But even this material soon turned pink when exposed to air. However, after several recrystallizations of the vacuum-distilled product from 70% alcohol the pyrrole was obtained in a form which remained colorless; m. p. 128–129°.[5]

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[5] The melting point has been reported to be 129° (ref. 4).

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ANN ARBOR, MICHIGAN
RECEIVED SEPTEMBER 30, 1943

Reactions of *t*-Butyl Cinnamate and *t*-Butyl Benzoate with Phenylmagnesium Bromide[1]

BY FRED FROSTICK, ERWIN BAUMGARTEN AND CHARLES R. HAUSER

Kohler and Heritage[2] showed that methyl cinnamate undergoes both 1,2- and 1,4-addition with phenylmagnesium bromide yielding a mixture of products. We have found that *t*-butyl cinnamate (in which the carbonyl group is relatively hindered) undergoes apparently only 1,4-addition yielding *t*-butyl β,β-diphenylpropionate.

$$C_6H_5CH{=}CHCOOC(CH_3)_3 \xrightarrow{C_6H_5MgBr} (C_6H_5)_2CHCH_2COOC(CH_3)_3$$

To a stirred solution of phenylmagnesium bromide, prepared from 5.6 g. (0.23 mole) of magnesium and 46.1 g. (0.23 mole) of bromobenzene in 100 ml. of dry ether, was added during twenty minutes 23.5 g. (0.115 mole) of *t*-butyl cinnamate.[3] The reaction mixture refluxed gently and a precipitate formed. After refluxing for three hours, the mixture was poured into an ice-cold saturated ammonium chloride solution. The ether layer was shaken with cold 10% sulfuric acid, and then with cold 5% potassium hydroxide solution. After drying with anhydrous sodium sulfate followed by "Drierite," the solvent was distilled, finally using the water aspirator. The solid residue (29.5 g.) was recrystallized from petroleum ether (b. p. 30–60°), yielding 15 g. (44%) of essentially pure *t*-butyl β,β-diphenylpropionate. Four recrystallizations yielded a product melting at 55.5–55.6°.

Anal.[4] Calcd. for $C_{19}H_{22}O_2$: C, 80.85; H, 7.86. Found: C, 80.93; H, 7.60.

The product was further identified by hydrolysis in the presence of concentrated hydrochloric acid to β,β-diphenylpropionic acid, which, after recrystallization from acetone–water mixture, melted at 152–154° (reported, 155°).[5]

Analogous to methyl or ethyl benzoate, *t*-butyl benzoate has been found to undergo the "normal" carbonyl addition reaction with phenylmagnesium bromide, yielding triphenylcarbinol. Some benzoic acid (which might have resulted from hydrolysis of the ester) was also isolated. Neither isobutene nor *t*-butylbenzene was found; these products would have resulted had the elimination or substitution reaction occurred.

To a stirred solution of phenylmagnesium bromide (prepared from 0.5 mole each of magnesium and bromobenzene in 150 ml. of ether), contained in a reaction flask equipped with a U-tube immersed in a dry ice-bath, was added during one-half hour 0.3 mole of *t*-butyl benzoate[6] in 100 ml. of ether. After standing overnight the reaction mixture was refluxed for five hours. The liquid condensed in the U-tube did not absorb an appreciable amount of bromine in carbon tetrachloride solution, indicating that no significant amount of isobutene was formed. After decomposition of the reaction mixture with ammonium chloride, the ether solution was shaken with bicarbonate (from which was isolated a 10% yield of benzoic acid), dried and the solvent distilled. The residue was subjected to steam distillation until oily material (containing diphenyl but apparently no *t*-butylbenzene) ceased to pass over, and then recrystallized from alcohol, yielding triphenylcarbinol (41%), m. p. 159–162°.

In a similar experiment, carried out with *t*-butyl benzoate and methylmagnesium iodide, no isobutene appeared to be formed.

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[1] This work was supported by a grant from the Duke University Research Council.

[2] Kohler and Heritage, *Am. Chem. J.*, **33**, 21 (1905); see also Allen and Blatt in "Organic Chemistry," Gilman, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 681.

[3] Abramovitch, Shivers, Hudson and Hauser, THIS JOURNAL, **65**, 986 (1943).

[4] Analysis by T. S. Ma, University of Chicago, Chicago, Illinois.

[5] Bacon, *Am. Chem. J.*, **33**, 84 (1905).

[6] Norris and Rigby, THIS JOURNAL, **54**, 2097 (1932).

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
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RECEIVED DECEMBER 6, 1943

Nature of Carotenes in Alfalfa

BY A. R. KEMMERER AND G. S. FRAPS

According to Beadle and Zscheile,[1] spinach and some other plants contain appreciable amounts of "neo-β-carotene," stereoisomer of β-carotene, which can be produced by heating β-carotene in petroleum ether. This pigment is the same as that termed pseudo-α-carotene by Gillam and El Ridi,[2] and neo-β-carotene B, by Polgár and Zechmeister.[3] Kemmerer and Fraps,[4] by chromatographic analysis with calcium hydroxide, found, besides β-carotene and this "neo-β-carotene" in plants, another pigment which they termed "carotenoid X." "Carotenoid X" did not possess vitamin A potency, while "neo-β-carotene" had one-half the potency of β-carotene. Polgár and Zechmeister,[4] by various treatments of β-carotene, secured about twelve neo-β-carotenes including neo-β-carotenes B and U. Since the identification of the carotenes in plants is of both practical and scientific importance, both the "neo-β-carotene" and "carotenoid X" in alfalfa were studied.

Neo-β-carotene B was prepared by refluxing a solution of 20 mg. of crystalline carotene in 100 ml. of hexane for one hour.[4] The solution was chromatographed on calcium hydroxide and the neo-β-carotene B was separated and extracted. Then it was purified by another chromatographic treatment. This pigment is just below the β-carotene band in the chromatogram. Neo-β-carotene U was prepared by dissolving about 10 mg. of crystalline carotene in petroleum naphtha (Skellysolve F), adding a small crystal of iodine, and allowing the solution to stand an hour.[4] The neo-β-carotene U was separated and purified by absorption on calcium hydroxide. The neo-β-carotene U is just above the β-carotene in the chromatogram.

"Carotenoid X" and "neo-β-carotene" were prepared from alfalfa leaf meal by extraction with alcholic potassium hydroxide and petroleum naphtha (Skellysolve F) and chromatographic separation on calcium hydroxide.[3]

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[1] B. W. Beadle and F. P. Zscheile, *J. Biol. Chem.*, **144**, 21 (1942).

[2] A. E. Gillam and M. S. El Ridi, *Biochem. J.*, **30**, 1735 (1936).

[3] A. Polgár and L. Zechmeister, THIS JOURNAL, **64**, 1856 (1942).

[4] A. R. Kemmerer and G. S. Fraps, *Ind. Eng. Chem., Anal. Ed.*, **15**, 714 (1943).

Solutions of neo-β-carotene U and "carotenoid X" were mixed and subjected to chromatographic analysis on calcium hydroxide. There was no separation of bands, showing that the two pigments were identical. By a similar experiment neo-β-carotene B and "neo-β-carotene" from alfalfa were found to be identical.

Direct comparisons of the absorption of light by the preparations were made by means of a quartz spectrograph. In petroleum naphtha (Skellysolve F) solutions, photographed at different settings of the photometer, "carotenoid X" and neo-β-carotene U both had absorption maxima at 468 and 443 mμ; "neo-β-carotene" from alfalfa and neo-β-carotene B likewise had the same absorption curve with maxima at 473 and 446 mμ.

The pigments were also compared by dissolving approximately equal quantities in hexane, treating with iodine and analyzing the product by chromatographic separation on calcium hydroxide. The colorimetric ratio of the pigments formed from neo-β-carotene U was, unknown pigment: neo-β-carotene U: β-carotene: neo-β-carotene B: neo-β-carotene E = 2:22:42:29:5 and from "carotenoid X" of alfalfa = 3:23:46:24:4. For neo-β-carotene B the ratio was, 2:25:45:28:0 and for neo-β-carotene from alfalfa 1:22:43:34:0. The ratios of stereoisomers produced by this treatment were nearly the same in the two comparisons, another evidence of the identity of the carotenes compared from alfalfa. The same carotenes have been found in the chromatographic analysis of other plants (spinach, collards, grasses, etc.).

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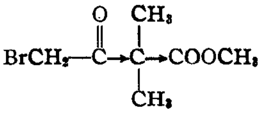
COLLEGE STATION, TEXAS
RECEIVED NOVEMBER 22, 1943

The Action of Sodium Cyanide on Methyl γ-Bromo-α,α-dimethylacetoacetate

BY C. F. KOELSCH

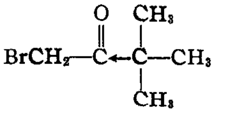
The reaction of sodium cyanide with an α-halogenated ketone usually leads to the formation of a β-ketonitrile; for example, bromopinacolone yields pivaloylacetonitrile.[1] A few α-haloketones, however, furnish α,β-oxidonitriles; for example, desyl chloride yields α,β-epoxy-α,β-diphenylpropionitrile.[2]

On the basis of the polarizations indicated in formulas I and II, it was anticipated that methyl γ-bromo-α,α-dimethylacetoacetate (I) might not parallel bromopinacolone (II) in its behavior toward sodium cyanide, but might suffer attack at its carbonyl group, leading to an oxide (IV).



$$BrCH_2-\overset{\overset{O}{\|}}{C}\rightarrow\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\rightarrow COOCH_3$$

I



$$BrCH_2-\overset{\overset{O}{\|}}{C}\leftarrow\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

II

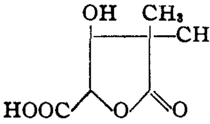
The reaction had been studied long ago[3,4,5] and the product had been assigned structure III. But a survey of the old data indicated that the properties of the product were more in accord with structure IV.

$CNCH_2COC(CH_3)_2COOCH_3$

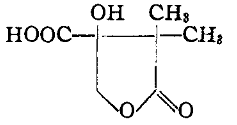
III

IV

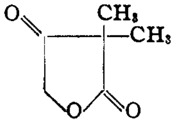
In the present work it was demonstrated that IV is correct. This was done by showing that the hydrolysis product of the nitrile, previously considered to be formed through hydration of the enol of III and formulated as V, actually is VI. The hydrolysis product was identical with the acid obtained by adding hydrogen cyanide to VII and hydrolyzing the resulting cyanohydrin, procedures which can lead only to VI.



V



VI



VII

2,4-Diketo-3,3-dimethyltetrahydrofuran[6] (VII), b. p. 200–210° (740 mm.) or 103–107° (16 mm.), was obtained in 86% yield when 25 g. of methyl γ-acetoxy-β-keto-α,α-dimethylbutyrate[7] was boiled for two hours with 5 g. of 10 molar alcoholic hydrogen chloride (contrary to the statement of Conrad and Gast,[6] the acetoxy ester was unchanged after it had been kept for three months; it also was unaffected when it was heated with potassium carbonate). When 1.3 g. of VII was shaken for fifteen minutes with a solution of 0.6 g. of sodium cyanide and 0.8 ml. of hydrochloric acid in 4 ml. of water, it furnished an oily cyanohydrin. This was removed with ether and boiled for one hour with 6 ml. of 20% hydrochloric acid; when the solution was cooled, it deposited 0.5 g. of VI, colorless prisms from water, m. p. 213–217° alone or mixed with the compound obtained from I by the procedure of Lawrence.[3] When it was boiled with methanol and sulfuric acid, VI gave a methyl ester that melted at 104–105° alone or mixed with Lawrence's ester.

Recognition of the correct structure (IV) for the nitrile previously considered to be III necessitates changes in the structures of substances derived from this compound. Simple esters, etc., need not be specifically mentioned here, but the following revisions must be pointed out. "3-Acetoxy-4,4-dimethyl-5-ketotetrahydro-furoic acid"[4] is actually 3-acetoxy-4,4-dimethyl-5-ketotetrahydrofuran-3-carboxylic acid; "4,4-dimethyl-5-ketotetrahydrofuroic acid"[4,5] is actually 4,4-dimethyl-5-ketotetrahydrofuran-3-carboxylic acid; "ethyl α′-chloro-β-hydroxy-α,α-dimethylglutarate"[3] is actually ethyl α-chloromethyl-α-hydroxy-β,β-dimethylsuccinate; "α,α-dimethyl glutaconic acid"[5] is actually[8] α,α-dimethylitaconic acid. Some doubt now attaches to the structures formerly assigned[3] to homologs of III and V, *viz.*, ethyl γ-cyano-β-keto-α-ethyl-α-

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[1] Widman and Wahlberg, *Ber.*, **44**, 2065 (1911).

[2] Kohler and Brown, THIS JOURNAL, **55**, 4299 (1933). Other examples may be found in the work of Justoni [*Gazz. chim. ital.*, **71**, 41 (1941), *Chem. Abs.*, **36**, 1016 (1942)] and of Delbaere [*Bull. soc. chim. Belg.*, **51**, 1 (1942), *Chem. Abs.*, **37**, 5018 (1943)].

[3] Lawrence, *J. Chem. Soc.*, **75**, 417 (1899).

[4] Conrad and Gast, *Ber.*, **32**, 137 (1899).

[5] Conrad, *ibid.*, **33**, 1920 (1900).

[6] Conrad and Gast, *ibid.*, **31**, 2728 (1898).

[7] Conrad and Kreichgauer, *ibid.*, **30**, 857 (1897).

[8] *Cf.* Perkin, *J. Chem. Soc.*, **81**, 249 (1902).