NOTES.

365. *Characteristic Absorption Bands in the* 10-μ. *Region of the Infra-red Spectra of* cyclo*Paraffin Derivatives.*

By L. W. Marrison.

Absorption bands in the infra-red region which appear to be characteristic of *cyclo*paraffinic structures have been reported by Derfer, Pickett, and Boord (*J. Amer. Chem. Soc.*, 1949, **71**, 3482) for *cyclo*propane homologues and monoalkyl*cyclo*butanes. An examination of published data of the absorption compounds in the 9—11-μ. region, supplemented by measurements made in this Laboratory, provides evidence for rather more extensive generalisation.

The observation by Derfer *et al.* (*loc. cit.*) that the homologues of *cyclo*propane have a band at 1000—1020 cm.$^{-1}$ applies also to vinyl*cyclo*propane (Van Wolkenberg *et al.*, *ibid.*, p. 3595), but not to *cyclo*propane itself, which has a band at 1028 cm.$^{-1}$.

The band between 909 and 917 cm.$^{-1}$, which occurs in the spectra of all monoalkyl*cyclo*butanes (Derfer *et al.*, *loc. cit.*) is not present in either methylene- or octafluoro-*cyclo*butane. A band between 960 and 1000 cm.$^{-1}$ is, however, present in the published spectra of all *cyclo*butane compounds ("Catalog of Infra-Red Spectrograms," A.P.I. Research Project 44, National Bur. Standards).

The spectra of all *cyclo*pentane derivatives have a band whose average position is at 977 cm.$^{-1}$. The variation in published data is so wide, however, that the significance of its presence or absence in an unknown compound is negligible (*e.g.*, *n*-butyl*cyclo*pentane 937; ethyl*cyclo*pentane 1020 cm.$^{-1}$).

The published spectra of *cyclo*hexane derivatives show two bands, one between 952 and 1005 cm.$^{-1}$, and the other between 1000 and 1055 cm.$^{-1}$. Among the 50 compounds listed there are only two exceptions: *cyclo*hexane itself (1041 cm.$^{-1}$ only), and the β-isomer of 1 : 2 : 3 : 4 : 5 : 6-hexachloro*cyclo*hexane (1055 cm.$^{-1}$ only) (*op. cit.*, Thompson, *J.*, 1948, 1432; Nielsen *et al.*, *Analyt. Chem.*, 1949, **21**, 369; Grédy, *Compt. rend.*, 1934, **198**, 89; Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 423). The following data (cm.$^{-1}$) were obtained in this Laboratory:

*cyclo*Hexanol	961;	1020
Chloro*cyclo*hexane	995;	1018
α-1 : 2 : 3 : 4 : 5 : 6-Hexachloro*cyclo*hexane	952;	1044
β- ,, ,, ,,		1055
γ- ,, ,, ,,	952;	1025
δ- ,, ,, ,,	955;	1036
α-Heptachloro*cyclo*hexane	957;	1005
β- ,, ,,	966;	1013
δ- ,, ,,	960;	1027

*cyclo*Hexanone and its derivatives, whose spectra have been described by Lecomte (*Compt. rend.*, 1945, **221**, 50) and Cherrier (*ibid.*, 1947, **225**, 1063), show several deviations from the generalisation proposed and it is clear that it cannot be applied to these compounds.

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366. *Organocobalt Compounds.*

By D. A. E. Briggs and J. B. Polya.

The preparation and properties of some organocobalt compounds have been described by Ingles and Polya (*Nature*, 1949, **164**, 447; *J.*, 1949, 2280). Circumstances have prevented a systematic extension of this work but the present note supplements previous information on some naphthylcobalt halides.

When α- and β-naphthylcobalt tri-iodides were prepared by the previously described methods except that highly purified solvents were used in the present experiments, light petroleum caused incomplete precipitation. Precipitation with dioxan afforded reduced but satisfactory yields and the filtrates gradually deposited small amounts of R_2CoI_2. In one case a somewhat impure material of the approximate formula R_3CoI_5 was obtained which recalls the $R_3Co_2Br_5$ previously described. These findings confirm the view that dioxan decomposes organocobalt halides of the type $RCoX_3$ to R_2CoX_2 which occasionally permits the isolation of $RCoX_3,R_2CoX_2$.

Reaction of the naphthylcobalt tri-iodides with methyl iodide gave dinaphthyls in place of the expected methylnaphthalenes. Acetyl chloride gave very poor yields of acetylnaphthalenes, but $(\beta\text{-}C_{10}H_7)_3Co_2I_5$ gave 47% of the ketone. α-Naphthylcobalt tri-iodide and benzoyl chloride gave good yields of 1-benzoylnaphthalene, but the reaction failed with the β-isomer and with $(\beta\text{-}C_{10}H_7)_3Co_2I_5$.

Experimental.—By use of pure solvents and of dioxan for precipitation were obtained, on a 0·1 molar scale:

(*a*) α-Naphthylcobalt tri-iodide, yellowish-green, decomp. 153° (48%) (Found: C, 21·0; H, 1·4; I, 66·4. Calc. for $C_{10}H_7I_3Co$: C, 21·0; H, 1·2; I, 67·5; Co, 10·3%), and di-α-naphthylcobalt di-iodide (2%) (Found: I, 45·1; Co, 9·7. Calc. for $C_{20}H_{14}I_2Co$: I, 44·8; Co, 10·3%).

(*b*) β-Naphthylcobalt tri-iodide, yellowish-green, decomp. 164—166° (15%) (Found: C, 20·8; H, 1·4; I, 67·7; Co, 10·0%), di-β-naphthylcobalt di-iodide (1%) (Found: I, 44·3; Co, 10·7%), and *tri-β-naphthyldicobalt pentaiodide*, greyish-green (15%) (Found: C, 30·2; H, 2·4; I, 53·3; Co, 10·8. $C_{30}H_{21}I_5Co_2$ requires C, 31·6; H, 2·3; I, 55·8; Co, 10·3%).

Reaction with acetyl chloride. When α-naphthylcobalt tri-iodide (1·0 g.) and acetyl chloride (5·0 c.c.) were mixed, cobalt halides and iodine were formed at once. After being kept for 1 hour at room temperature and then heated for 2 hours on the water-bath, the mixture was treated with ice-water (15 c.c.) and extracted with ether. The extract was washed successively with aqueous sodium carbonate and thiosulphate and with water and then evaporated. The residual brown oil gave 1-acetylnaphthalene semicarbazone, m. p. 235° (from ethanol) (3—4%). Similarly was obtained 2-acetylnaphthalene, m. p. 52—53° (semicarbazone, m. p. 236—237°), in 6—8% yield from $RCoI_3$ or 47% yield from R_3CoI_5.

Reaction with benzoyl chloride. 1-Naphthylcobalt tri-iodide (1·0—5·0 g.) and benzoyl chloride (5—20 c.c.) were set aside for 1 hour and then refluxed gently for 90 minutes. The product was extracted with ether and washed as above. The residues from the ethereal solution were recrystallised three times from aqueous alcohol and afforded 1-benzoylnaphthalene, m. p. 72—73°, identified as the oxime, m. p. 140—141°, in yields which varied between 54 and 75% in a number of experiments.

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367. 4 : 6-*Dimethyl* β-*Methylglucoside and Some Derivatives of* β-*Methylglucoside.*

By J. C. DENNISON and D. I. MCGILVRAY.

4 : 6-DIMETHYL β-METHYLGLUCOSIDE was synthesised by Bell and Synge (*J.*, 1937, 1711) by methylation of β-methylglucoside 2 : 3-dinitrate and subsequent hydrolysis. Later, Bell and Lorber (*J.*, 1940, 453) prepared the α-isomeride from 2 : 3-dibenzyl α-methylglucoside; and application of this synthesis in a slightly modified form has now enabled us to obtain 4 : 6-dimethyl β-methylglucoside in a higher-melting form than previously reported.

Experimental.—2 : 3-*Dibenzyl* 4 : 6-*benzylidene* β-*methylglucoside.* 4 : 6-Benzylidene β-methylglucoside (cf. Mathers and Robertson, *J.*, 1933, 698) (30 g.), powdered potassium hydroxide (25 g.), and benzyl chloride (100 ml.) were stirred in a closed vessel at 100° for 5 hours. After isolation and purification (cf. Bell and Lorber, *loc. cit.*), the *dibenzyl* compound crystallised from ethanol (95%) as fine needles, m. p. 119—120°, $[\alpha]_D^{20}$ −35·8° (*c*, 3·02 in chloroform) (Found: OMe, 6·6. $C_{28}H_{30}O_6$ requires OMe, 6·7%).

2 : 3-*Dibenzyl* β-*methylglucoside.* This was prepared from the benzylidene derivative in 95% yield, by the procedure of Bell and Lorber (*loc. cit.*). This *glucoside* crystallised from light petroleum (b. p. 60—80°) in fine needles, m. p. 122—123°, $[\alpha]_D^{20}$ −13·3° (*c*, 2·7 in chloroform) (Found: OMe, 8·8. $C_{21}H_{26}O_6$ requires OMe, 8·2%).

2 : 3-*Dibenzyl* 4 : 6-*dimethyl* β-*methylglucoside.* The foregoing compound (7·0 g.) was twice methylated with Purdie's reagents. The *product* (7·6 g.) crystallised overnight in a vacuum-desiccator and had m. p. 40—41°, $[\alpha]_D^{20}$ +32·0° (*c*, 2·52 in chloroform) (Found: OMe, 23·0. $C_{23}H_{30}O_6$ requires OMe, 23·1%).

4 : 6-*Dimethyl* β-*methylglucoside.* The benzyl groups were removed from the benzyl ether (7·6 g.) with sodium in ethanol (cf. Bell and Lorber, *loc. cit.*). The crude product (2·7 g.; m. p. 69—71°), after recrystallisation from light petroleum (b. p. 60—80°), melted at 77—79° and had $[\alpha]_D^{20}$ −27·0° (*c*, 2·74 in chloroform) (Found: OMe, 40·5. Calc. for $C_9H_{18}O_6$: OMe, 41·8%). Bell and Synge (*loc. cit.*) and Peat and Wiggins (*J.*, 1938, 1813) gave m. p. 50—52°, and Reeves (*J. Amer. Chem. Soc.*, 1949, **71**, 217) stated that the m. p. was initially 52—55°, but that after being kept the compound had m. p. 67—68°. The properties of the 2 : 3-ditoluene-*p*-sulphonyl derivative agreed with those recorded by other workers.

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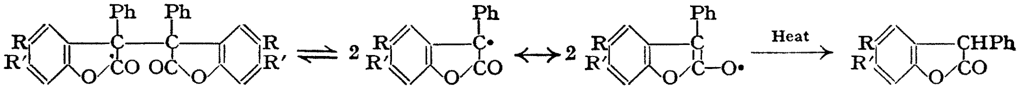
368. *Reactions of Diaryldicoumaranonyls and* 2 : 2′-*Diphenylthioindigo-white.*

By AHMED MUSTAFA and AHMED MEDHAT ISLAM.

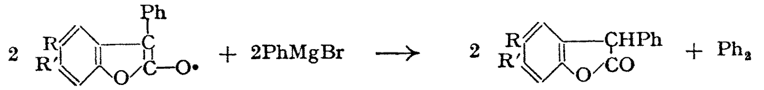
SCHÖNBERG AND MUSTAFA (*J.*, 1949, 889) have found that 2 : 2′-diketo-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*a*) and 2 : 2′-diphenylthioindigo-white (III) form the corresponding reduction products, (II*a*) and (IV), when heated at 270° without a solvent. The analogues (I*b*, *c*, and *d*) are known to form, in solution, free radicals that may be regarded as resonance hybrids (see below) (Löwenbein, *Ber.*, 1925, **58**, 601; Arventi, *Ann. Sci. Univ. Jassy*, 1938, **24**, 219). When heated at 270°, they too gave the reduction products, namely, (II*b*, *c*, and *d*), which we believe to be produced from the free radicals by disproportionation (cf. Schönberg and Mustafa, *loc. cit.*).



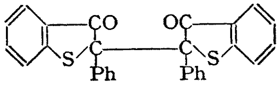
(I*a*; R = R′ = H.)
(I*b*; R = H; R′ = Me.)
(I*c*; R = Me; R′ = H.)
(I*d*; R = Cl; R′ = H.)

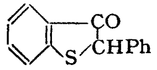
(II*a*; R = R′ = H.)
(II*b*; R = H, R′ = Me.)
(II*c*; R = Me, R′ = H.)
(II*d*; R = Cl, R′ = H.)

When a benzene solution of (I*a*) was added to an ethereal phenylmagnesium bromide solution and the mixture was decomposed with aqueous ammonium chloride, (II*a*) was obtained in almost quantitative yield, together with diphenyl, whereas (I*a*) was recovered unchanged when shaken with an aqueous ammonium chloride solution for 3 hours at room temperature [cf. the action of phenylmagnesium bromide on *s*-tetraphenyldibenzoylethane (Löwenbein and Schuster, *Annalen*, 1930, **481**, 106)]. The action of phenylmagnesium bromide is similar with (I*b*, *c*, and *d*) and with (III). This is an example of reductive fission of the C–C linkage by the Grignard reagent (cf. Mustafa, *J.*, 1949, 1662).



(III.)





(IV.)

Experimental.—Thermal decompositions. (*a*) 2 : 2′-Diketo-6 : 6′-dimethyl-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*b*) (1 g.) (Löwenbein, *loc. cit.*) was heated in a test-tube connected by a bent tube to a test-tube cooled by ice–salt. Dry carbon dioxide was passed through the apparatus. Pyrolysis (bath-temp. 270°) was carried out for ½ hour. Colourless crystals which appeared on the walls of both test-tubes were collected and recrystallised from ethyl alcohol; they had m. p. 122° (0·8 g., *ca.* 80%) and were shown to be the lactone of 6-methyl-3-phenylcoumaran-2-one (II*b*) (identity : mixed m. p. and colour reaction with sulphuric acid; Bistrzycki and Flatau, *Ber.*, 1897, **30**, 130).

(*b*) When 2 : 2′-diketo-5 : 5′-dimethyl-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*c*) (1 g.) (Löwenbein, *loc. cit.*) was similarly pyrolysed, oily drops of 5-methyl-3-phenylcoumaran-2-one (II*c*) appeared which solidified on cooling. The solid crystallised from ethyl alcohol in colourless crystals, m. p. 106° (0·75 g., *ca.* 75%) (identity : mixed m. p. and colour reaction with sulphuric acid; *idem*, *Ber.*, 1895, **28**, 989).

(*c*) 5 : 5′-Dichloro-2 : 2′-diketo-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*d*) (1 g.) (Arventi, *loc. cit.*) similarly afforded 5-chloro-3-phenylcoumaran-2-one (II*d*) as colourless crystals (from ethyl alcohol), m. p. 124° (0·82 g., *ca.* 82%) (identity: mixed m. p. and colour reaction with sulphuric acid; Stoermer, *Ber.*, 1911, **44**, 1863).

Reactions with phenylmagnesium bromide. (*a*) An ethereal solution of phenylmagnesium bromide [from magnesium (1·8 g.), bromobenzene (18·8 g.), and dry ether (100 c.c.)] was filtered and divided into two portions. To one portion, 2 : 2′-diketo-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*a*) (1·5 g.) (Schönberg and Mustafa, *J.*, 1945, 657) and dry benzene (30 c.c.) were added. To the second portion, only dry benzene (30 c.c.) was added. The two portions were then refluxed for 2 hours, kept overnight at room temperature, decomposed with cold aqueous ammonium chloride, and extracted with ether. The ethereal solutions were washed with water, dried (Na_2SO_4), and evaporated. The oily residue obtained from the first portion was subjected to steam-distillation, and the aqueous distillate extracted with ether, dried, and evaporated, giving diphenyl as colourless crystals, m. p. 71° (0·7 g.) alone or mixed with an authentic specimen. The non-volatile oil solidified on cooling and crystallised from benzene–light petroleum (b. p. 30—50°) as colourless crystals, m. p. 114° (1·26 g., *ca.* 87%); it was 3-phenylcoumaran-2-one (II*a*) (mixed m. p. and colour reaction with sulphuric acid) (Found : C, 79·7; H, 4·8. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%) (Bistrzycki and Flatau, *loc. cit.*).

The oily residue obtained from the evaporation of the second ethereal solution, similarly treated, gave only diphenyl, m. p. 71° (0·21 g.).

In a blank experiment a solution of (I*a*) (1·5 g.) in dry benzene (30 c.c.) was refluxed for 2 hours in a stream of dry carbon dioxide and kept over-night at room temperature. On concentration of the benzene solution, (I*a*) was recovered completely or almost completely unchanged (m. p. and mixed m. p.).

(*b*) 2 : 2′-Diphenylthioindigo-white (III) (Kalb and Baeyer, *Ber.*, 1913, **46**, 3879) (1·5 g.), when similarly treated, gave 2 : 3-dihydro-3-keto-2-phenylthionaphthen (IV) (1·1 g., *ca.* 75%), m. p. 105° (from ethyl alcohol) (mixed m. p. and colour reaction with sulphuric acid; Kalb and Baeyer, *loc. cit.*) (Found : C, 74·1; H, 4·0; S, 13·8. Calc. for $C_{14}H_{10}OS$: C, 74·3; H, 4·4; S, 14·1%), and diphenyl, m. p. 71° [from light petroleum (b. p. 40—60°)] (0·67 g.).

(*c*) 2 : 2′-Diketo-6 : 6′-dimethyl-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*b*) (1·5 g.) afforded 6-methyl-3-phenylcoumaran-2-one (II*b*) (1·17 g., *ca.* 80%), m. p. 122° (from ethyl alcohol) (identity : mixed m. p. and colour reaction with sulphuric acid; Bistrzycki and Flatau, *loc. cit.*), together with diphenyl (0·64 g.).

(*d*) 2 : 2′-Diketo-5 : 5′-dimethyl-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*c*) (1·5 g.) similarly gave 5-methyl-3-phenylcoumaran-2-one (II*c*), m. p. 106° (from ethyl alcohol) (1·1 g., *ca.* 73%) (identity : mixed m. p. and colour reaction with sulphuric acid; Bistrzycki and Flatau, *loc. cit.*), and diphenyl (0·68 g.).

(*e*) 5 : 5′-Chloro-2 : 2′-diketo-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (I*d*) (1·5 g.) similarly gave 5-chloro-3-phenylcoumaran-2-one (II*d*), m. p. 124° (from ethyl alcohol) (1·13, *ca.* 76%) (identity : mixed m. p. and colour reaction with sulphuric acid; Stoermer, *loc. cit.*), and diphenyl (0·60 g.).

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