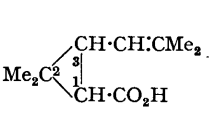
The Chrysanthemumcarboxylic Acids. Part VI. The Configurations of the Chrysanthemic Acids.*

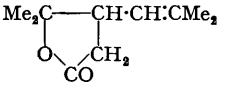
By LESLIE CROMBIE and STANLEY H. HARPER.

[Reprint Order No. 4502.]

THE recent optical resolution of the racemic chrysanthemic acids (3-*iso*but-1′-enyl-2 : 2-dimethyl*cyclo*propane-1-carboxylic acids) (I) (Campbell and Harper, *J. Sci. Food Agric.*, 1952, **3**, 189) and their conversion into pyrocin, shown to be the lactone (II) (Crombie, Harper, and Thompson, *ibid.*, 1951, **2**, 421; Part V*), has made possible the deduction of the configurations of the optically active chrysanthemic acids.



(I)



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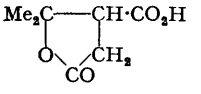

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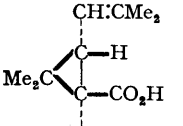

(IV)

(+)-*trans*-Chrysanthemic acid, the naturally occurring isomer (the acidic component of cinerin-I and pyrethrin-I), is transformed by heat into (−)-pyrocin (Matsui, *Botyu-Kagaku*, 1950, **15**, 1; Part V, *loc. cit.*) with rupture of the *cyclo*propane ring between $C_{(1)}$ and $C_{(2)}$ and consequent loss of asymmetry at $C_{(1)}$ but retention of activity at $C_{(3)}$. Ozonisation of (−)-pyrocin yields (+)-terebic acid (III) (Matsui, Ohno, Kitamura, and Toyao, *Bull. Chem. Soc. Japan*, 1952, **25**, 210). Now Fredga obtained (+)-terebic acid on oxidation of (−)-*iso*propylsuccinic acid (*Svensk Papperstidn.*, 1947, **50**, No. 11, *B*, 91) and has related the configuration of the latter to that of (−)-methylsuccinic acid (Fredga and Leskinen, *Arkiv Kemi, Min., Geol.*, 1944, **19**, *B*, No. 1). From this a formal path of transformations to L-glyceraldehyde has been traced out which would relate $C_{(3)}$ of the chrysanthemic acids to glyceraldehyde and lead to the formula (IV) for (+)-*trans*-chrysanthemic acid (the $C_{(1)}$–$C_{(3)}$ bond is in the plane of the paper). However, these transformations involve several arbitrary correlations whose significance has been discussed by us previously (Crombie and Harper, *J.*, 1950, 2685).

To complete the interrelating of the chrysanthemic acids we have now converted (+)-*cis*-chrysanthemic acid into a pyrocin, shown to be the hitherto unknown (+)-isomer by admixture in equal parts with (−)-pyrocin of the same melting point (84°), when depression of melting point occurred to that of (±)-pyrocin (59°), not further depressed on admixture with (±)-pyrocin. Mixtures containing a slight excess of (+)- or (−)-pyrocin had melting points below that of (±)-pyrocin, showing this to be a racemic compound. The enantiomorphic (−)-*cis*-chrysanthemic acid is therefore the epimer of (+)-*trans*-chrysanthemic acid about $C_{(1)}$.

Experimental.—(+)-*Pyrocin.* (+)-*cis*-Chrysanthemic acid (2 × 0·5 g.; Campbell and Harper, *loc. cit.*), after fusion and sealing in Pyrex tubes evacuated to 10^{-2} mm., was heated at 310° for 3 hr. After cooling, the contents were rinsed out with ether, washed with aqueous sodium hydroxide, dried (Na_2SO_4), and distilled (b. p. 128—131°/16 mm.), to give a partly crystalline product which was freed from oil and crystallised from light petroleum (b. p. 40—60°). (+)-*Pyrocin* (125 mg.) was thus obtained as irregular prisms, m. p. 83·5—84·5° (Found: C, 71·7; H, 9·6. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%), $[\alpha]_D^{20}$ +62° (*c*, 0·764) in sodium-dried ether (*l*, 2), $[\alpha]_D^{20}$ +64° (*c*, 0·608) in ethanol (*l*, 2). Matsui (*loc. cit.*) records $[\alpha]_D^{21}$ −75·5° in ether, while Matsui *et al.* (*loc. cit.*) record $[\alpha]_D^{25}$ −57·7° in alcohol for (−)-pyrocin.

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* Part V, *J. Sci. Food Agric.*, 1952, **3**, 230.

The Synthesis of 2-*Phenyl*cyclo*heptatrienone from* 2-*Phenyl*cyclo*hept*-2-*enone.*

By Dov Elad and David Ginsburg.

[Reprint Order No. 4666.]

2-Phenyl*cyclo*heptatrienone has been prepared by the reaction of tropolone methyl ether or 2-chloro*cyclo*heptatrienone with phenylmagnesium bromide (Nozoe, Mukai, and Minegishi, *Proc. Japan. Acad.*, 1951, **27**, 419; Doering and Hiskey, *J. Amer. Chem. Soc.*, 1952, **74**, 5688) and of tropolone with phenyl-lithium. Since 2-phenyl*cyclo*hept-2-enone was readily available (Ginsburg and Pappo, *J. Amer. Chem. Soc.*, 1953, **75**, 1094) the synthesis has been performed from this alicyclic intermediate.

Bromination of 2-phenyl*cyclo*hept-2-enone with one mol. of *N*-bromosuccinimide proceeded sluggishly over a period of 9 hr. Dehydrobromination with 2 : 6-lutidine afforded a mixture, the oximes from which were separable by chromatography. The major oxime had m. p. 113—115°, $\lambda_{max.}$ 2400 Å (log ε 3·93 in EtOH), and a small amount of an isomer, m. p. 122—124°, $\lambda_{max.}$ 2250 Å (log ε 4·18 in EtOH), was obtained. On the basis of these absorption data the former is considered 2-phenyl*cyclo*hepta-2 : 4-dienone oxime, and the latter 2-phenyl*cyclo*hepta-2 : 6-dienone oxime (cf. Evans and Gillam, *J.*, 1943, 565). This assignment is supported by the general observation that, with *N*-bromosuccinimide, bromination in the position allylic to the double bond is preferred to that α to a carbonyl group, in αβ-ethylenic ketones (Djerassi, *Chem. Reviews*, 1948, **43**, 284).

Repetition of the bromination (now rapid) and dehydrobromination with the mixed 2-phenyl*cyclo*heptadienones yielded 2-phenyl*cyclo*heptatrienone.

Attempted oxidation of 2-phenyl*cyclo*hepta-2 : 4-dienone to 3-phenyltropolone by selenium dioxide in dioxan failed although the crude product gave a positive ferric chloride test : 2-phenyl*cyclo*heptatrienone was again obtained. Such dehydrogenations are known, *e.g.*, in the case of 2-methyl*cyclo*hexanone (Godchot and Cauquil, *Compt. rend.*, 1936, **202**, 326) and 2-phenyl*cyclo*hexanone (Elad and Ginsburg, *J.*, 1953, 2664).

Experimental.—2-*Phenyl*cyclo*heptatrienone.* 2-Phenyl*cyclo*hept-2-enone (0·93 g.), *N*-bromosuccinimide (0·98 g.), and a catalytic amount of benzoyl peroxide were heated under reflux in carbon tetrachloride (15 ml.) for 9 hr. The succinimide was removed by filtration and the solvent evaporated in a vacuum. The residue was refluxed with 2 : 6-lutidine (15 ml.) for 2 hr. The solvent was removed in a vacuum and the residue was taken up in ether, washed with dilute hydrochloric acid and with water, and dried (Na_2SO_4), and the ether was evaporated. The residue (0·84 g.) was refluxed in carbon tetrachloride (15 ml.) with *N*-bromosuccinimide (0·98 g.) and a catalytic amount of benzoyl peroxide for 2 hr. After treatment as described above the residue was chromotographed in benzene over acid-washed alumina (Merck). Elution was by benzene–chloroform (1 : 1) and finally chloroform. The middle fraction which consisted of 2-phenyl*cyclo*heptatrienone crystallised as yellow needles, m. p. 81—82° (from heptane) (101 mg.). Recrystallisation from *iso*octane raised the m. p. to 82·5—83·5°. The infra-red absorption spectrum was identical with that reported (Doering and Hiskey, *loc. cit.*).

Oximes of 2-*phenyl*cyclo*hepta*-2 : 4- *and* -2 : 6-*dienone.* The residue obtained from the first bromination (see above) was treated with hydroxylamine hydrochloride in ethanol–pyridine, and an oily mixture of oximes was obtained in the usual way. The oil was dissolved in ether and the solution was washed with Claisen's alkali. The alkaline layer was acidified with acetic acid and kept overnight in the refrigerator. The precipitate was chromatographed in benzene over acid-washed alumina. Benzene–chloroform (1 : 1) and finally chloroform were used for elution. The first fraction upon evaporation gave needles of 2-*phenyl*cyclo*hepta*-2 : 4-*dienone oxime*, m. p. 113—115° (from aqueous ethanol) (Found : C, 78·3; H, 6·8. $C_{13}H_{13}ON$ requires C, 78·4; H, 6·6%). The second fraction yielded rosettes of 2-*phenyl*cyclo*hepta*-2 : 6-*dienone oxime*, m. p. 122—124° (from aqueous ethanol) (Found : C, 78·1; H, 6·7%). Each of the oximes gave a large m. p. depression when admixed with 2-phenyl*cyclo*hept-2-enone oxime.

Selenium dioxide oxidation of the dienone mixture. The residue from the first bromination step (from 0·93 g. of 2-phenyl*cyclo*hept-2-enone) was dissolved in dioxan (20 ml.). Selenium dioxide (0·62 g.) was added and the solution was refluxed for 8 hr. The precipitated selenium

was filtered off and the dioxan was removed in a vacuum. The residue was taken up in ether and was washed with dilute silver nitrate solution and with water. After evaporation, the oily residue was chromatographed in benzene over acid-washed alumina. Only one fraction crystallised after evaporation of the solvent. Recrystallisation gave 2-phenyl*cyclo*hepta-trienone, m. p. 82·5—83·5° (from *iso*octane), identical with the product obtained as above.

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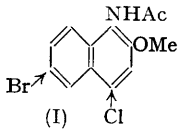
REHOVOTH, ISRAEL. [*Received, September 21st*, 1953.]

The Halogenation of 2-Methoxy-1-acetonaphthalide.

By F. BELL.

[Reprint Order No. 4693.]

To the examples already given (*J.*, 1953, 3035) of difference in position of substitution by chlorine and bromine can be added that of 2-methoxy-1-acetonaphthalide (I). Davis (*Chem. News*, 1896, **74**, 302) established that bromination occurs in position 6. He found, also, that chlorination with sulphuryl chloride yielded a crystalline monochloro-derivative, m. p. 167°, but this was not oriented. In a patent (I. G. Farbendind., G.P. 491,022) it is stated that 2-methoxy-1-acetonaphthalide in acetic acid is chlorinated in position 4 but the chloro-compound is not described nor is evidence given for the structure. It is now found that by interaction with one mol. of sulphuryl chloride there is obtained a monochloro-derivative, m. p. 197°, identical with that obtained by chlorination in acetic acid. The chlorine atom is shown to be present in position 4 by alternative preparation from 4-amino-2-methoxy-1-acetonaphthalide, the constitution of which was established by Bradley and Robinson (*J.*, 1934, 1488).



(I)

No such difference is found for 2-methoxy-1-toluene-*p*-sulphonamidonaphthalene, which undergoes bromination, chlorination, and nitration uniformly in position 4. Further bromination occurs in position 6. Although the yield of mononitro-derivative is fairly good (about 50% compared with less than 25% in the nitration of the corresponding acetyl derivative) it was not possible to hydrolyse off smoothly the toluene-*p*-sulphonyl residue. A similar difficulty was experienced with 1-formamido-2-methoxy-4-nitronaphthalene.

EXPERIMENTAL

Chlorination of 2-Methoxy-1-acetonaphthalide.—(*a*) Chlorine (1 mol.) was passed into a slightly warm solution of the amide (Bradley and Robinson, *loc. cit.*) in acetic acid, and the resultant solution diluted with water. The precipitated 4-*chloro*-derivative formed needles, m. p. 197°, from ethanol (Found: C, 62·6; H, 4·3. $C_{13}H_{12}O_2NCl$ requires C, 62·5; H, 4·8%). (*b*) Sulphuryl chloride (1 mol.), diluted with chloroform, was dropped into a slightly warm solution of the compound in chloroform. The chloroform was distilled off and the residue crystallised several times from ethanol (50% yield of monochloro-derivative, m. p. 197°). Addition of excess of sulphuryl chloride to the monochloro-compound gave a plastic mass from which no crystalline material was isolated.

Synthesis of 4-Chloro-2-methoxy-1-acetonaphthalide.—The product obtained from 4-amino-2-methoxy-1-acetonaphthalide by the usual Sandmeyer procedure was extracted with boiling acetone. On cooling, the extract deposited the 4-chloro-compound in needles, m. p. 197°, in good yield.

Bromo-compounds.—An acetic acid solution of 2-methoxy-1-nitronaphthalene (5 g.) and bromine (4 g.) was gently boiled for 1 hr. and then left overnight. The crystals deposited (2·2 g.) gave pure 6-bromo-2-methoxy-1-nitronaphthalene after one recrystallisation from acetic acid. On slight dilution of the mother-liquor there was obtained a sticky solid, which consisted mainly of 1 : 6-dibromo-2-methoxynaphthalene. Addition of excess of zinc dust to a boiling suspension of the bromonitro-compound (3·2 g.) in ethanol (64 c.c.) and hydrochloric acid (30 c.c.) gave a colourless solution, which after filtration from zinc and addition of hydro-

chloric acid gave an almost quantitative yield of the base hydrochloride. Decomposition of this with ammonia solution gave 6-bromo-2-methoxy-1-naphthylamine, m. p. 70—73°, which with toluene-*p*-sulphonyl chloride in pyridine gave *6-bromo-2-methoxy-1-toluene*-p-*sulphonamidonaphthalene* as needles, m. p. 219°, from acetic acid or chloroform (Found: C, 53·9; H, 3·6. $C_{18}H_{16}O_3NSBr$ requires C, 53·2; H, 3·9%).

Bromine (1 g.) in chloroform was added to a solution of 2-methoxy-1-toluene-*p*-sulphonamidonaphthalene (2 g.) in hot chloroform. After a few minutes' boiling the mixture was diluted with light petroleum, and the product crystallised from acetic acid. *4-Bromo-2-methoxy-1-toluene*-p-*sulphonamidonaphthalene* formed needles, m. p. 187—188° (1·5 g.) (Found: C, 52·9; H, 3·5%).

4 : 6-*Dibromo-2-methoxy-1-toluene*-p-*sulphonamidonaphthalene* was obtained by the bromination in chloroform solution of the 6-bromo-derivative or, in poorer yield, of the 4-bromo-derivative. It formed needles, m. p. 212°, from acetic acid (Found: Br, 32·6. $C_{18}H_{15}O_3NSBr_2$ requires Br, 33·0%).

2-Methoxy-1-toluene-p-*sulphonamidonaphthalene*, from 2-methoxy-1-naphthylamine and toluene-*p*-sulphonyl chloride in pyridine, crystallised from chloroform in needles, m. p. 200° (Found: C, 65·2; H, 5·5. $C_{18}H_{17}O_3NS$ requires C, 66·1; H, 5·2%).

Nitro-compounds.—*2-Methoxy-4-nitro-1-toluene*-p-*sulphonamidonaphthalene*, obtained by heating 2-methoxy-1-toluene-*p*-sulphonamidonaphthalene (5 g.) on a steam-bath for 5 hr. with concentrated nitric acid (5 c.c.) and water (50 c.c.), crystallised from acetic acid in bright yellow needles, m. p. 199° (2·6 g.) (Found: C, 58·2; H, 4·5. $C_{18}H_{16}O_5N_2S$ requires C, 58·1; H, 4·3%). It was recovered after being boiled with concentrated hydrochloric acid, ethanolic hydrogen chloride, or 60% sulphuric acid and was sulphonated by concentrated sulphuric acid even in the cold.

2-Methoxy-4-nitro-1-acetonaphthalide was obtained by Bradley and Robinson's method. The mother-liquor from the purification of the crude nitro-compound deposited needles, m. p. 184—185°, of 2-methoxy-1 : 4-naphthaquinone. When 2-methoxy-4-nitro-1-acetonaphthalide was boiled with ethanol–hydrochloric acid it slowly yielded a yellow hydrochloride, which on decomposition with ammonia solution gave crude *2-methoxy-4-nitro-1-naphthylamine*, which formed orange needles, m. p. 199°, from acetic acid (Found: C, 61·6; H, 4·8. $C_{11}H_{10}O_3N_2$ requires C, 60·6; H, 4·6%). This base did not interact in pyridine solution with toluene-*p*-sulphonyl chloride.

2-Methoxy-1-naphthylamine with boiling formic acid afforded needles of the *formyl* derivative, purified by recrystallisation from ethanol, to yield colourless needles, m. p. 165° (Found: C, 71·0; H, 5·3. $C_{12}H_{11}O_2N$ requires C, 71·6; H, 5·5%). 1 G. was added slowly to a mixture of concentrated nitric acid (0·5 c.c.) and acetic acid (2·5 c.c.) and the resultant paste set aside for 2 hr. Addition of water gave a precipitate which was first boiled with alcohol and then recrystallised from pyridine, to yield *2-methoxy-4-nitro-1-formamidonaphthalene* as bright yellow needles, m. p. 245° (Found: C, 58·2; H, 4·1. $C_{12}H_{10}O_4N_2$ requires C, 58·5; H, 4·1%).

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Friedelin and epi*Friedelinol from* Ceratopetalum apetalum *D.Don.*

By P. R. JEFFERIES.

[Reprint Order No. 4697.]

Ceratopetalum apetalum D.Don (Cunoniaceae), commonly known as coachwood, occurs in the rain forests of New South Wales. The odour of the freshly broken bark has been ascribed to the presence of coumarin (Maiden, " The Forest Flora of N.S.W.," 1906, Vol. I, p. 128). Extraction of the bark with light petroleum affords the triterpene ketone, friedelin, and an alcohol, m. p. 279—283°. Friedelin has been previously isolated from cork where it occurs associated with the hydroxy-ketone cerin (Elsevier, " Encyclopædia of Organic Chemistry," Elsevier Publ. Co., New York, 1940, Vol. XIV, p. 588).

The new alcohol, characterised as its acetate and benzoate, yields friedelin when oxidised with copper powder and is named *epi*friedelinol to distinguish it from the epimer obtained by sodium–amyl alcohol reduction of friedelin. *epi*Friedelinol has also been

obtained by platinum-catalysed reduction of friedelin in acetic acid and is probably identical with the low-melting friedelinol which Lander and Svirbely (*J. Amer. Chem. Soc.*, **1944**, **66**, 235) obtained by an undisclosed method.

In a personal communication Dr. J. R. Price informs me that he and A. W. McKenzie have isolated both friedelin and *epi*friedelinol from *Balanops australiana* F. Muell.

Experimental.—Light petroleum refers to the fraction of b. p. 60—80°. B.D.H. aluminium oxide for chromatographic analysis was used throughout. The solvent for determinations of rotation was chloroform.

Isolation of friedelin and epi*friedelinol.* The dried powdered bark (7 kg.) was exhausted by continuous extraction with light petroleum, and the concentrated extract separated from crystalline material and evaporated. Digestion of the residue with a little ether afforded a second crop and the combined material (44 g.) crystallised from benzene, to give the less soluble epi*friedelinol* (5·2 g.) which, crystallised thrice from chloroform, formed plates, m. p. 279—283°, $[\alpha]_D^{13}$ +24° (*c*, 0·36) (Found: C, 83·8; H, 12·3. $C_{30}H_{52}O$ requires C, 84·1; H, 12·2%). The m. p. was unaffected by admixture with a sample obtained by reduction of friedelin. Evaporation of the benzene mother-liquors gave the crude ketone which was dissolved in benzene–light petroleum (1 : 9) and poured on alumina (500 g.). Elution with the same solvent and crystallisation of the product from benzene gave friedelin (36 g.), m. p. 261—265°, $[\alpha]_D^{14}$ −22° (*c*, 0·812) (Found: C, 84·8; H, 11·6. Calc. for $C_{30}H_{50}O$: C, 84·5; H, 11·8%), identical with a sample derived from cork. Elution of the column with chloroform gave a further crop (1·5 g.) of *epi*friedelinol.

Friedelin enol benzoate, prepared according to the method of Drake and Jacobsen (*J. Amer. Chem. Soc.*, 1935, **57**, 1570), had m. p. and mixed m. p. 262—267°, $[\alpha]_D^{13}$ +62° (*c*, 0·68). Friedelin oxime, prepared by means of hydroxylamine hydrochloride in pyridine at 100°, had m. p. and mixed m. p. 290—292°.

Oxidation of epi*friedelinol.* The alcohol (0·3 g.) was heated with copper powder (2·0 g.) under nitrogen at 290—300° for a few minutes. The cold melt was digested with chloroform and filtered, and the extract evaporated. Dissolution of the residue in benzene–light petroleum (1 : 5) and filtration through alumina (10 g.) afforded a crystalline residue which, after crystallisation from benzene, had m. p. 261—265° alone or mixed with authentic friedelin. The identity was confirmed by comparison of samples of the enol benzoate.

Reduction of friedelin. The ketone (0·7 g.) and platinum oxide (0·1 g.) were suspended in pure acetic acid (100 ml.) and hydrogenated at 100°/500 lb. The mixture was diluted with water, and solid collected and extracted with hot chloroform. Evaporation and crystallisation from benzene gave *epi*friedelinol, m. p. and mixed m. p. 279—283°.

Derivatives of epi*friedelinol.* (*a*) The *acetate* was obtained from both samples with boiling acetic anhydride. It crystallised from benzene–alcohol in plates, m. p. and mixed m. p. 290—294°, $[\alpha]_D^{13}$ +45° (*c*, 0·435) (Found: C, 82·0; H, 11·8. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). (*b*) Treatment of the alcohol (both samples) with benzoyl chloride in pyridine for 1 hr. at 100° gave the *benzoate*, crystallising from benzene–alcohol as plates, m. p. 254—257°, $[\alpha]_D^{13}$ +40° (*c*, 0·48) (Found: C, 83·8; H, 10·7. $C_{37}H_{56}O_2$ requires C, 83·4; H, 10·6%).

Acknowledgment is made to Dr. J. R. Price for supplying samples of friedelin and its enol benzoate and oxime, and to Dr. H. J. Rodda of this Department and Messrs. Webb and Tracey of C.S.I.R.O., Brisbane, for making available the plant material.

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The Rearrangement of N-*Acetylhydrazobenzene.*

By D. W. Davies and D. Ll. Hammick.

[Reprint Order No. 4721.]

The rearrangement of *N*-acetylhydrazobenzene in the presence of concentrated hydrochloric acid has been examined by Pongratz and Scholtis (*Ber.*, 1942, **75**, 138). They obtained a product, m. p. 201—203°, which they described as *N*-acetylbenzidine, m. p. 199°. They did not, however, take a mixed m. p. with an authentic sample, or try to discover whether any other products were formed. In the present investigation confirmation of the formation of *N*-acetylbenzidine was obtained, and the absence of other products was proved.

The rearrangement was also investigated in dilute hydrochloric acid, and in a solution of hydrogen chloride in 95% ethanol. The products were found to be benzidine and diphenyline in aqueous acid of a greater strength than 5N, and in ethanolic acid of any strength, no *N*-acetylbenzidine being detectable. This is readily explained as being due to hydrolysis of the acetyl group, followed by rearrangement. This difference in the effect of the acids presumably occurs because the arrangement is of second order with respect to acid (Hammond and Shine, *J. Amer. Chem. Soc.*, 1950, **72**, 220), whereas the hydrolysis is of first order with respect to acid. Thus, only in concentrated aqueous acid does the rearrangement become sufficiently fast to occur before appreciable hydrolysis.

Experimental.—The results described in the last paragraph were obtained as follows: the appropriate solution was made up and set aside overnight; its optical density was measured in the range of wave-lengths 200—320 mμ, the solution being then neutralized and the measurements repeated. The curves obtained were compared with those previously determined for *N*-acetylhydrazobenzene, *N*-acetylbenzidine, and benzidine in neutral and acid solution. The instrument used was a Beckman ultra-violet Spectrophotometer, Model DU. To test the reliability of the method, the products of some of the rearrangements were isolated and identified by mixed m. p. determinations with authentic samples. These results always agreed with those obtained by the spectral methods.

N-Acetylhydrazobenzene was prepared by the action of acetic anhydride on hydrazobenzene (Ritter and Ritter, *J. Amer. Chem. Soc.*, 1930, **52**, 2815.), and *N*-acetylbenzidine by the action of acetic anhydride on benzidine (Cain, *J.*, 1909, **95**, 717.). Commercial benzidine was purified by recrystallizarion from ethanol in the presence of animal charcoal. The m. p.s obtained agreed with those given in the literature.

The Dyson Perrins Laboratory, University of Oxford. [*Received, October* 14*th*, 1953.]