Experiments on Halogenated Ketones. The Conversion of 1-*Bromo-*1 : 3-*diphenylpropan*-2-*one into* 1-*Phenylindan*-2-*one.*

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1-Bromo-1 : 3-diphenylpropan-2-one undergoes Friedel–Crafts type reactions in the presence of aluminium chloride; with benzene it affords some 1 : 1 : 3-triphenylpropan-2-one (19%). In the absence of benzene, intramolecular reaction yields 1-phenylindan-2-one (80%); 1-bromo-3-phenylpropan-2-one is not cyclised thus. In the presence of hydrogen bromide, 1-bromo-3-phenylpropan-2-one rearranges to 1-bromo-1-phenylpropan-2-one; each isomer forms a distinctive 2-aminothiazole derivative when treated with thiourea. β-Bromo-propiophenone, which is believed to be identical with a product described by Grignard and Perrichon as 1-bromo-3-phenylpropan-2-one, with semicarbazide gives an unstable semicarbazone which cyclises to a carbamoylpyrazoline; the latter is synthesised by an alternative method.

α-HALOGENATED ketones often undergo Friedel–Crafts reactions with aromatic compounds; in particular, ketones (I) with benzene and aluminium chloride have given the *gem*-diphenyl compounds (II) [R = Me: Ruggli, Dahn, and Wegmann, *Helv. Chim. Acta*, 1946, **29**, 113; Schultz and Mickey, *Org. Synth.*, 1949, **29**, 38; R = Ph (chloroketone): MacKenzie and Lesslie, *Ber.*, 1928, **61**, 158], and α-alkyl *gem*-diphenyl ketones have been obtained similarly (Schultz, Bicking, Mickey, and Crossley, *J. Amer. Chem. Soc.*, 1953, **75**, 1072).

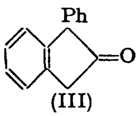
Treatment of crude 1-bromo-1 : 3-diphenylpropan-2-one (I; R = CH_2Ph) with benzene and aluminium chloride gave a mixture from which 1 : 1 : 3-triphenylacetone (II; R = CH_2Ph) was isolated in only 19% yield. The product was identified by the oxime and by comparison with an authentic sample made by rearrangement of 1 : 2 : 3-triphenylpropane-1 : 2-diol (Orékhoff, *Bull. Soc. chim. France*, 1919, **25**, 108). It seemed probable that the low yield of triphenylacetone was due to an intramolecular condensation affording 1-phenylindan-2-one (III) and its transformation products. Indan-2-ones are relatively uncommon, but Kohler and Weiner (*J. Amer. Chem. Soc.*, 1934, **56**, 434) obtained 1-methyl-1 : 3-diphenylindan-2-one by heating 1-hydroxy-1-methyl-1 : 3 : 3-triphenylpropan-2-one with hydriodic acid; this appears to be the only recorded example of the formation of an indan-2-one by a reaction formally analogous to (I) ⟶ (III).

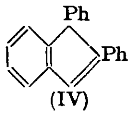
Attempts were therefore made to cyclise α′-bromo-α-phenylalkyl ketones to indan-2-ones. Bromination of 1 : 3-diphenylacetone by an improved method afforded crystalline 1-bromo-1 : 3-diphenylpropan-2-one (I; R = CH_2Ph) which was characterised by conversion into 2-amino-4-benzyl-5-phenylthiazole, and into the corresponding anilino-ketone

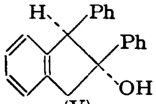
(McGeoch and Stevens, *J.*, 1935, 1032; Julian, Meyer, Magnani, and Cole, *J. Amer. Chem. Soc.*, 1945, **67**, 1203). Francis (*J.*, 1899, 865) claimed to have obtained the anilino-ketone anil (m. p. 127·5°; hydrochloride, m. p. 176°) from the bromo-ketone and aniline. There is little doubt that Francis's product was the anilino-ketone, which has m. p. 127—129° and forms a hydrochloride m. p. 172—174°. We obtained no evidence of anil formation; furthermore, the Bischler mechanism for indole synthesis which postulates intermediate anilino-ketone anils has been criticised recently (Crowther, Mann, and Purdie, *J.*, 1943, 58; *Annual Reports*, 1946, **43**, 242). 1-Bromo-1 : 3-diphenylpropan-2-one and sodium iodide in acetone afforded the unstable α-iodo-ketone, which rapidly liberated iodine on warming or on ultraviolet irradiation in light petroleum solution. This bromo-ketone also condensed readily with 1 : 3-diphenylacetone in alkaline media, giving an unidentified compound $C_{30}H_{26}O_2$, m. p. 200—202°. 1-Bromo-1 : 3-diphenylpropan-2-one in presence of aluminium chloride in cold carbon disulphide gave 1-phenylindan-2-one (III), m. p. 51—53°, in 80% yield. The indanone formed a 2 : 4-dinitrophenylhydrazone (m. p. 199°) and a semicarbazone (m. p. 200—202°), reduced ammoniacal silver nitrate solutions, and slowly dissolved in cold aqueous sodium hydroxide. The indanone somewhat resembles 1 : 2-diphenylpropaldehyde for which Burton and Shoppee (*J.*, 1937, 546) give m. p. 54°, two 2 : 4-dinithrophenylhydrazones of m. p. 148—152° and 199°, semicarbazone of m. p. 125° (see also Ramart-Lucas and Salmon-Lecagneur, *Bull. Soc. chim. France*, 1932, **51**, 1084, who made a semicarbazone, m. p. 120—121°). Although 1-bromo-1 : 3-diphenylpropan-2-one might have given 1 : 2-diphenylpropaldehyde by a type of retro-Danilov rearrangement, this structure was excluded because the product did not afford αβ-diphenylpropionic acid on oxidation with silver oxide (cf. Ramart-Lucas and Salmon-Lecagneur, *loc. cit.*). Confirmation of the 1-phenylindan-2-one structure was obtained by treatment with phenylmagnesium bromide and dehydration of the intermediate alcohol [not isolated, but presumably the *cis*-diphenyl compound (V)] to 1 : 2-diphenylindene (IV), which was identical with a specimen made from 1 : 2 : 3-triphenylpropane-1 : 2-diol (Orékhoff and Tiffeneau, *Bull. Soc. chim. France*, 1922, **31**, 253; cf. McKenzie and Roger, *Ber.*, 1929, **62**, 284). By a similar sequence of reactions, Koelsch and Johnson (*J. Org. Chem.*, 1941, **6**, 534) converted 2-phenylindan-1-one into 2 : 3-diphenylindene. All the indane derivatives encountered in our experiments give the expected intense blue or green solutions in concentrated sulphuric acid. The reducing properties and alkali-solubility (with ring scission) of 1-phenylindan-2-one are a little unexpected, but recall the behaviour of some other indanones (*e.g.*, 2-phenylindan-1-one; von Miller and Rohde, *Ber.*, 1892, **25**, 2095; von Auwers and Auffenberg, *Ber.*, 1919, **52**, 92). Attempts were made unsuccessfully to convert 1-phenylindan-2-one into the known 1-phenylindane-2 : 3-dione or its dioxime (Pfeiffer and de Waal, *Annalen*, 1935, **520**, 185; Koelsch, *J. Amer. Chem. Soc.*, 1936, **58**, 1321).

(I) $Ph\cdot CHBr\cdot COR$

$Ph_2CH\cdot COR$ (II)


(III)


(IV)



(V)

(VI) $Ph\cdot CH_2\cdot CO\cdot CH_2Br$

$Ph\cdot CHBr\cdot COMe$ (VII)

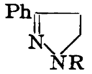
For the conversion of α-bromo-α′-phenylalkyl ketones into indan-2-ones, activation of the bromine by a suitable α-substituent appears to be necessary Thus, no indanone was obtained from 1-bromo-3-phenylpropan-2-one (VI), which was recovered unchanged after treatment with aluminium chloride. The preparation of 1-bromo-3-phenylpropan-2-one (VI) from phenylacetyl chloride and diazomethane followed by treatment with hydrogen bromide (Catch, Elliott, Hey, and Jones, *J.*, 1948, 287; cf. Diesbach, Capponi, and Farquet, *Helv. Chim. Acta*, 1949, **32**, 1226) was attended by unexpected complications, as the bromomethyl ketone (VI) was found to rearrange to 1-bromo-1-phenylpropan-2-one (VII) in the presence of hydrogen bromide. The latter bromo-ketone was also obtained by direct bromination of phenylacetone. The two isomeric bromo-ketones were characterised by treating them with thiourea, which gave thiazole derivatives having the expected light-absorption properties. A preliminary account of the rearrangement of 1-bromo-3-phenylpropan-1-one has already been given (Smith, Wilson, and Woodger, *Chem. and Ind.*, 1954, 309); the light-absorption of thiazoles will be discussed in a forthcoming communication. The above rearrangement is believed to occur by debromination–bromination (Smith, Wilson, and Woodger, *loc. cit.*; Newman, *J. Amer. Chem. Soc.*, 1951, **73**, 4993; Stevens and Lenk, *J. Org. Chem.*, 1954, **19**, 528).

Grignard and Perrichon (*Ann. Chim.*, 1926, **5**, 5) obtained several bromomethyl ketones by hydrating 1-bromoalkynes. The product from 1-bromo-3-phenylprop-1-yne (VIII) had m. p. 58°, formed a semicarbazone m. p. 225—230°, and was claimed to be 1-bromo-3-phenylpropan-2-one (VI). However, the calculated percentage composition and " found " analytical figures are incorrect, and no analysis is given for the semicarbazone. We believe that Grignard and Perrichon's product was actually β-bromopropiophenone (X), which has m. p. 58° (Foreman and McElvain, *J. Amer. Chem. Soc.*, 1940, **62**, 1435), a rearrangement (*e.g.*, VIII ⟶ IX) having taken place during their synthesis. Little progress was made in repeating their reaction, as the intermediate benzylacetylene was not easily obtained and isomerised or polymerised readily. We prepared a sample of β-bromopropiophenone, m. p. 58°, by a method used for the corresponding chloro-ketone (Kohler, *Amer. Chem. J.*, 1909, **42**, 389), and studied its reaction with semicarbazide. No compound of m. p. 225—230° was obtained; however, Grignard and Perrichon's unanalysed " semicarbazone " of this m. p. may well have been impure hydrazodicarboxyamide, for which various m. p.s from 245° to 270° have been quoted. Authentic β-bromopropiophenone with semicarbazide under mild conditions yielded an unstable semicarbazone, m. p. 130°; at higher temperatures cyclisation occurred, and 1-carbamoyl-3-phenyl-Δ^2-pyrazoline (XI; R = $CO{\cdot}NH_2$) was obtained (cf. Maire, *Bull. Soc. chim. France*, 1908, **3**, 272). The structure of this product was confirmed by an independent preparation from 3-phenyl-Δ^2-pyrazoline (XI; R = H) and cyanic acid (cf. von Auwers and Heimke, *Annalen*, 1927, **458**, 194).

$Ph{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}Br$ (VIII)

$Ph{\cdot}C{\vdots}C{\cdot}CH_2Br$ (IX)

$Ph{\cdot}CO{\cdot}CH_2{\cdot}CH_2Br$ (X)



(XI)

EXPERIMENTAL

Reaction of 1-*Bromo*-1 : 3-*diphenylpropane*-2-*one with Benzene.*—Bromine (16 g.) was added dropwise during 90 min. to a stirred solution of 1 : 3-diphenylpropan-2-one (21 g.) in dry, thiophen-free benzene (75 c.c.) at 20°. A stream of dry nitrogen was then blown through the solution for 2 hr. to expel hydrogen bromide. The resulting benzene solution of crude 1-bromo-1 : 3-diphenylpropan-2-one was dropped during 1 hr. into a gently refluxing and stirred mixture of pure benzene (60 c.c.) and powdered aluminium chloride (27 g.). The mixture was refluxed for a further hour, cooled, and treated with ice (175 g.) and concentrated hydrochloric acid (40 c.c.), and the organic layer was separated, washed with sodium hydrogen carbonate solution, and dried (Na_2SO_4). Distillation afforded a main fraction (19·5 g.), b. p. 90—180°/0·1 mm. Further distillation gave unidentified oils and a fraction, b. p. 160—180°/0·06 mm., which solidified; recrystallisation from ethanol afforded 1 : 1 : 3-triphenylpropan-2-one (5·3 g., 17%), m. p. 79—81°, raised to 80—81° on a further crystallisation. The m. p. was not depressed by admixture with a specimen, m. p. 81—82°, prepared from 1 : 2 : 3-triphenylpropane-1 : 2-diol and concentrated sulphuric acid (Orékhoff, *loc. cit.*). (The ketone is most conveniently obtained by the latter method.) The oxime, obtained in pyridine, had m. p. 133—135° (Orékhoff, *loc. cit.*, gives m. p. 134—135°).

1-*Bromo*-1 : 3-*diphenylpropan*-2-*one.*—Bromine (7·7 c.c.) was added during 1 hr. to a stirred mixture of 1 : 3-diphenylpropan-2-one (31·5 g.), carbon disulphide (150 c.c.), and finely powdered calcium carbonate (15 g.). The mixture was stirred for a further hour, then treated with water, and the carbon disulphide layer dried and evaporated. The residue (42 g., 97%), recrystallised twice from light petroleum (b. p. 40—60°), gave the bromo-ketone (27 g., 62%) as colourless needles, m. p. 45—47° (Bourcart, *Ber.*, 1889, 22, 1368, gives m. p. 43—44°; Francis, *J.*, 1899, 865, m. p. 49°; and Veksler, *J. Gen. Chem.*, *U.S.S.R.* 1950, **20**, 1289, m. p. 48—48·5°). Distillation of the bromo-ketone is not recommended.

2-Amino-4-benzyl-5-phenylthiazole.—The above bromo-ketone (2·9 g.), thiourea (0·76 g.), and ethanol (25 c.c.) were refluxed for 3 hr. The *thiazole hydrobromide* (59%), m. p. 215—218° (with previous sintering), was recrystallised from ethanol (Found: S, 8·85. $C_{16}H_{15}N_2SBr$ requires S, 9·25%). The free base had m. p. 143—144° (King and Hlavacek, *J. Amer. Chem. Soc.*, 1950, **72**, 3722, give m. p. 139—140°).

1-Anilino-1 : 3-diphenylpropan-2-one.—Reaction of aniline (2 mols.) with the above bromo-ketone for ½ hr. afforded the anilino-ketone (97%), m. p. 127—129° (McGeoch and Stevens, *loc. cit.* give m. p. 125°). The *hydrochloride*, m. p. 172—174°, obtained from the base and alcoholic hydrogen chloride (Found: N, 4·1. $C_{21}H_{19}ON,HCl$ requires N, 4·15%), was decomposed by hot ethanol, and the free base crystallised on cooling. The anilino-ketone was the sole product from several reactions carried out at higher temperatures.

Condensation of 1-Bromo-1 : 3-diphenylpropan-2-one with 1 : 3-Diphenylpropan-2-one.—A mixture of the bromo-ketone (210 mg.), ketone (150 mg.), and ethanol (5 c.c.) was treated with one drop of 10N-sodium hydroxide. The solid *substance* (50 mg.) produced had m. p. 200—202° (Found: C, 86·2, 86·1; H, 6·3, 6·3. $C_{30}H_{26}O_2$ requires C, 86·1; H, 6·25%).

Reaction of 1-Bromo-1 : 3-diphenylpropan-2-one with Sodium Iodide.—The bromo-ketone (2·9 g.), sodium iodide (1·5 g.), and acetone (110 c.c.) were mixed and left at 20° for about ½ hr., then poured into water. The solid (3 g.; m. p. 70—72°) obtained was recrystallised carefully from light petroleum (b. p. 40—60°). However, some decomposition occurred, and the iodo-ketone, m. p. 74—76°, was not obtained pure (Found: I, 28·65. Calc. for $C_{15}H_{13}OI$: I, 37·8%). The impure iodo-ketone (157 mg.) was dissolved in light petroleum (b. p. 40—60°) in a quartz flask and irradiated with an ultra-violet lamp for 5 hr. Thiosulphate titration indicated that 59% of the iodine had been liberated. Refluxing a solution of the iodo-ketone in light petroleum (b.p. 40—60°) in diffused daylight for 5 hr. liberated 15% of the iodine.

1-Phenylindan-2-one.—A solution of recrystallised 1-bromo-1 : 3-diphenylpropan-2-one (8·7 g.) in carbon disulphide (60 c.c.) was added during 35 min. to a cold stirred mixture of carbon disulphide (30 c.c.) and powdered aluminium chloride (8·1 g.). The mixture was then stirred for a further 75 min., again at room temperature, and treated with cold dilute hydrochloric acid. The carbon disulphide layer was separated. Distillation afforded an oil, b. p. 130—135°/0·2 mm. (5 g., 80%), which solidified; recrystallisation from light petroleum (b. p. 40—60°), yielded *1-phenylindan-2-one* as large colourless prisms, m. p. 51—53° (Found: C, 86·3; H, 5·9. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%). The *2 : 4-dinitrophenylhydrazone*, m. p. 199° (decomp.), was orange-yellow and almost insoluble in ethanol (Found: C, 64·7; H, 4·45; N, 14·0. $C_{21}H_{16}O_4N_4$ requires C, 64·95; H, 4·15; N, 14·45%). The *semicarbazone* (obtained by using semicarbazide hydrochloride in aqueous ethanol) had m. p. 200—202° (with previous sintering) (Found: N, 15·2. $C_{16}H_{15}ON_3$ requires N, 15·85%). The indanone reacted readily with nitrous acid (*n*-butyl nitrite and aqueous hydrochloric acid in ethanol); the product was a brownish-yellow solid, crystallising as a pinkish powder, m. p. 157° (approx.), from ethanol (Found: C, 84·3; H, 4·9; N, 0·75%), which gave an amorphous product with hydroxylamine acetate. The indanone reacted vigorously with *p*-nitrosodimethylaniline in ethanol; no crystalline product was obtained from the dark green solution, and 3-phenylindane-1 : 2-dione was not formed when the product was boiled with aqueous hydrochloric acid. 1-Phenylindan-2-one was shaken overnight with moist silver oxide, suspended in ether; metallic silver was formed, together with an unidentified pink solid, m. p. 80° (indefinite), which was insoluble in aqueous sodium hydroxide, reduced ammoniacal silver nitrate, and gave a deep blue colour with concentrated sulphuric acid. The indanone slowly dissolved in aqueous sodium hydroxide, and on acidification an unidentified acid, m. p. 130°, was obtained. The indanone readily reduced ammoniacal silver nitrate solution, gave an intense green colour, changing to intense blue on warming, with concentrated sulphuric acid, and gave no derivative with benzaldehyde in acid or alkaline media.

1 : 2-Diphenylindene.—1-Phenylindan-2-one (200 mg.) in ether (2 c.c.) was added to a Grignard solution made from bromobenzene (800 mg.), magnesium (150 mg.), and ether (5 c.c.). When the vigorous reaction subsided the mixture was refluxed for 2 hr., cautiously treated with cold dilute hydrochloric acid, and steam-distilled to remove ether and traces of diphenyl and bromobenzene. Ether-extraction of the residue gave an oil which was dissolved in glacial acetic acid (5 c.c.) containing water (2 drops) and concentrated sulphuric acid (0·5 c.c.), warmed at 75° for only 5 min., then cooled to 15°. The crystalline product (100 mg.; m. p. 150—155°) was filtered off and washed thoroughly with water. Recrystallisation from benzene–light petroleum

(b. p. 40—60°) afforded 1 : 2-diphenylindene, as needles, m. p. 172—174°, not depressed on admixture with a specimen (m. p. 173—175°) prepared from 1 : 2 : 3-triphenylpropane-1 : 2-diol and acetyl chloride (Orékhoff and Tiffeneau; McKenzie and Roger, *locc. cit.*). The indene gave an intensely green solution in warm concentrated sulphuric acid.

1-*Bromo*-3-*phenylpropan*-2-*one*.—Phenylacetyl chloride was treated with diazomethane in pure ether, and dry hydrogen bromide passed into the mixture (cf. Catch, Elliott, Hey, and Jones, *loc. cit.*). The ether solution was immediately washed with dilute aqueous sodium hydrogen carbonate, dried, and distilled, to give the bromo-ketone, b. p. 88—90·5°/0·15 mm., m. p. 15—20°, n_D^{23} 1·5586 (Catch, Elliott, Hey, and Jones, *loc. cit.*, give b. p. 106°/0·2 mm., $n_D^{15 \cdot 5}$ 1·5593). The bromo-ketone with thiourea in ethanol afforded 2-amino-4-benzylthiazole hydrobromide, m. p. 88—89° ($\lambda_{max.}$ 259 mμ, ε 7600 in acid ethanol); the free base had m. p. 93—94° (Libermann and Moyeux, *Bull. Soc. chim. France*, 1950, 301, give m. p. 96—97°). Semicarbazide hydrochloride (0·35 g.), the bromo-ketone (0·67 g.), and cold aqueous ethanol (10 c.c.) soon deposited a solid (0·65 g.; m. p. 136—137°); recrystallisation from ethanol gave the fairly stable *semicarbazone*, m. p. 137—138° (Found: Br, 30·0. $C_{10}H_{12}ON_3Br$ requires Br, 29·6%). Under similar conditions, 1-phenylpropan-2-one also formed a semicarbazone, but 1-bromo-1-phenylpropan-2-one and 1-bromo-1 : 3-diphenylpropan-2-one did not.

Attempted Cyclisation of 1-*Bromo*-3-*phenylpropan*-2-*one*.—The bromo-ketone (3·35 g.) in carbon disulphide (25 c.c.) was added during 1 hr. to a refluxing mixture of carbon disulphide (15 c.c.) and powdered aluminium chloride (4·25 g.). The mixture was stirred and refluxed for a further 1½ hr., then poured into cold dilute hydrochloric acid and worked up in the usual way. This gave unchanged bromo-ketone (3·25 g., 97%), b. p. 55—60°/0·01 mm., which gave a copious precipitate with alcoholic silver nitrate, and with semicarbazide hydrochloride in cold ethanol gave the semicarbazone (75% yield), m. p. and mixed m. p. 136—137°.

1-*Bromo*-1-*phenylpropan*-2-*one*.—(a) *From* 1-*phenylpropan*-2-*one*. Bromine (25 g.) was added with stirring to a solution of phenylacetone (20 g.) in benzene at 20° during 30 min. Hydrogen bromide was removed in a stream of nitrogen during 2 hr. The liquid was washed with water and distilled; the bromo-ketone (14·4 g., 45%) had b. p. 122—126°/8 mm. (Babichev, *Ukrain. Chem. J.*, 1950, **16**, 188, gives b. p. 122—123°/5 mm.). This bromo-ketone (5 g.), thiourea 1·7 g.), and ethanol (17 c.c.), refluxed for 3½ hr., gave 2-*amino*-4-*methyl*-5-*phenylthiazole hydrobromide*, m. p. 213—215° (from ethanol), $\lambda_{max.}$ 281 mμ, (ε 12,900 in acid ethanol) (Found: C, 44·3; H, 4·1. $C_{10}H_{10}N_2S,HBr$ requires C, 44·3; H, 4·1%). The free base had m. p. 166—168° (Kopp, *Bull. Soc. chim. France*, 1950, 582, gives m. p. 164—166°).

(b) *By rearrangement of* 1-*bromo*-3-*phenylpropan*-2-*one*. 1-Bromo-3-phenylpropan-2-one (1·08 g.) was dissolved in undried ether (5 c.c.) containing 285 g. of dissolved hydrogen bromide per l. After being kept in the dark for 52 hr. the red-brown solution was diluted with ether (100 c.c.) washed with sodium hydrogen carbonate solution and water, then dried (Na_2SO_4). Removal of the solvent gave an oil (1·03 g.); this was refluxed with thiourea (0·37 g.) in ethanol (25 c.c.) for 3 hr.; the resulting solution (acidified) had pronounced light absorption at 278 mμ with an inflexion at 245 mμ. The ethanol was removed, and the solid product crystallised from ethanol–ether, affording impure 2-amino-4-methyl-5-phenylthiazole hydrobromide (0·76 g., 55%), m. p. 183—193°, raised to 215—217° on three further crystallisations. The m. p. was not depressed on admixture with the authentic hydrobromide, and the free base had m. p. 164—166°. In other experiments, the rearranged bromo-ketone was distilled; the product gave 2-amino-4-methyl-5-phenylthiazole with thiourea.

β-*Bromopropiophenone* (cf. Mannich and Heilner, *Ber.*, 1922, **55**, 360).—β-Dimethylaminopropiophenone hydrochloride was dissolved in water, and steam-distilled for several hours, a little quinol being added to the solution and to the distillate. Crude 1-phenylprop-2-en-1-one (67%) was isolated from the distillate by careful ether-extraction. This unsaturated ketone (1·93 g.) was immediately dissolved in anhydrous ether (20 c.c.) and ethereal hydrogen bromide (21 c.c. of a solution containing 90 g. of acid per l. of ether) added. After 20 hr. the ether was removed. The solid product (2·9 g., 92%) was recrystallised from light petroleum (b. p. 40—60°), to give β-bromopropiophenone (2·3 g., 73%) as white crystals, m. p. 57—59° (Foreman and McElvain, *J. Amer. Chem. Soc.*, 1940, **62**, 1435, give m. p. 58—59°).

Reaction of β-*Bromopropiophenone with Semicarbazide*.—(*a*) The bromo-ketone (520 mg.) was dissolved in cold ethanol (12 c.c.) containing water (2·5 c.c.), and semicarbazide hydrochloride (270 mg.) added. The mixture was shaken for 1 hr., then sodium acetate trihydrate (335 mg.) was added. After 12½ hr., the crystals were filtered off and washed with cold water, giving impure bromo-ketone semicarbazone (220 mg.), m. p. 130° (decomp., with previous sintering) (Found: N, 14·3. Calc. for $C_{10}H_{12}ON_3Br$: N, 15·55%). The compound liberated hydrogen bromide on attempted recrystallisation. (*b*) The bromo-ketone (455 mg.) in ethanol (9·5 c.c.) and water (2 c.c.) was shaken with semicarbazide hydrochloride (240 mg.) at 20° for 1½ hr. Sodium acetate trihydrate (290 mg.) was added, and the solution refluxed for 2 hr. The mixture was evaporated to dryness and the residue extracted with benzene. Evaporation of the benzene extract afforded a solid (260 mg., 65%), which was recrystallised from benzene. 1-*Carbamoyl*-3-*phenyl*-Δ^2-*pyrazoline* formed white crystals (Found: N, 21·4. $C_{10}H_{11}ON_3$ requires N, 22·2%), m. p. 157—160° not depressed by admixture with sample made as follows:

3-Dimethylamino-1-phenylpropan-2-one and hydrazine hydrate afforded 3-phenyl-Δ^2-pyrazoline (Beech, Turnbull, and Wilson, *J.*, 1952, 4686), characterised by the nitroso-derivative, m. p. 154—156°. The pyrazoline (1·06 g.) was dissolved in 2N-hydrochloric acid (7·5 c.c.) at 40° (bath), and potassium cyanate (680 mg.) in water (2 c.c.) was added. The precipitated yellowish solid (440 mg.) was recrystallised from benzene, affording the carbamoyl compound, m. p. 157—160°.

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