

The entire ethanol solution boiling higher than 70° was saponified with 10 g. of potassium hydroxide by refluxing overnight. After distillation of the ethanol and acidification of the residues with excess sulfuric acid, the solution was extracted with ether five times. The ether solution was dried and concentrated by distillation. The residue, approximately 3 ml., was treated with excess phosphorus trichloride and the acid chloride distilled. The *p*-toluidide, prepared in the usual manner, melted at 122–124° alone or when mixed with the *p*-toluidide of propionic acid. Identification of hydrogen cyanide, acetone and propionic acid from the ozonization of the monoadduct proved that the structure was 2-ethyl-3-methyl-2-butenitrile.

Structure of the Diadduct.—In the same manner described above for the monoadduct, the diadduct was ozonized and the products identified as propionyl cyanide and methyl propyl ketone, showing that the diadduct was 2-ethyl-3-methyl-2-hexenenitrile. This structure was confirmed by the congruency of its infrared spectrum with that of a sample of 2-ethyl-3-methyl-2-hexenenitrile, previously reported by Osman and Cope.³

Reaction of Ethylene with Mesityl Oxide.—The crude product obtained by heating 100 g. of mesityl oxide with an excess of ethylene at 3000 atm. and 280° for 3 hr. was distilled to obtain 20 g. of recovered mesityl oxide and 33 g. of higher boiling material. Fractional distillation of the

latter gave 5 g. of monoadduct I, b.p. 144–148°, n_D^{25} 1.4294 (*Anal.* Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.3; H, 11.3); 8 g. of monoadduct II, b.p. 163–165°, n_D^{25} 1.4456 (*Anal.* Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.1; H, 11.2); and 5 g. of diadduct, b.p. 118–121° (100 mm.), n_D^{25} 1.4412 (*Anal.* Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 78.2; H, 11.8).

The monoadduct boiling at 164° was dissolved in ethanol and ozonized for 3 hr. Excess ozone was removed with a stream of nitrogen and the ozonization mixture was hydrogenated at 2 atm. pressure using 10% palladium-on-charcoal catalyst. The reaction mixture was filtered, the ethanol was removed by distillation, and the distillate was treated with 2,4-dinitrophenylhydrazine and sulfuric acid to obtain a derivative which melted at 124–126° alone or when mixed with acetone 2,4-dinitrophenylhydrazone. This indicated that the higher boiling monoadduct was 3-ethyl-4-methyl-3-pentene-2-one.

Attempts to isolate a recognizable ozonization fragment from the lower boiling monoadduct were unsuccessful. This suggests that it may be dihydropyran derivative. The low refractive index also suggests a very different structure.

No effort was made to establish the structure of the product corresponding to the addition of two moles of ethylene to one mole of mesityl oxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

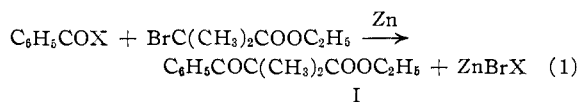
A Reformatsky Type Condensation of Aroyl Chlorides with Ethyl α -Bromoisobutyrate by Means of Zinc to Form β -Keto Esters^{1,2}

BY P. L. BAYLESS AND CHARLES R. HAUSER

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A Reformatsky type condensation between aroyl chlorides and ethyl α -bromoisobutyrate by means of zinc has been realized. The reaction furnishes a convenient method for preparing certain β -keto esters and, through ketonic cleavage, certain ketones. Ethyl mesityldimethylacetate was cleaved by acid to form mesitylene instead of the ketone.

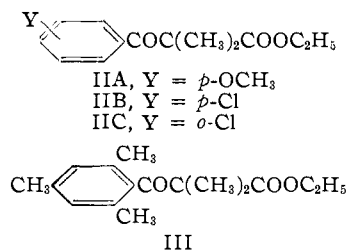
It has previously been shown in this Laboratory³ that a Reformatsky type condensation may be effected between phenyl benzoate and ethyl α -bromoisobutyrate by means of zinc to form ethyl benzoyldimethylacetate (I) in 52% yield. This condensation involves, presumably, the intermediate formation of the zinc bromoester which is benzoylated, the over-all reaction being represented by equation 1 ($X = OC_6H_5$)



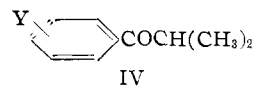
We have now realized this type of acylation with benzoyl chloride to form β -keto ester I in 57% yield (equation 1, $X = Cl$), and with four appropriately substituted benzoyl chlorides to give β -keto esters IIA–C and III in yields of 65–72% (Table I). Also, corresponding acylations were carried out with phenyl *p*-methoxybenzoate and phenyl *p*-chlorobenzoate, but the yields were lower than those obtained with the acid chlorides (see note c, Table I). Phenyl mesitoate failed to react under similar conditions.

The reactions with the substituted benzoyl chlorides were effected in refluxing ether, whereas those with benzoyl chloride and the phenyl esters

were carried out in a refluxing mixture of benzene and toluene. At least with the acid chloride, ether would presumably also be suitable.⁴



β -Keto esters I and IIA–C underwent the expected ketonic cleavage on refluxing with mixtures of sulfuric and acetic acids,⁵ ketones of type IV being obtained in good yields (Table II).



However, under the same conditions, ethyl mesityldimethylacetate (III) gave mesitylene (87%). Apparently this hydrocarbon resulted

(4) In the reactions with acid chlorides, the zinc became coated with a dark oil which appeared to be kept at a minimum in ether. Although benzoyl chloride reacted in the refluxing benzene-toluene mixture, *p*-methoxy- and *p*-chlorobenzoyl chlorides failed to react appreciably under the same conditions, and the starting materials or their hydrolysis products were largely recovered.

(5) B. E. Hudson, Jr., and C. R. Hauser, *THIS JOURNAL*, **63**, 3163 (1941).

(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) Paper LIII on condensations.

(3) M. S. Bloom and C. R. Hauser, *THIS JOURNAL*, **66**, 152 (1944).

TABLE I
 β -KETO ESTERS FROM AROYL CHLORIDES AND ETHYL α -BROMOISOBUTYRATE WITH ZINC

Acid chloride	β -Keto ester	B.P.		Yield, %	n_D^{25}	Carbon, %		Hydrogen, %		Chlorine, %	
		$^{\circ}\text{C}$.	Mm.			Calcd.	Found	Calcd.	Found	Calcd.	Found
Benzoyl	I	151-152 ^a	15	57	1.503 ^b						
<i>p</i> -Methoxybenzoyl	IIA	182-183	10	65	1.520	67.16	66.84	7.24	7.02		
<i>p</i> -Methoxybenzoate ^c	IIA	182-183	10	59	1.521	67.16	67.63	7.24	7.47		
<i>p</i> -Chlorobenzoyl	IIB	161-163	10	71	1.517	61.21	61.48	5.94	6.05	13.92	13.90
<i>p</i> -Chlorobenzoate ^c	IIB	179-180	20	35	1.518 ^d	61.21	61.45	5.94	5.89	13.92	13.88
<i>o</i> -Chlorobenzoyl	IIC	169-172	12	72	1.506 ^e	61.21	61.00	5.94	5.88	13.92	13.79
Mesityl	III	180-182	15	68		73.28	73.62	8.39	8.37		

(M.p. 42.0-42.5)

^a Reported b.p. 145-146 $^{\circ}$ at 13 mm. (A. Haller and E. Bauer, *Compt. rend.*, 152, 553 (1911)). ^b At 26 $^{\circ}$. ^c Phenyl ester. ^d At 23 $^{\circ}$. ^e At 24 $^{\circ}$.

TABLE II

β -Keto ester	Ketone IV, Y	B.P.		Yield, %		n_D^{25}		Carbon, %		Hydrogen, %		Chlorine, %		Semicarbazone, m.p., $^{\circ}\text{C}$.
		$^{\circ}\text{C}$.	Mm.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found			
I	H	109-110	15 ^a	84									161.5-162 ^b	
IIA	<i>p</i> -OCH ₃			41									188-189 ^c	
IIB	<i>p</i> -Cl	142-143	19	75	1.534 ^d	65.75	65.85	6.06	6.20	19.41	19.35	19.41	19.35	184-184.5 ^e
IIC	<i>o</i> -Cl	121-122	17	75	1.520	65.75	65.84	6.06	6.12	19.41	19.28	19.41	19.28	106-106.5 ^f

^a Reported b.p. 102 $^{\circ}$ at 15 mm.⁵ ^b 2,4-Dinitrophenylhydrazones; reported m.p. 163 $^{\circ}$, R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 263. ^c The melting point was not lowered by admixture with a sample of the semicarbazone of *p*-methoxyisobutyrophenone prepared from anisole and isobutyryl chloride with trifluoroacetic acid (*cf.* M. S. Newman, *THIS JOURNAL*, 67, 345 (1949)). The ketone boiled at 150 $^{\circ}$ at 14 mm. *Anal.* Calcd. for C₁₁H₁₄O₂: C, 74.00; H, 7.86. Found: C, 74.00; H, 7.84. A. Sosa (*Ann. chim.*, 14, 5 (1940)) reported 193-194 $^{\circ}$ as the melting point of the semicarbazone. ^d At 23 $^{\circ}$. ^e *Anal.* Calcd. for C₁₁H₁₄ClN₃O: C, 55.11; H, 5.89. Found: C, 55.28; H, 6.28. ^f *Anal.* Calcd. for C₁₁H₁₄ClN₃O: Cl, 14.79. Found: Cl, 14.75.

from direct cleavage of the β -keto ester, involving a reverse Friedel-Crafts type of acylation, and not from the possible intermediate isobutyromesitylene or mesitoic acid since these compounds were recovered unchanged after similar treatment.

The aroylations of ethyl α -bromoisobutyrate described above furnish a convenient method of preparation of β -keto esters of type II and, when followed by ketonic cleavage, of certain ketones of type IV for which the Friedel-Crafts acylation is not suitable. Two of the ketones listed in Table II, *o*- and *p*-chloroisobutyrophenones, appear to be new.

However, attempts to condense benzoyl chloride with ethyl α -bromoacetate or α -bromopropionate employing zinc and a mixture of benzene and toluene gave products that were difficult to separate. Apparently β -keto esters were formed but they underwent further condensation involving their α -hydrogen. Similar results were obtained previously with phenyl benzoate,³ although low yields (19-31%) of ethyl benzoylacetate have been reported from ethyl α -bromoacetate with benzoyl bromide or chloride employing magnesium.⁶

Experimental⁷

Acylation to Form β -Keto Esters (Table I). (A) With Substituted Benzoyl Chlorides.—In a 500-ml. round-bottomed three-necked flask equipped with a mercury sealed stirrer, a reflux condenser and an addition funnel was placed 13.1 g. (0.10 g. atom) of zinc foil (sanded and cut into small strips). Approximately 50 ml. of a solution of 0.1 mole each of the acid chloride and ethyl α -bromoisobutyrate in 200 ml. of anhydrous ether was added, the mixture stirred and warmed until reaction began (cloudiness or foaming), and the remainder of the solution then added at such a rate

that the mixture refluxed gently. After stirring and refluxing until practically all of the zinc had reacted (usually two to three hours), the mixture was cooled and poured with stirring into excess 20% sulfuric acid containing ice. More ether (50 ml.) was added and, after shaking, the ether layer (combined with which was an ether extract of the aqueous layer) was extracted with saturated sodium bicarbonate solution, followed by water and dried over Drierite. The solvent was removed and the residue fractionated *in vacuo*. The product from the reaction with mesityl chloride solidified on cooling, and was recrystallized from petroleum ether (at -70 $^{\circ}$).

The acid chlorides employed in these experiments were freshly distilled products obtained commercially or from the corresponding acids and thionyl chloride. The mesitoic acid was prepared from bromomesitylene.⁸

(B) With Benzoyl Chloride or Phenyl Esters.—These acylations were carried out on the 0.2 mole scale essentially as described above for the substituted benzoyl chlorides, except that a mixture of benzene (100 ml.) and toluene (150 ml.) was employed as the solvent instead of ether. In the reactions with the phenyl esters, the ether-benzene-toluene solution of the products was extracted with sodium hydroxide (instead of bicarbonate) until practically free from phenol.

The phenyl esters used in these experiments were prepared from the corresponding acid chlorides and phenol in the presence of magnesium.⁹

Cleavage of β -Keto Esters.—A mixture of 0.05 mole of β -keto ester, 10 ml. of concentrated sulfuric acid, 30 ml. of glacial acetic acid and 10 ml. of water was refluxed until carbon dioxide ceased to be evolved (8-12 hours) essentially as described previously.⁴ The yields and other data for the resulting ketones are summarized in Table II.

Ethyl mesityldimethylacetate (III) (0.05 mole) gave 5.23 g. (87%) of mesitylene, b.p. 65-66 $^{\circ}$ at 20 mm., 162-164 $^{\circ}$ at atmospheric pressure (reported 164 $^{\circ}$)¹⁰; dinitro derivative, m.p. 87 $^{\circ}$ (reported 86 $^{\circ}$).¹⁰

When mesitoic acid (m.p. 152.5-153 $^{\circ}$) was treated similarly, 91% of it (having the same melting point) was re-

(8) N. S. Drake, *Org. Syntheses*, 21, 77 (1941).

(9) E. H. Man, F. W. Swamer and C. R. Hauser, *THIS JOURNAL*, 73, 901 (1951).

(10) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 259.

(6) R. Meyer and K. Tügel, *Ann.*, 347, 81 (1906).

(7) Boiling points and melting points are uncorrected. Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

covered. When isobutyromesitylene, b.p. 142–143° at 19 mm. (prepared in 75% yield by the Friedel–Crafts acylation of mesitylene with isobutyryl chloride),¹¹ was refluxed even

for 20 hours with the acid mixture, 82% of the original ketone was recovered. A 2-g. residue was obtained, but no mesitylene was found.

(11) A. Klages, *Ber.*, **37**, 928 (1904).

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1856]

cis-trans Isomeric 1,6-Diphenylhexatrienes

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1,6-Diphenylhexatriene^{1,2,3} may assume six spatial configurations of which five were observed upon partial stereoisomerization of the ordinary (all-*trans*) form (m.p. 203°) and subsequent chromatographic resolution of the fluorescent stereoisomeric mixture. One of the new isomers, termed *cis*-I, has crystallized, two others (*cis*-II and -III) were isolated as oils in the pure state, while the existence of the minor isomer *cis*-IV could be ascertained by qualitative observations only. Some ultraviolet spectral characteristics including the fine structure and *cis*-peak effect of the individual spatial forms are given; the relative stabilities of the stereoisomers are discussed, including the behavior in iodine-catalyzed solutions; it is shown that when both hindered and unhindered *cis* double bonds are present, the former type is rearranged first. Configurations for three *cis* forms are proposed.

Although the three steric forms of diphenylbutadiene have been studied extensively² and some pertinent data are also available for diphenyloctatetraene,³ so far as we know the stereoisomerization of 1,6-diphenylhexatriene-1,3,5, $C_6H_5 \cdot CH=CH \cdot CH=CH \cdot CH=C_6H_5$, has not yet been investigated.

That the preparations obtained by synthesis represent the all-*trans* form, was demonstrated by X-ray analysis.⁴

As pointed out earlier, the *cis* forms of a diphenylpolyene may be subdivided into sterically "unhindered" and "hindered" types. When a terminal double bond of the open chain undergoes *trans* → *cis* rearrangement, a spatial conflict arises between a H-atom of the side chain and a ring hydrogen located in *o*-position to the aliphatic section.⁵ Diphenylhexatriene offers the feature, unique in this series, that all but one of its possible *cis* configurations (2 mono-*cis*, 2 di-*cis* and 1 tri-*cis*) are "hindered," the sole exception being the central mono-*cis* isomer (*cf.* Fig. 5).

We find that ordinary (all-*trans*-) diphenylhexatriene can be partially converted into a mixture of stereoisomers by exposing its solutions to sunshine ("insolation"), by iodine catalysis in light, by melting crystals, or by the formation and subsequent cleavage of its boron trifluoride complex.⁶ Refluxing in darkness does not produce sizable amounts of *cis* forms (Table I).

(1) Smith-Mundt Research Fellow (from the University of Oslo).

(2) F. Straus, *Ann.*, **342**, 190 (1905); C. Kelber and A. Schwarz, *Ber.*, **45**, 1946 (1912); E. Ott and R. Schröter, *ibid.*, **60**, 624 (1927); A. Sandoval and L. Zechmeister, *THIS JOURNAL*, **69**, 553 (1947); J. H. Pinckard, B. Wille and L. Zechmeister, *ibid.*, **70**, 1937 (1948).

(3) L. Zechmeister and A. L. LeRosen, *ibid.*, **64**, 2755 (1942).

(4) J. Hengstenberg and R. Kuhn, *Z. Kryst. Min.*, **75**, 301 (1930); **76**, 174 (1930).

(5) See Fig. 2 given in reference 3. For the existence of hindered *cis* forms of isoprenic polyene structures, *cf.* C. H. Eugster, C. F. Garbers and P. Karrer, *Helv. Chim. Acta*, **35**, 1179 (1952); **35**, 1850 (1952); **36**, 562 (1953). General discussion, L. Zechmeister, *Experientia*, **10**, 1 (1954).

(6) The interaction of diphenylpolyenes and BF₃ is under investigation. As Table I shows, in spite of progressive irreversible destruction the amount of the *cis* forms obtained after 10 min. and 60 min. is remarkably constant. For conversions of carotenoid pigments *via* their BF₃-complexes, *cf.* L. Wallcave, J. Leemann and L. Zechmeister, *Proc. Nat. Acad. Sci.*, **39**, 604 (1953); L. Wallcave and L. Zechmeister, *THIS JOURNAL*, **75**, 4495 (1953).

TABLE I

COMPOSITION OF SOME STEREOISOMERIC MIXTURES OBTAINED FROM ALL-*trans*-DIPHENYLHEXATRIENE BY *trans* → *cis* REARRANGEMENT

Treatment	Un- changed all- <i>trans</i>	Content in the mixture, %			Destruction products (by diff.)
		<i>cis</i> -I	<i>cis</i> -II	<i>cis</i> -III + <i>cis</i> -IV	
Iodine catalysis ^a	93.5	1.7	3.7	0.3	1
Iodine catalysis ^a	93.9	1.8	3.8	.3	0.5
Insolation (60 min.) ^b	65.0	3.5	6.3	.5	25
Insolation (60 min.) ^b	62.0	3.3	6.6	.5	28
Refluxing (45 min.) ^c	Only traces of <i>cis</i> forms were obsd.				
Melting crystals ^d	10.5	0.5	2.3	0.1	87
<i>Via</i> the BF ₃ complex ^e (10 min.)	24	.48	0.27	.48	75
<i>Via</i> the BF ₃ complex ^e (60 min.)	2	.48	.34	.46	96

^a For conditions *cf.* the Experimental part. ^b In hexane, 3 mg. per 100 ml. ^c In *n*-propyl alcohol, b.p. 97°, 7 mg. per 100 ml.; in darkness. ^d In a boiling diphenyl ether bath, b.p. 259°; duration, 15 min. (evacuated capillary tube). ^e The time given refers to the duration of the interaction of the substance and boron trifluoride etherate terminated by the addition of 95% methanol; *cf.* the Experimental part.

Of the five possible *cis* isomers, four have been observed in the present study; they are located below the all-*trans* zone on the chromatographic column and termed, in the order of decreasing adsorption affinities, *cis*-I to *cis*-IV. The differences between the adsorbabilities as well as the fluorescence behavior in ultraviolet light, made possible a chromatographic resolution of stereoisomeric mixtures. *cis*-I has been crystallized (m.p. 107°); the *cis* forms II and III were isolated as chromatographically homogeneous and spectroscopically pure oils, while the existence of the minor isomer *cis*-IV was secured by qualitative observations only.

All-*trans*-diphenylhexatriene is the most thermostable among the stereoisomers but it is light-sensitive to a limited extent. Under the conditions of refluxing in darkness, the *cis*-I configuration is definitely less resistant than those of the all-*trans* and *cis*-II compounds. In scattered light the stability of *cis*-I is comparable to that of the all-*trans*