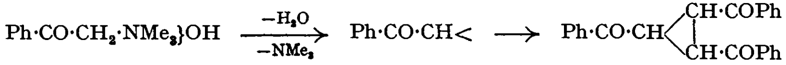
NOTES.

The Thermal Decomposition of Phenacyltrimethylammonium Hydroxide. By J. Harley-Mason.

It was observed by Stevens *et al.* (*J.*, 1928, **3193**) that phenacylbenzyldimethylammonium hydroxide rearranges in alkaline solution with migration of the benzyl group. Under the same conditions phenacyltrimethylammonium hydroxide (I) does not rearrange. In an attempt to determine whether a methyl group was capable of migration under more drastic conditions, (I) was submitted to thermal decomposition at 200°. The products were trimethylamine, water, and *cis*-1 : 2 : 3-tribenzoyl*cyclo*propane, identical with the product obtained by Paal and Schulze (*Ber.*, **1903**, **36**, 2425) by the action of sodium on phenacyl iodide, together with a small amount of an intensely red substance not identified. No products of rearrangement could be isolated. The decomposition is thus parallel to the thermal decomposition of diazoacetophenone (Grundmann, *Annalen*, 1938, **536**, 29), and the product presumably arises from the trimerisation of the radical Ph·CO·CH< :



To a solution of phenacyltrimethylammonium chloride (15 g.) in water (30 c.c.), silver oxide (15 g.) was added with vigorous shaking. After 10 minutes the mixture was filtered and the residue washed with water. The chloride-free filtrate and washings were concentrated in a vacuum to a thick syrup of the quaternary hydroxide, and this was then slowly heated in an oil-bath. When the temperature reached 180° a vigorous decomposition commenced and trimethylamine and steam were evolved. The reaction subsided after 5 minutes and the temperature was then raised to 200° for a further 5 minutes. The deep red melt was allowed to cool somewhat, ethanol (50 c.c.) was added, and the mixture was refluxed for 1 hour. After cooling, the product, which consisted of colourless crystals contaminated with a small amount of an intensely red substance, was collected. Three recrystallisations from glacial acetic acid removed the red material, which remained in the mother liquors, and gave 3·9 g. of colourless needles, m. p. 217°, undepressed by admixture with a sample of *cis*-1 : 2 : 3-tribenzoyl*cyclo*propane prepared by the method of Paal and Schulze (*loc. cit.*).—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, May* 12*th*, 1948.]

A Comparative Study of the Würtz–Fittig and the Clemmensen Method for the Preparation of Aromatic Hydrocarbons. By HUSSEIN A. FAHIM and AHMED MUSTAFA.

THE aim of the present investigation is to study how far the Würtz–Fittig and the Clemmensen method may be applied satisfactorily to the preparation of *n*-alkylbenzenes.

Eisenlohr and Schulz (*Ber.*, 1924, **57**, 1808), Schmidt, Hopp, and Schoeller (*Ber.*, 1939, **72**, 1893), and Shen and Wood (*J. Inst. Petroleum*, 1940, **26**, 514) reported that, in general, the Clemmensen method proved to be unsatisfactory for the preparation of *n*-alkylbenzenes. Consequently, this method has been carefully tested by the synthesis of different *n*-alkylbenzenes and high yields have been obtained (Table I). It should be added, too, that the use of pure as well as commercial zinc granules, in the Clemmensen method did not alter the result.

TABLE I.

n-Alkylbenzene.	Clemmensen method, % yield.	Würtz–Fittig method, % yield.	*n*-Alkylbenzene.	Clemmensen method, % yield.	Würtz–Fittig method, % yield.
Propylbenzene	82	55	Heptylbenzene	90	70
Butylbenzene	88	70	Octylbenzene	91	40
Amylbenzene	90	55	Nonylbenzene	92	—
Hexylbenzene	91	62			

It seems that in the Würtz–Fittig method the yield of *n*-alkylbenzenes is influenced particularly by the nature of the halogen present in the reacting molecules. The highest yield of hydrocarbon is always obtained when the alkyl and aryl bromides are used, whereas the yield is much less from either alkyl and aryl iodides, or alkyl and aryl chlorides. Furthermore, the amount of the hydrocarbon obtained by the action of bromobenzene and alkyl halide, butyl chloride, bromide, and iodide, invariably follows the sequence : Br > I > Cl. This order is also observed in the synthesis of higher hydrocarbons, *e.g.*, *n*-heptylbenzene. The results obtained are given in Table II.

TABLE II.

Temp.	Solvent.	Aryl halide.	Alkyl halide.	% Yield (based on aryl halide used).
		n-*Propylbenzene.*		
20°	Ether	Chlorobenzene	*n*-Propyl chloride	7
20	Ether	Iodobenzene	*n*-Propyl iodide	8
20	Ether	Bromobenzene	*n*-Propyl chloride	20
25	Benzene	Bromobenzene	*n*-Propyl iodide	30
20	Ether	Chlorobenzene	*n*-Propyl bromide	32
20	Ether	Bromobenzene	*n*-Propyl bromide	50—55
		n-*Butylbenzene.*		
30—35	Ether	Iodobenzene	*n*-Butyl iodide	7
25	Ether	Chlorobenzene	*n*-Butyl chloride	10
30—40	Benzene	Bromobenzene	*n*-Butyl chloride	20
30—40	Benzene	Chlorobenzene	*n*-Butyl bromide	25
30—40	Benzene	Bromobenzene	*n*-Butyl iodide	40
25	Ether	Bromobenzene	*n*-Butyl bromide	70
30—40	Benzene	Bromobenzene	*n*-Butyl bromide	62—70
		n-*Amylbenzene.*		
30	Ether	Chlorobenzene	*n*-Amyl chloride	5
30	Ether	Iodobenzene	*n*-Amyl iodide	6
30—40	Benzene	Bromobenzene	*n*-Amyl chloride	15
30—40	Benzene	Chlorobenzene	*n*-Amyl bromide	42
30—40	Benzene	Bromobenzene	*n*-Amyl iodide	46
30—40	Benzene	Bromobenzene	*n*-Amyl bromide	50—55

These results lead to the conclusion that the Clemmensen method is more favourable than the Würtz–Fittig method for the preparation of *n*-alkylbenzenes. The latter method, however, may give satisfactory results when the interaction takes place between alkyl and aryl bromides.

Experimental.—The Würtz–Fittig reaction was carried out in a three-necked flask containing the reactants, aryl halide (1 mol.), alkyl halide (1·1 mols.), and finely powdered sodium metal (2·5 atoms), in the presence of a solvent. The mixture was left for 48 hours at room temperature and then fractionated. The benzene solution of the products, prepared from aryl and alkyl chlorides, acquired a greenish fluoresence.

For the preparation of *n*-alkylbenzenes by the Clemmensen method, the corresponding phenyl alkyl ketones were prepared by Friedel–Crafts method in very satisfactory yields. The acid chloride in each case was prepared in almost quantitative yield by refluxing the corresponding acid with excess of thionyl chloride for 24 hours.

The following new derivatives of the ketones have been prepared :

Phenyl n-*butyl ketone* p-*nitrophenylhydrazone*, orange crystals from ethyl alcohol, m. p. 121—122° (Found : C, 68·2; H, 6·7; N, 14·1. $C_{17}H_{19}O_2N_3$ requires C, 68·7; H, 6·4; N, 14·1%); 2 : 4-*dinitrophenylhydrazone*, orange-red crystals from ethyl alcohol, m. p. 123—124° (Found : C, 59·2; H, 5·5; N, 16·4. $C_{17}H_{18}O_4N_4$ requires C, 59·6; H, 5·3; N, 16·4%).

Phenyl n-*amyl ketone* p-*nitrophenylhydrazone*, orange crystals from ethyl alcohol, m. p. 102° (Found : C, 69·3; H, 6·5; N, 13·4. $C_{18}H_{21}O_2N_3$ requires C, 69·4; H, 6·8; N, 13·5%); 2 : 4-*dinitrophenylhydrazone*, orange-red crystals from ethyl alcohol, m. p. 129° (Found : C, 60·6; H, 5·4; N, 15·4. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·6; N, 15·7%).

Phenyl n-*hexyl ketone* 2 : 4-*dinitrophenylhydrazone*, orange-red crystals from ethyl alcohol, m. p. 131° (Found : C, 61·2; H, 5·7; N, 15·4. $C_{19}H_{22}O_4N_4$ requires C, 61·6; H, 5·9; N, 15·1%).

Phenyl n-*heptyl ketone* p-*nitrophenylhydrazone*, orange crystals from ethyl alcohol, m. p. 113—114° (Found : C, 70·7; H, 7·2; N, 12·0. $C_{20}H_{25}O_2N_3$ requires C, 70·8; H, 7·4; N, 12·4%); 2 : 4-*dinitrophenylhydrazone*, orange-red crystals from ethyl alcohol, m. p. 122° (Found : C, 62·6; H, 6·3; N, 14·3. $C_{20}H_{24}O_4N_4$ requires C, 62·5; H, 6·2; N, 14·6%).

Phenyl n-*octyl ketone* p-*nitrophenylhydrazone*, orange crystals from ethyl alcohol, m. p. 100° (Found : C, 71·3; H, 7·6; N, 12·0. $C_{21}H_{27}O_2N_3$ requires C, 71·3; H, 7·6; N, 11·9%); 2 : 4-*dinitrophenylhydrazone*, orange-red crystals from ethyl alcohol, m. p. 121—122° (Found : C, 63·1; H, 6·7; N, 13·9. $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·5; N, 14·1%).—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, ABBASSIA, CAIRO, EGYPT. [*Received, May* 10*th*, 1948.]

Some pp′-*Dialkylbenzophenones, and Derivatives of* p-*Alkylbenzoic Acids.* By HUSSEIN A. FAHIM.

BOTH *pp*′-dialkylbenzophenones and *p*-alkylbenzoic acids have been prepared by the Friedel–Crafts condensation of benzene homologues with oxalyl chloride.

pp′-*Dimethylbenzophenone* (Limpricht, *Annalen*, 1900, **312**, 91). A mixture of toluene (10 g., 1·3 mols.), oxalyl chloride (12·5 g., 1 mol.), and carbon disulphide (30 c.c.) was gradually treated with aluminium chloride (21 g., 1·6 mol.) at room temperature, with stirring. The mixture was left overnight, carbon disulphide was removed, and the residue decomposed with ice-cold water. The mass was extracted with ether, and the ethereal solution was shaken repeatedly with dilute alkali. The combined alkali extracts gave, on acidification, *p*-toluic acid (m. p. 180°) in 33% yield. The ether solution, on evaporation of the solvent, furnished *pp*′-dimethylbenzophenone (m. p. 95°) in 55% yield. The p-*nitrophenylhydrazone* crystallised from alcohol in golden yellow crystals, m. p. 153° (Found : C, 73·0; H, 5·5; N, 11·9. $C_{21}H_{19}O_2N_3$ requires C, 73·0; H, 5·5; N, 12·2%), and the *semicarbazone* from benzene–light petroleum in white prisms, m. p. 140° (Found : C, 71·7; H, 6·3; N, 16·1. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·4; N, 15·7%).

pp′-*Diethylbenzophenone* (Koslow, Fedossejew, and Olifsson, *J. Gen. Chem. Russia*, 1936, **6**, 259). A mixture of ethylbenzene (14 g., 1·3 mols.), oxalyl chloride (12·5 g., 1 mol.), and carbon disulphide (30 c.c.) was gradually treated with aluminium chloride (21 g., 1·5 mols.). The yields of *p*-ethylbenzoic acid (m. p. 112—113°) and *pp*′-diethylbenzophenone were 30 and 45% respectively. Schönberg and Kraemer (*Ber.*, 1922, **55**, 1174) isolated *p*-ethylbenzoic acid as the sole product. The ketone, which solidified when kept in the cold for some days, crystallised from alcohol in white needles, m. p. 47° (Found : C, 85·6; H, 7·5. Calc. for $C_{17}H_{18}O$: C, 85·7; H, 7·5%). The p-*nitrophenylhydrazone* crystallised from alcohol in orange needles, m. p. 99—100° (Found : C, 73·8; H, 6·2; N, 10·8. $C_{23}H_{23}O_2N_3$ requires C, 73·9; H, 6·2; N, 11·3%).

pp′-*Di*-n-*propylbenzophenone*. A mixture of *n*-propylbenzene (24 g., 2 mols.), oxalyl chloride (12·5 g., 1 mol.), and carbon disulphide (30 c.c.) was gradually treated with aluminium chloride (33·5 g., 2·5 mols.). *p*-*n*-Propylbenzoic acid (m. p. 140—141°) was obtained in 1% yield. The *ketone*, which solidified when kept in the cold for some time, was obtained in 30% yield. It crystallised from methyl alcohol in white crystals, m. p. 69° (Found : C, 85·4; H, 8·1. $C_{19}H_{22}O$ requires C, 85·7; H, 8·2%), the *oxime* crystallised from light petroleum in white silky needles, m. p. 93° (Found : N, 4·99. $C_{19}H_{23}ON$ requires N, 4·98%), the *semicarbazone* crystallised from dilute alcohol in white needles, m. p. 122—123° (Found : C, 74·7; H, 7·8; N, 13·0. $C_{20}H_{25}ON_3$ requires C, 74·3; H, 7·7; N, 13·0%), and the p-*nitrophenylhydrazone* crystallised from alcohol in orange-yellow crystals, m. p. 126° (Found : C, 74·5; H, 6·6; N, 10·3. $C_{25}H_{27}O_2N_3$ requires C, 74·8; H, 6·7; N, 10·5%).

pp′-*Di*-n-*butylbenzophenone*. This was obtained from *n*-butylbenzene (27 g., 2 mol.), oxalyl chloride (12·5 g., 1 mol.), aluminium chloride (33·5 g., 2·5 mols.), and carbon disulphide (30 c.c.), in 40% yield, as a yellowish oil, b. p. 258—262°/26 mm. No acid could be isolated. The *oxime* crystallised from light petroleum in white crystals, m. p. 70—71° (Found : C, 81·1; H, 8·7. $C_{21}H_{27}ON$ requires C, 81·5; H, 8·7%), and the p-*nitrophenylhydrazone* crystallised from alcohol in orange-yellow crystals, m. p. 138° (Found : C, 75·2; H, 7·3; N, 9·4. $C_{27}H_{31}O_2N_3$ requires C, 75·5; H, 7·2; N, 9·7%).

n-*Alkylbenzoic acids.* Some of these acids have been prepared by oxidation of the corresponding *p*-*n*-alkylphenyl methyl ketone with sodium hypobromite solution (Zaki and Fahim, *J.*, 1942, 307). They have also been obtained, in satisfactory yields, by a modification of the method described above for the preparation of the dialkylbenzophenones: a solution of the *n*-alkylbenzene (1 mol.) and oxalyl chloride (1 mol.) in carbon disulphide (4 mols.) was gradually treated with aluminium chloride (1 mol.) at room temperature, with stirring. The product was left overnight, carbon disulphide was removed, and the residue was decomposed with ice-cold water. The mass was collected and digested with hot N/2-sodium hydroxide for ½ hour. Any undissolved oil was extracted with ether and the acid precipitated on acidification.

p-*Ethylbenzoyl chloride.* This was obtained, by heating *p*-ethylbenzoïc acid (9 g.) and thionyl chloride (13 g.) under reflux for 3½ hours, as a colourless fuming liquid, b. p. 235—236°. 1-p-*Ethylbenz*-2-p-*nitrophenylhydrazide* was obtained by heating under reflux for a short time an ethereal solution of equimolecular amounts of *p*-nitrophenylhydrazine and *p*-ethylbenzoyl chloride, filtering the solution from an insoluble product, and removing the solvent. The hydrazide crystallised from benzene–light petroleum in yellowish tiny needles, m. p. 220—221° (Found: C, 63·5; H, 5·3; N, 14·6. $C_{15}H_{15}O_3N_3$ requires C, 63·2; H, 5·3; N, 14·7%).

p-n-*Propylbenzoyl chloride.* Propylbenzoyl chloride, obtained by heating under reflux *n*-propylbenzoic acid (8 g.) and thionyl chloride (10 g.) for 4½ hours, was a yellowish fuming liquid, b. p. 135—136°/20 mm. The amide crystallised from benzene–light petroleum in white silky needles, m. p. 152° (Willard and Maresh, *J. Amer. Chem. Soc.*, 1940, **62**, 1253, give m. p. 128·4°) (Found: C, 73·8; H, 7·9; N, 8·4. Calc. for $C_{10}H_{13}ON$: C, 73·6; H, 7·9; N, 8·5%). N-*Methyl*-p-n-*propylbenzamide* was obtained by shaking together the cooled acid chloride and aqueous methylamine, and crystallised from benzene–light petroleum in white feathery-like crystals, m. p. 100—101° (Found: C, 74·5; H, 8·4; N, 8·2. $C_{11}H_{15}ON$ requires C, 74·5; H, 8·5; N, 7·9%). 1-p-n-*Propylbenz*-2-p-*nitrophenylhydrazide* crystallised from acetone–light petroleum in whitish crystals, m. p. 201° (Found: C, 64·4; H, 5·6; N, 14·3. $C_{16}H_{17}O_3N_3$ requires C, 64·2; H, 5·7; N, 14·0%).

p-n-*Butylbenzoyl chloride.* This was prepared by heating under reflux *n*-butylbenzoic acid (7·5 g.) and thionyl chloride (9 g.) for 4½ hours, and formed a yellowish liquid, b. p. 155—156°/26 mm. The amide crystallised from alcohol in white crystals, m. p. 136° (Willard and Maresh, *loc. cit.*, give m. p. 121·5°) (Found: C, 74·3; H, 8·2; N, 7·8. Calc. for $C_{11}H_{15}ON$: C, 74·5; H, 8·4; N, 7·9%). N-*Methyl*-p-n-*butylbenzamide* crystallised from benzene–light petroleum in white crystals, m. p. 70—71° (Found: C, 75·3; H, 9·0; N, 7·2. $C_{12}H_{17}ON$ requires C, 75·4; H, 8·9; N, 7·3%).—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, ABBASSIA, CAIRO, EGYPT. [*Received, May* 11*th*, 1948.]

The Bromination of Dimethoxystilbenes. By FELIX BERGMANN.

IN our recent paper on this subject (*J.*, 1947, 1450) we stated that "in all known cases the speed of addition of bromine to the central double bond of a stilbene is greater than that of nuclear substitution". Prof. H. Erdtman calls our attention to the fact observed by him (*Ber.*, 1941, **74**, 50) that pinosylvine dimethyl ether (3 : 5-dimethoxystilbene) is dibrominated in the ring before saturation of the double bond. It is of great interest that introduction of a second methoxyl group into the anisole ring increases the rate of nuclear substitution over that of addition to the olefinic double bond. We regret having overlooked Erdtman's observation, the original publication of which was not available to us.—DEPARTMENT OF PHARMACOLOGY, THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL. [*Received, May* 6*th*, 1948.]