with the racemic acid[3,4] and with the cyclopentane acid.[2] The bromo acid chloride was hydrolyzed by refluxing with 85% formic acid. The crude bromo acid, m.p. 115–125°, was recrystallized twice from petroleum ether to give the pure compound, m.p. 141–142.3°.

Anal. Calcd. for $C_9H_{15}O_2Br$: C, 45.97; H, 6.43; Br, 33.99. Found: C, 45.81; H, 6.56; Br, 34.10.

A bromo acid which had the same m.p. and mixed m.p. was obtained from II but the yield was only 47%. Presumably inversion occurred through the acid chloride of the unsubstituted acid.

2,6-Dimethyl-1-cyclohexenecarboxylic acid was obtained in 90% yield by dehydrohalogenation of the bromo acid by refluxing for four hours in saturated methanolic potassium hydroxide, m.p. 88.2–89.7° (from petroleum ether).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15; neut. equiv., 154.2. Found: C, 70.33; H, 9.19; neut. equiv., 154.5.

This acid was not pure enough for reduction at low pressures over Adams catalyst, but at 120 atmospheres it gave a crude acid, m.p. 50–70°. Purification by the sodium bicarbonate technique gave 30% of II, m.p. 86–87.5°. The acids recovered from the sodium bicarbonate solution were low melting but had a neutral equivalent of 155.3 (calcd. 156.2). Isomerization with hydrochloric and acetic acids gave III, m.p. 99–101°, which indicates that the hydrogenation product was mainly II and III. Very little of the starting material was present because the crude product did not react with bromine or neutral permanganate.

2,6-Dibromoheptane was prepared by the von Braun reaction.[15] N-Benzoyl-2,6-dimethylpiperidine was obtained in 60–90% yield, and the dihalide was formed from this in 35% yield, b.p. 94–94.5° (10 mm.).

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(15) Leonard and Nommensen, This Journal, **71**, 2808 (1949).

Los Angeles, California Received March 26, 1951

[Contribution from the Department of Chemistry, University of Michigan]

Unsymmetrical 1,3-Diarylpropenes[1]

By Christian S. Rondestvedt, Jr.

A series of unsymmetrical 1,3-diarylpropenes was prepared by dehydrating 1,3-diaryl-1-propanols. The latter were conveniently prepared in high yields by lithium aluminum hydride reduction of the corresponding chalcones. The method is more convenient than those in the literature.

In connection with an investigation of the mechanism of the reaction of maleic anhydride with olefins,[2] a series of unsymmetrical 1,3-diarylpropenes was needed. An examination of the literature revealed a number of possible syntheses, but some of them are not experimentally attractive. 1,3-Diaryl-1-propanols can be prepared from an aromatic aldehyde and a β-arethylmagnesium halide, but the requisite β-arethyl halide must first be synthesized. An alternate route from an arylmagnesium halide and a β-arylpropionaldehyde again requires preparation of the latter. More simply, commercially available aromatic aldehydes and substituted acetophenones may be condensed to chalcones which can then be reduced to the desired hydrochalcols.[3] The hydrochalcol can be dehydrated to the olefin directly or through the derived chloride.[4a,b]

Other routes described in the literature include coupling of an arylmagnesium halide with a substituted cinnamyl bromide[5a] and a Perkin condensation of an aromatic aldehyde with a β-arylpropionic acid accompanied or followed by decarboxylation.[4b,5b] Both methods require synthesis of one of the reaction components, the other in general being commercially available.

Some of these methods have been explored as routes to the desired unsymmetrical 1,3-diarylpropenes. Boeseken and Elsen[5a] recorded a low yield of 1,3-diphenylpropene in the coupling of phenylmagnesium bromide with cinnamyl bromide. In our hands, the corresponding reaction of *p*-tolylmagnesium bromide with cinnamyl bromide gave a poor yield of unsaturated material which could not be readily purified. Since the method appeared unpromising, no further experiments were tried with related compounds.

Addition of commercially available hydrocinnamaldehyde to *p*-methoxyphenylmagnesium bromide formed the carbinol in excellent yield. Substitution of *p*-tolylmagnesium bromide gave only low yields of impure carbinol, accompanied by small amounts of 4,4′-bitolyl and considerable toluene and unreacted aldehyde. With prolonged refluxing in ether or in benzene, the yields were still poor, but the recovery of starting material was less. This procedure was also abandoned as unpromising.

The synthesis of chalcones has been thoroughly studied, and all members of the series desired are known compounds. Although their reduction to hydrochalcols has been accomplished with hydrogen and platinum and with sodium amalgam, they are reduced by lithium aluminum hydride[6] much more conveniently, in good yield, and with no danger of hydrogenolysis of sensitive benzyl-type hydroxyls or ring halogens. The initial addition is evidently 1,4- to the conjugated system,[7] since in the reduction of anisalacetophenone, a small quantity of β-anisylpropiophenone was isolated. The matter was not further investigated, but it appears that 1,2- and 1,4-reduction of α,β-unsaturated carbonyl compounds by lithium aluminum hydride follows the same pattern that Kohler observed in addition of Grignard reagents.[8] This evidence supports the

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(1) Presented at the Meeting of the American Chemical Society in Boston, April, 1951.

(2) K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 51 (1943).

(3) P. Pfeiffer, E. Kalckbrenner, W. Kunze and K. Levin, *J. prakt. Chem.*, [2] **119**, 109 (1928).

(4) (a) M. Tuot and M. Guyard, *Bull. soc. chim.*, 1087 (1947); (b) W. Dieckmann and H. Kammerer, *Ber.*, **39**, 3049 (1906).

(5) (a) J. Boeseken and G. Elsen, *Rec. trav. chim.*, **48**, 364 (1929); (b) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **121**, 2381 (1922); C. K. Ingold and C. W. Shoppee, *ibid.*, 447 (1929).

(6) R. F. Nystrom and W. G. Brown, This Journal, **69**, 1197 (1947).

(7) R. E. Lutz and J. S. Gillespie, *ibid.*, **72**, 2002 (1950).

(8) *Cf.* F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948); R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

TABLE I

1,3-DIARYL-1-PROPANOLS, $RCHOHCH_2CH_2R'$

R	R′	Yield, %[a]	M.p., °C.	Calcd., %		Found, %		Derivative				
				C	H	C	H	M.p., °C.	Calcd., % C	H	Found, % C	H
C_6H_5	p-$C_6H_4OCH_3$	88	65.6–65.8	79.31	7.49	79.15	7.21					
p-$C_6H_4OCH_3$	C_6H_5	90[b]	52.3–53.3	79.31	7.49	79.22	7.19					
C_6H_5	p-C_6H_4Cl	88	71.8–72.3	72.72	6.10	73.27	6.10	114.5–115.0[d]	59.94	3.89	60.19	3.82
p-C_6H_4Cl	C_6H_5	95	44.5–45.2	72.72	6.10	72.41	5.96	69.8–70.2[c]	66.75	4.58	67.48	4.54
p-$C_6H_4CH_3$	C_6H_5	97	30.3–30.8[e]	84.91	8.02	84.86	7.93	93.9–94.2[c]	73.58	5.64	73.44	5.59

[a] Crude yield after removal of ether at 100° (10 mm.). [b] Crude yield in the reaction $C_6H_5CH_2CH_2CHO + p\text{-}CH_3OC_6H_4MgBr$ was 89%. [c] p-Nitrobenzoate. [d] 3,5-Dinitrobenzoate. [e] Reported by P. Mastagli, *Compt. rend.*, **204**, 1656 (1937), as a liquid.

TABLE II

1,3-DIARYLPROPENES, $RCH{=}CHCH_2R'$

R	R′	%[a]	M.p., °C. of solid form	B.p. of liquid form °C.	Mm.	$n^t{}_D$	t, °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
C_6H_5	p-$CH_3OC_6H_4$	73	31.6–32.5					85.67	7.19	85.03	6.92
				199–201	10[b]	1.5581	28	85.67	7.19	85.20	6.94
p-$CH_3OC_6H_4$	C_6H_5	72	29.6–30.0					85.67	7.19	85.60	7.04
				201–203	11[b]	1.6002	26	85.67	7.19	84.85	6.91
C_6H_5	p-ClC_6H_4	66	23.6–24.4					78.77	5.73	78.59	5.47
				189–191	8	1.5571	24	78.77	5.73	78.05	5.57
p-ClC_6H_4	C_6H_5	58	....					...	..	...	..
				190–192	12	1.5576	24	78.77	5.73	78.10	5.74
p-$CH_3C_6H_4$	C_6H_5	62	....					...	..	...	..
				175.5–177.5	10	1.5573	22	92.26	7.74	91.90	7.67

[a] Combined yield of purified solid and liquid forms, based on chalcone. [b] These are known compounds, but were reported with somewhat different constants; see ref. 5b.

contention of Brown and co-workers that lithium aluminum hydride reacts like an organometallic compound by nucleophilic displacement.[9]

Dehydration occurred when a hydrochalcol was distilled from potassium bisulfate or upon refluxing with 50% sulfuric acid, the former procedure giving better yields and being more convenient. The two anisyl compounds dehydrated extensively on distillation without an acid catalyst; the others dehydrated partially on distillation at 1–2 mm.

The alcohols were usually low-melting solids, characterized by analysis and by p-nitro- or 3,5-dinitrobenzoate esters. The olefins were usually liquids, but some could be separated into liquid and solid forms by chilling. Presumably the liquid form was *cis* and the solid *trans*, based on the usual rule. Isomerization appears to be light-induced, since samples of the liquid anisyl compounds which had stood for six months in diffuse daylight deposited additional quantities of solid olefin. Since the planned use of these olefins did not require sterically homogeneous material, the *cis–trans* isomers were not further investigated.

The experimental results are recorded in the tables.

Experimental[10]

Chalcones.—Commercially available aldehydes were purified by washing with sodium carbonate solution, drying and distilling. Commercial ketones were purified by distillation. The condensations were carried out by the general procedure of Kohler and Chadwell.[11] In the condensation of p-chlorobenzaldehyde with acetophenone, the time of contact was reduced to one-half hour.[12] The melting points agreed with values in the literature.

Hydrochalcols.—The chalcone, in an extraction thimble, was placed in an apparatus similar to a Soxhlet extractor but designed to provide continuous return of the extracting liquid. Lithium aluminum hydride (0.6 mole per mole of chalcone) was dissolved in absolute ether (one liter per mole). By heating on the steam-bath, the ether extracted the chalcone from the thimble. This device was necessary since the substituted chalcones were only sparingly soluble in ether. An intermediate purple color was sometimes observed. Refluxing was continued until the solution in the flask was colorless, then for an additional half-hour. The excess reagent was decomposed with water, then 5% sulfuric acid was added with swirling until all solid was dissolved. The ether layer was washed with water and dried with anhydrous potassium carbonate. The ether was evaporated, finally by heating to 100° at 10 mm. pressure.

Some of the hydrochalcols could be distilled at 0.5 mm. Others were recrystallized from ether–petroleum ether or from aqueous methanol.

p-Nitrobenzoate esters were prepared according to Shriner and Fuson.[13] If these did not crystallize, the 3,5-dinitrobenzoate was formed by the procedure of Wild.[14]

Dehydration.—The hydrochalcol (50 g. or less) was heated to 200° by a Glas-Col mantle. Then freshly fused and powdered potassium bisulfate (5% by weight) was added all at once, and the apparatus was immediately arranged for vacuum distillation. The olefin was distilled at or below 15 mm., as rapidly as possible consistent with keeping the head temperature not more than 10° above the indicated boiling point. The distillate, usually yellow, was redistilled from 5% of potassium bisulfate.

Upon refrigeration, solid separated from three of the five liquids. It was removed by filtration and recrystallized from petroleum ether, b.p. 30–40°, containing 5–10% of ethyl ether. The two anisyl compounds yielded further solid on standing in diffuse daylight for six months. In-

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[9] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[10] Analyses by Clark Microanalytical Laboratory, Urbana, Illinois. Melting points are uncorrected.

[11] A. H. Blatt, ed., "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 78.

[12] L. C. Raiford, THIS JOURNAL, **50**, 161 (1928).

[13] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 164, Proc. 7A.

[14] F. Wild, "Characterization of Organic Compounds," Cambridge University Press, Cambridge, England, 1947, p. 53, Proc. (2).

gold, *et al.*,[5] have reported both these as liquids; possibly their method gave sterically homogeneous material. However, their measurement of the position of the prototropic equilibrium point by refractometric means is open to some doubt, in view of the unknown stereoisomer composition of their reference compounds and their equilibrium mixtures.

During crystallization of 3-anisyl-1-phenylpropene, a small amount of the less soluble β-anisylpropiophenone was isolated and identified by its melting point 67.5–67.9° and its oxime, m.p. 87–89°.[15]

1-Phenyl-3-p-anisylpropane.—In hopes of obtaining a solid for derivative purposes, a sample of solid 1-phenyl-3-p-anisylpropene was hydrogenated in methanol at 1 atm. pressure over 5% palladium–charcoal. Absorption of hydrogen was very rapid and quantitative. The methanol was evaporated and the residue recrystallized from petroleum ether (b.p. 30–40°). It melted at 2–4°. It was then distilled, b.p. 184–185° (10 mm.), $n^{26}\text{D}$ 1.5578.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.00; H, 7.74.

No picrate could be formed.[16] An attempt to prepare a sulfonamide[17] gave solid material which was alkali-soluble, but which could not be purified. It melted at 130–140°, depending on the rate of heating, then immediately solidified, to remelt at 180–183°.

Acknowledgment.—The author is indebted to Miss Kathleen Hsu, Mr. Richard Scribner, Mr. Moe Wassermann and Mr. Max Boudakian for preparing some of the chalcones and for some preliminary experiments.

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[15] P. Pfeiffer, *J. prakt. Chem.*, [2] **108**, 350 (1924), reports melting points of 69° and 89°, respectively.

[16] Ref. 13, p. 190, Proc. 32.

[17] *Ibid.*, p. 189, Proc. 31.

ANN ARBOR, MICHIGAN RECEIVED MARCH 22, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Reaction of Menthofuran with p-Toluenediazonium Sulfate[1]

BY RICHARD H. EASTMAN AND FRANCIS L. DETERT

Menthofuran (I) reacts with p-toluenediazonium sulfate in acetate-buffered methanol to yield an unstable intermediate containing a molecule of methanol. Treatment of the unstable intermediate with aqueous acid causes loss of the molecule of methanol and conversion to N-(2-azabicyclo[4,3,0]3-keto-4,8-dimethyl-4,9-nonadienyl-2)-p-toluidine. The structure of the latter has been established by autohydrogenolysis to p-toluidine and 3,6-dimethyloxindole, and by comparison of its ultraviolet absorption spectrum with that of a model compound. An unambiguous synthesis of 3,6-dimethyloxindole is reported, and a mechanism for the reaction of furans with diazonium salts in buffered alcoholic media is proposed.

In an earlier communication[2] we have described the course of the reaction between p-nitrobenzenediazonium chloride and 2,5-dimethylfuran. The present communication deals with the reaction between p-toluenediazonium sulfate and menthofuran (I), and proposes a mechanism for the reaction.

When menthofuran (I) and p-toluenediazonium sulfate were permitted to react in an aqueous, methanolic solution of potassium acetate there was obtained a bright-yellow, crystalline substance, $C_{18}H_{24}N_2O_2$ (II) which was converted to N-(2-azabicyclo[4,3,0]3-keto-4,8-dimethyl-4,9-nonadienyl-2)-p-toluidine (III) on treatment with acid. The evidence for the structure of III is as follows: (1) Treatment of III with nitrous acid gave a pale-yellow nitroso compound (IV) which was an N-nitroso derivative since treatment of it with ammonium sulfide regenerated III. (2) III showed one active hydrogen on treatment with methylmagnesium iodide. (3) When III was heated with palladized charcoal there was obtained, in good yield, p-toluidine and 3,6-dimethyloxindole (V). The identity of 3,6-dimethyloxindole was established by comparison with an authentic sample and by its ultraviolet absorption spectrum (Fig. 1). (4) The ultraviolet absorption spectrum of III (Fig. 2) is nearly identical with that of IX (Fig. 2), prepared as described below, and with the calculated sum (Fig. 2) of the absorptions of VII[3] (Fig. 3) and p-toluidine.

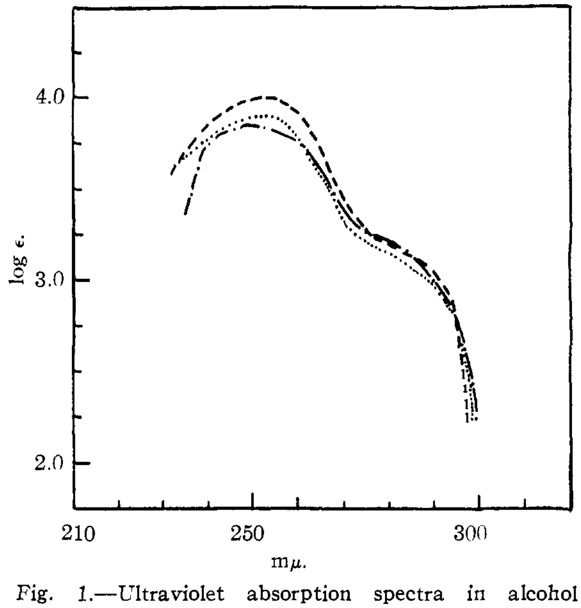

Fig. 1.—Ultraviolet absorption spectra in alcohol: — —, 3,6-dimethyloxindole (V); — · —, 1,3,3-trimethyloxindole [Ramart-Lucas and Biquard, *Bull. soc. chim.*, 2, 1387 (1935)]; .... 3,4-dimethyloxindole.

The results of this investigation, taken with the earlier work on 2,5-dimethylfuran,[2] make it possible to propose a scheme for the coupling of furans with diazonium salts in alkaline alcoholic media which is based upon the accepted mechanism of aromatic substitution, and which accounts for the participa-

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[1] The work reported here is taken from the Dissertation of Francis L. Detert for the degree of Doctor of Philosophy in Chemistry at Stanford University, and was presented in part at the 1949 Spring Meeting of the American Chemical Society in San Francisco, Calif.

[2] Eastman and Detert, THIS JOURNAL, **70**, 962 (1948).

[3] VII has been prepared by dehydration of the autoxidation product VI of menthofuran (I) (Woodward and Eastman, *ibid.*, **72**, 399 (1950). Desoxypatulin which possesses the same chromophoric system as VII has λ_{max} 273, log ϵ 4.17 (Woodward and Singh, *ibid.*, **71**, 758 (1949).