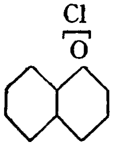
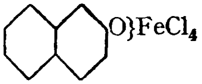
NOTES.

iso*Benzpyrylium Ferrichloride.* By B. K. Blount and Robert Robinson.

The unsubstituted pyrylium analogues of pyridinium and *iso*quinolinium salts have not yet been described, although Decker and von Fellenberg (*Annalen*, 1907, **356**, 281) have reported



(I.)



(II.)

(III.)

the preparation of benzpyrylium chloride (I), the simplest substance of the type analogous to quinolinium salts. Any glutacondialdehyde, or related ketone, or a derived enol should afford a pyrylium salt on treatment with a mineral acid, but we have not yet found the correct conditions for the conversion of glutacondialdehyde itself (Baumgarten, *Ber.*, **1926**, **59**, 1166) into pyrylium chloride (III).

On the other hand, the iso*benzpyrylium ferrichloride* (II) has been obtained without difficulty by the action of hydrogen chloride and ferric chloride on homophthalaldehyde.

The latter substance was not isolated, but the crude product of the oxidation of *trans*-1 : 2-hydrindenediol by Criegee's method (*Ber.*, 1931, **64**, 260; cf. Dimroth and Schweizer, *Ber.*, 1923, **56**, 1375) was directly employed.

Treatment of the salt with ammonia affords *iso*quinoline.

iso*Benzpyrylium Ferrichloride* (II).—A mixture of *trans*-1 : 2-hydrindenediol (4·5 g.) and C_6H_6 (100 c.c.) was distilled until 10 c.c. was collected. The dry mixture, containing glycol in suspension, was treated near its b. p. with $Pb(OAc)_4$ (13·3 g.) during 5 min. and constantly shaken. After boiling for a few sec. to ensure completion of the reaction, and cooling, the $Pb(OAc)_2$ was filtered off and the clear solution conc. in vac. The oily residue, dissolved in AcOH (20 c.c.), was cooled while a solution, obtained by adding anhyd. $FeCl_3$ (8 g.) to AcOH (12 c.c.) and saturating it with HCl, was added. Considerable heat was evolved and the iso*benzpyrylium* salt separated at once in flat yellow needles. It was washed with AcOH and Et_2O (yield, 7·5 g., or 76%) (Found: C, 32·1; H, 2·6; Cl, 42·4. $C_9H_7OCl_4Fe,\frac{1}{2}H_2O$ requires C, 32·0; H, 2·4; Cl, 42·0%).

The substance decomposed at 205—208°. Its solution in boiling AcOH rapidly darkened, and a pure product was not obtained on recrystn. from this solvent. A trace of the substance dissolves in conc. H_2SO_4 to a colourless solution exhibiting intense violet fluorescence. NH_3 aq. (5 drops of *d* 0·880) was added to the ferrichloride (1 g.), along with H_2O (1 c.c.), and the mixture warmed on the steam-bath for 1 min.; the characteristic odour of *iso*quinoline was observed. Solid KOH (2 g.) was added, and the mixture distilled in steam. The milky distillate was heated to boiling, hot aq. picric acid added, and, after cooling, the ppt. collected and recryst. from H_2O: m. p. 222°, alone or mixed with an authentic specimen (Found: N, 16·0. Calc. for $C_{15}H_{10}O_7N_4$: N, 15·6%).—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, March 9th*, 1933.]

Organic Compounds of Boron. By THOMAS THOMSON and THOMAS S. STEVENS.

ACCORDING to modern theories, the group BR_4 must represent a univalent anion. Attempts, however, to prepare salts of the type $[BR_4]M$, where R is a hydrocarbon radical, by heating trimethylboron with ethyl-lithium, phenyl-lithium, methylsodium, ethylsodium, or benzylsodium, and triphenylboron with all except the first and last of these, at temps. up to 120°, were unsuccessful. In each expt. the part of the reaction product insol. in the inert solvent used (frequently ligroin) was free from B. Schlenk's technique was generally followed in the prepn. and manipulation of the alkali-organic compounds.

When heated in ligroin at 120°, ethyl-lithium yielded a solid which on hydrolysis gave nearly pure H corresponding to a content of 50% of lithium hydride. Ethylsodium decomposes similarly (Carothers and Coffman, *J. Amer. Chem. Soc.*, 1929, **51**, 588).

The authors are indebted to the Carnegie Trustees for a Teaching Fellowship held by one of them (T. S. S.) and for a Research Scholarship held by the other (T. T.).—THE UNIVERSITY, GLASGOW. [*Received, February 8th*, 1933.]

The Methylation of Ethyl αβ-Dimethylglutaconate. By JOHN PACKER and JOHN D. SARGENT.

ACCORDING to Thorpe and Wood (J., 1913, **103**, 1759) the so-called " labile " ethyl αβ-dimethylglutaconate, prepared by the action of NaOEt and MeI on ethyl *iso*dehydracetate (Bland and Thorpe, J., 1912, **101**, 1557), undergoes methylation to ethyl αβγ-trimethylglutaconate when treated with alc. NaOEt and MeI at room temp. for 3 hr., and the latter ester yields on hydrolysis αβγ-trimethylglutaconic acid, m. p. 127°. On the other hand, Feist and Beyer (*Annalen*, 1906, **345**, 117) state that they could not introduce a methyl group into the αβ-ester.

The present authors could not methylate " labile " ethyl αβ-dimethylglutaconate to any appreciable extent by treatment with ethyl- or methyl-alc. NaOEt or NaOMe respectively and MeI in the cold, at the b. p., and heated under press. in an autoclave, αβ-dimethylglutaconic acid being the only cryst. product isolated after hydrolysis of the resultant ester. Methylation, however, was readily effected as follows : The αβ-ester (1 mol.) in Et_2O was added to dispersed Na (1 atom) in dry Et_2O and MeI was added carefully, finally in excess, to the orange-yellow sodium derivative formed. NaI separated with evolution of heat and the reaction was completed by warming on the steam-bath for ½ hr. The resultant ester, b. p. 136—138·5°/20 mm., was mainly, if not wholly, ethyl ααβ-trimethylglutaconate : it is likely that no appreciable quantity of ethyl αβγ-trimethylglutaconate was formed, since no ethyl pyruvate could be detected amongst the products of oxidation with neutral $KMnO_4$.

Hydrolysis of the ester with boiling 10% HCl gave a mixture, m. p. 96—100°, of *cis*- and *trans*-ααβ-trimethylglutaconic acids (Found : C, 55·8; H, 6·9. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0%), partly separable into two fractions by crystn. from C_6H_6 or Et_2O. The mixture of acids, boiled with AcCl containing 5% PCl_3, gave (50% yield) the anhydride of *cis*-ααβ-trimethylglutaconic acid, m. p. 106—107° (Found : C, 62·2; H, 6·7. Calc. for $C_8H_{10}O_3$: C, 62·3; H, 6·5%) (see Perkin and Thorpe, J., 1897, **71**, 1185). The anhydride gave no colour with $FeCl_3$, further proving it not to be the hydroxy-anhydride of αβγ-trimethylglutaconic acid, which melts at 119° (Rogerson and Thorpe, J., 1905, **87**, 1705). Distillation under reduced press. of the ammonium salts of the mixed acids yielded no trace of 2 : 6-dihydroxy-3 : 4 : 5-trimethylpyridine, which is formed by the distillation of ammonium αβγ-trimethylglutaconate (Rogerson and Thorpe, *loc. cit.*).

Hydrolysis of the trimethylglutaconic ester with boiling 20% aq. KOH appeared to go in two stages, one portion of the ester being more readily hydrolysed than the other. The acid obtained from the more readily hydrolysed portion would not crystallise, but that from the other portion crystallised readily from Et_2O and had m. p. 147—148° after recrystn. from H_2O (Found : C, 56·1; H, 7·3. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0%). It was proved to be *trans*-ααβ-trimethylglutaconic acid by direct comparison with a specimen of this acid synthesised by the method of Perkin and Thorpe (J., 1897, **71**, 1182) from dimethylacetoacetic ester and bromoacetic ester.—CANTERBURY UNIVERSITY COLLEGE, NEW ZEALAND. [*Received, April 7th,* 1933.]

The Refractive Dispersion of Eugenol and iso*Eugenol.* By GARTHA THOMPSON.

THE author has already located the absorption bands of eugenol and *iso*eugenol at 2820 and 2610 A.U. respectively (J., 1923, **123**, 1596). The following values are now given for the refractive indices of the two isomerides at 20° (cf. Eykman, *Ber.*, 1890, **23**, 855).

	Eugenol.		*iso-*
Wave-length.	Series 1.	Series 2.	Eugenol.
Li 6708	1·5349	1·5350	1·5647
Cd 6438	1·5366	1·5368	1·5671
Na 5896	1·5411	1·5412	1·5728
Hg 5789	1·5419	1·5421	1·5742
Hg 5461	1·5454	1·5455	1·5789
Cd 5086	1·5506	1·5506	1·5861
Cd 4800	1·5554	1·5554	1·5929
Cd 4678	1·5579	1·5580	1·5964
Hg 4359	1·5655	1·5655	1·6077

[*Received, February 3rd,* 1933.]