Chlorophenyl-1,2-diphenyl-1-bromoethylene on similar treatment gives only *trans*-2-*p*-chlorophenyl-1,2-diphenyl-1-carboxyethylene or *trans*-1-*p*-chlorophenyl-1,2-diphenylethylene. The *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenyl-1-lithiumethylenes have thus been shown to retain their configurations under the reaction conditions.

Koelsch[1] first isolated the two 2-*p*-chlorophenyl-1,2-diphenyl-1-bromoethylenes (I) by bromination of 1-*p*-chlorophenyl-1,2-diphenylethanol and separation by fractional crystallization. The two isomeric bromides (*cis*- and *trans*-I) were reported to melt at 158 and 105° but the configurations were not established. Bergmann[2] on repeating this work, obtained two solid fractions, m.p. 160 and 113°, and measured the dipole moments. The higher melting isomer had $\mu = 2.61\ D$ and was assigned the *cis*- configuration. The lower melting isomer had $\mu = 1.57\ D$. Since Bergmann's calculated moment for the *trans*-isomer was nearly zero he concluded that the solid, m.p. 113°, was a mixture of *cis*- and *trans*-I.

We prepared *cis*- and *trans*-I by the method of Koelsch and obtained compounds which after purification by crystallization and chromatography had melting points in agreement with those of Bergmann. We have accepted the configurational assignment of Bergmann for the *cis*-isomer but in view of our method of purification and the reactions to be reported in this paper we feel that our product, m.p. 113°, is essentially pure *trans*-I.

When *cis*-I in a benzene–ether mixture was treated with butyllithium at −20° for ten minutes and the reaction mixture added to Dry Ice an 82% yield of *cis*-2-*p*-chlorophenyl-1,2-diphenyl-1-carboxyethylene (*cis*-II) was obtained. Under similar conditions, *trans*-I gave a 69% yield of *trans*-II. *cis*- and *trans*-II had been prepared previously by Koelsch[1] who had established their configurations.

The two lithium reagents prepared as above were also treated with methanol. That from *cis*-I gave a 100% yield of crude *cis*-1-*p*-chlorophenyl-1,2-diphenylethylene (*cis*-III) (82% yield after recrystallization). The lithium reagent from *trans*-I gave a 100% yield of crude *trans*-III (72% after purification).

Since *cis*- and *trans*-III had not previously been reported they were prepared by the decarboxylation of *cis*- and *trans*-II with copper chromite in boiling quinoline. The decarboxylation of each acid gave a single olefin in 55–65% yield. This decarboxylation has been shown with similar compounds to proceed with retention of configuration at the double bond.[3] We feel, therefore, that the structure of the olefin from *cis*-II is established as *cis*-III and that from *trans*-II as *trans*-III.

These reactions are summarized for the *cis*-series.

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[1] C. F. Koelsch, THIS JOURNAL, **54**, 2487 (1932).

[2] E. Bergmann, *J. Chem. Soc.*, 402 (1936).

[3] P. Ruggli and A. Staub, *Helv. Chim. Acta*, **20**, 37 (1937); T. W. J. Taylor and C. E. J. Crawford, *J. Chem. Soc.*, 1130 (1934); M. L. Sherrill and E. S. Matlack, THIS JOURNAL, **59**, 2134 (1937).