371. *Application of the Darzens Glycidic Ester Synthesis to Indan-1-one and Related Ketones.*

By A. H. Bone and L. A. Cort.

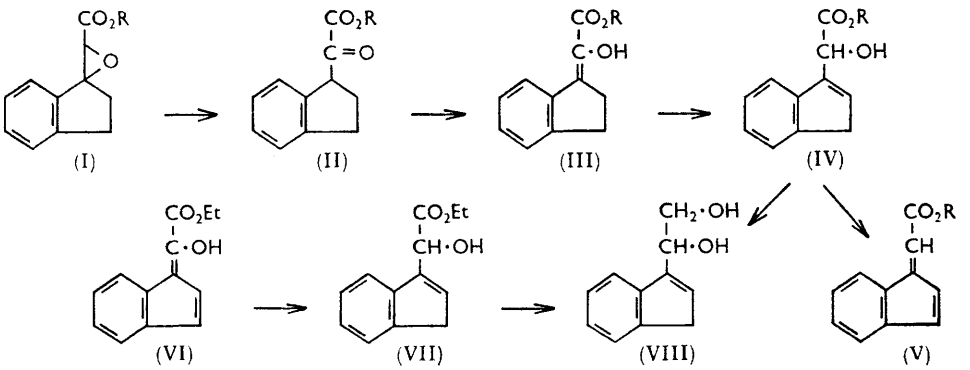
The tendency of glycidic esters to rearrange, to enol- or α-keto-esters, is shown to exist to a very marked extent when the preparation of such esters is attempted with a series of indan-1-ones by the Darzens reaction. The compound previously formulated as indane-1-spiro-2′-oxiran-3′-carboxylic acid is shown to be inden-1(?3)-ylglycollic acid.

The Darzens reaction with phenethyl phenyl ketone proceeds normally, and the expected glycidic acid and derived aldehyde can be obtained.

Condensation of indan-1-one with ethyl chloroacetate in the presence of potassium t-butoxide would be expected [1] to yield ethyl indane-1-spiro-2′-oxiran-3′-carboxylate

[1] Newman and Magerlein, *Org. Reactions*, 1949, **5**, 413.

(I; R = Et), but when the ester product (*A*) is hydrolysed by Claisen's method [2,3] two carboxylic acids are obtained, orange and colourless, respectively. The former of these has been identified [4] by direct comparison as inden-1-ylideneacetic acid (V; R = H). The colourless acid is now shown to be inden-1(?3)-ylglycollic acid (IV; R = H) by direct comparison with the authentic acid synthesised in the following manner: ethyl inden-1-ylideneglycollate [5] (VI) (from indene and diethyl oxalate) on reduction with aluminium amalgam gives [6] ethyl inden-1(?3)-ylglycollate (VII). Hydrolysis of this ester with aqueous or alcoholic alkali is accompanied by the development of a deep purple colour, and the acid produced on acidification is inden-1-ylideneacetic acid.[6] However, if hydrolysis is carried out by Claisen's method and the sodium salt(s) produced treated as described [4] for working-up of the Darzens condensation product, two acids are obtained: one is inden-1-ylideneacetic acid, and the other (colourless) is clearly inden-1(?3)-ylglycollic acid. The latter gave the same *p*-bromophenacyl ester as that obtained on the hydrolysis, etc., of the ester (*A*).

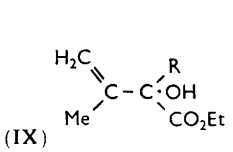


It was thought originally [4] that the colourless acid from the ester (*A*) was indane-1-spiro-2′-oxiran-3′-carboxylic acid, for it gave no immediate reaction with Brady's reagent [and hence could not be the α-keto-acid (II; R = H)], and it could be decarboxylated to yield 1-formylindane (characterised as the known semicarbazone). In accord with its identification as the glycollic acid, the acid is found to have two active hydrogen atoms per molecule and to show strong absorption in the ultraviolet region. Glycidic esters do not absorb selectively at these wavelengths; [7] in cases where the molecule contains a non-conjugated benzene nucleus, only low-intensity (ε ~200) broad-band absorption is found between 250 and 270 mμ, and this absorption by such compounds is ignored in the present work.

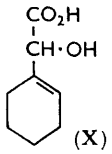
The behaviour of the ester (*A*) with Brady's reagent and with ferric chloride, together with the ultraviolet absorption, suggests that it is a mixture containing a large proportion of the glycollate (IV; R = Et); that is, rearrangements have occurred before treatment with acid or alkali. It is likely that the glycidic ester (I) is formed initially, and that this then rearranges to the keto-ester (II), a thermal rearrangement of this type being known.[8] Enolisation of the product would give a compound (III) in which there is an exocyclic double bond, and in the indane series there is evidence [9] that such a double bond migrates into the ring [to give in the present instance (IV)]. This accounts for the two products

[2] Claisen, *Ber.*, 1905, **38**, 693.
[3] Allen and Allan, *Org. Synth.*, 1944, **24**, 87.
[4] Bone and Cort, *Chem. and Ind.*, 1961, 22.
[5] Thiele, *Ber.*, 1900, **33**, 851.
[6] Thiele and Rüdiger, *Annalen*, 1906, **347**, 280.
[7] House and Blaker, *J. Amer. Chem. Soc.*, 1958, **80**, 6389.
[8] Kohler, Richtmyer, and Hester, *J. Amer. Chem. Soc.*, 1931, **53**, 211.
[9] Ahmed and Campbell, *J.*, 1960, 4115; Taylor, *J.*, 1960, 2805.

isolated after Claisen hydrolysis. It has been observed [10,11] that with some indenes there is difficulty in locating the olefinic double bond at either the 1,2- or the 2,3-position, especially after treatment with alkali.



(IX)



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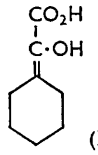


(XI)

In related experiments, it has been reported [12] that use of ethyl α-halogeno-esters and acetone in the Darzens reaction leads in some instances to products containing substances thought to be 2-hydroxy-3-methylbut-3-enoates (IX) on the basis of infrared absorption; and it has been shown [13] that cyclohexane-1-spiro-2′-oxiran-3′-carboxylic acid can be converted into cyclohex-1-enylglycollic acid (X) and into cyclohexylideneglycollic acid (XI) by treatment with hydrochloric acid. It is stated that neither acid (X) nor (XI) can be decarboxylated readily, and the latter is isolated from a solution in 0·23N-acid that has been boiled for 94 hr. It is somewhat surprising that inden-1(?3)-ylglycollic acid should be readily decarboxylated and yield 1-formylindane, but, since this does occur, a feasible preparative route to this aldehyde would be by condensation of indene with diethyl oxalate, etc. If the Claisen hydrolysis were carried out rapidly, and in dilute solution, better yields should be obtainable at this step. An attempt was made to follow spectroscopically the conversion of inden-1(?3)-ylglycollic into inden-1-ylideneacetic acid in alkaline solution, but the results merely establish generally that the conversion is relatively slow; quantitatively the results are not easy to interpret.

Ethyl inden-1(?3)-ylglycollate (from indene) was reduced to inden-1(?3)-ylethylene glycol (VIII) by lithium aluminium hydride; the constitution of this product follows from the fact that after hydrogenation the saturated glycol underwent scission with periodic acid to give 1-formylindane. The ester (*A*) similarly gave the same olefinic glycol (in slightly lower yield), confirming the view that the ester product contains little, if any, of the glycidic ester, which would be expected to give by this treatment a saturated 1,3-glycol (cf. ref. 14).

Use of 5-methoxyindan-1-one in the Darzens reaction with ethyl chloroacetate gave a solid product (in very low yield), identified as ethyl 5-methoxyindan-1-ylglyoxylate (XII); the absorption at 235 and 322 mμ suggests some enolisation, but it is difficult to explain in this case the non-migration of the olefinic double bond. After isolation of this ester, the remainder of the product was hydrolysed by Claisen's method, the derived acid proving to be 5-methoxyinden-1-ylideneacetic acid; no other acid product was found.

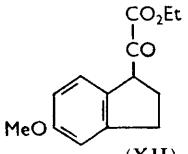
Since it is undesirable to use 5- or 6-methoxyindene for the unequivocal synthesis of 5- or 6-methoxyinden-1-ylideneacetic acid (the methoxyindenes apparently being mutually interconvertible under some experimental conditions [11]), the identity of the 5-methoxyinden-1-ylideneacetic acid was established by catalytic hydrogenation to 5-methoxyindan-1-ylacetic acid, which was directly compared with the acid prepared by a Reformatzky reaction, etc., from 5-methoxyindan-1-one.

When 6-methoxyindan-1-one was used in the Darzens reaction, a solid product was again isolated. This is the glycollate (XIII) (or the tautomer ethyl 6-methoxyinden-1-ylglycollate). Claisen hydrolysis of the product remaining after the initial condensation yielded only 6-methoxyinden-1-ylideneacetic acid.

[10] Koelsch and Scheiderbauer, *J. Amer. Chem. Soc.*, 1943, **65**, 2311.
[11] Ingold and Piggott, *J.*, 1923, **123**, 1469.
[12] Morris and Young, *J. Amer. Chem. Soc.*, 1955, **77**, 6678.
[13] Johnson, Belew, Chinn, and Hunt, *J. Amer. Chem. Soc.*, 1953, **75**, 4995.
[14] Billimoria and Maclagan, *J.*, 1951, 3067.

In view of these results it seemed of interest to attempt the Darzens reaction with 2,2-dimethylindan-1-one and with phenethyl phenyl ketone; the former of these could not give rise to an inden-1-ylidene derivative, and the latter (XIV) is the open-chain analogue of indan-1-one.

With 2,2-dimethylindan-1-one, the same reaction conditions as for indan-1-one gave 70% recovery of ketone. With forcing conditions condensation occurred, but no pure



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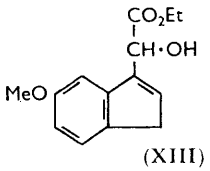

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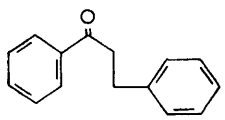

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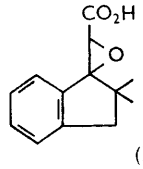

(XV)

ester could be isolated. After Claisen hydrolysis, the sodium salt yielded a *p*-bromophenacyl ester which is considered to be the derivative of 2,2-dimethylindane-1-spiro-2′-oxiran-3′-carboxylic acid (XV). The free acid, obtained from the sodium salt, gave with Brady's reagent a yellow 2,4-dinitrophenylhydrazone which was (when freshly prepared) completely soluble in aqueous potassium hydrogen carbonate. This rearrangement to the α-keto-acid in the presence of hydrogen ions occurs more readily than with ethyl β-methyl-β-phenylglycidate.

An appreciable by-product when forcing conditions are used for the Darzens condensation is ethyl ethoxyacetate; thus some alcohol exchange between potassium t-butoxide and ethyl chloroacetate must occur, the potassium ethoxide produced then reacting with more ethyl chloroacetate.

With phenethyl phenyl ketone the Darzens reaction proceeded normally, giving the glycidic ester in good yield. Application of the same hydrolysis conditions as used in the indane series (*viz.*, those of Claisen) led to a low yield of the glycidic acid, which showed no significant absorption above 215 mμ. Decarboxylation in the presence of soft-glass powder gave the expected 2,4-diphenylbutan-1-al. There were no indications that rearrangements comparable with those leading to olefinic alcohols in the indane series occur with the open-chain ketone.

It should be noted that all the products from the Darzens condensation in the present work have been subjected to heat (during distillation), except that from 5-methoxyindan-1-one, and that even in this case no glycidic acid or ester was isolated. The low yields throughout, and the rearrangements of the glycidic esters so far detected in this series, lead to the conclusion that the Darzens condensation with indan-1-ones and ethyl monochloroacetate is of very limited practical application.

Experimental

M. p.s are corrected. Light petroleum refers to the fraction of b. p. 60—80°. "Polyphosphoric" acid (cf. Arcus and Barrett [15]) refers to the solution from equal weights of phosphoric oxide and phosphoric acid (65% P_2O_5). Raney nickel refers to the B.D.H. "stabilised" catalyst. Spectra were determined in ethanol; log ε, in parentheses, follows $\lambda_{max.}$. A period of at least 12 hr. was taken for each preparation of free acids by Claisen hydrolysis, etc.

Inden-1(?3)-ylglycollic Acid.—(*a*) Ethyl inden-1-ylideneglycollate, m. p. 85—87°, was prepared according to Thiele's method,[5] better yields (85%) being obtained by condensation at 0°. It had $\lambda_{max.}$ 242 (3·95), 280 (4·19), and 338 mμ (4·15); the figures for the acid obtained by Claisen hydrolysis were 242 (3·97), 280 (4·19), and 335 mμ (4·15) (cf. the absorption of 1-benzylideneindene [16]). Reduction [6] gave ethyl inden-1(?3)-ylglycollate, b. p. 183—184°/15 mm., $\lambda_{max.}$ 250 mμ (3·92).

[15] Arcus and Barrett, *J.*, 1958, 2740.

[16] Bergmann, Berthier, Hirshberg, Loewenthal, Pullman, and Pullman, *Bull. Soc. chim. France*, 1951, 669.

Hydrolysis by the method [6] of Thiele and Rüdiger gave inden-1-ylideneacetic acid only, but Claisen hydrolysis (of 6·7 g.) and fractional precipitation (cf. ref. 4) gave inden-1-ylidene acetic acid (0·3 g.; m. p. and mixed m. p. of the *p*-bromophenacyl ester 153°), and inden-1(?3)-ylglycollic acid (4·2 g.). After crystallisation from chloroform the latter (1·6 g.) had m. p. 112° (decomp.), $\lambda_{max.}$ 250 mμ (3·94).

(*b*) After condensation of indan-1-one with ethyl chloroacetate as previously described,[4] the distilled ester product (*A*), b. p. 120—122°/0·35 mm., showed $\lambda_{max.}$ 245, 250, and 315 mμ ($E_{1\,cm}^{1\%}$ 310, 310, and 145). Product (*A*) gave only a transient colour with ferric chloride, and on prolonged contact with Brady's reagent it gave only a little gummy solid (under the same conditions ethyl β-methyl-β-phenylglycidate gave a 2,4-dinitrophenylhydrazone).

Hydrolysis of the product (A) gave *inden-1(?3)-ylglycollic acid*, m. p. 112° (decomp.), $\lambda_{max.}$ 250 mμ (3·94) (Found: active H, 1·11. $C_{11}H_{10}O_3$ requires 2H, 1·06%). Mixtures of acids from the two preparations, and mixtures of the derived *p*-bromophenacyl esters (m. p.s 128—129°), showed no m. p. depression. The acid gave no colour with ferric chloride, did not yield a semicarbazone, absorbed bromine from carbon tetrachloride solution without evolution of hydrogen bromide (the product decomposed on attempted isolation), and on decarboxylation [3] in hydrochloric acid yielded 1-formylindane. The semicarbazone (0·9 g. from 1·0 g. of acid) was obtained as needles, m. p. 168—169°, from ethanol (lit.,[17] m. p. 168°) (Found: C, 64·95; H, 6·35; N, 20·4. Calc. for $C_{11}H_{13}N_3O$: C, 65·0; H, 6·45; N, 20·7%). The *4-phenylsemicarbazone*, m. p. 137—138°, was obtained as needles from aqueous ethanol (Found: C, 72·9; H, 6·1; N, 15·1. $C_{17}H_{17}N_3O$ requires C, 73·1; H, 6·1; N, 15·05%). It was necessary to extract the aldehyde and distil it to obtain derivatives which were not sticky.

After the pure acid had been esterified with ethereal diazoethane, the product on hydrolysis still gave the deep purple colour and the acids already described were obtained. The *p*-bromophenacyl ester with warm aqueous sodium hydroxide gave a reddish-yellow colour, and under the same conditions inden-1-ylideneacetic acid gave a brown-red colour.

Treatment of the ester (*A*) with hydrazine hydrate in methanol led to the *hydrazide* of inden-1(?3)-ylglycollic acid, m. p. 155—156°, needles from ethanol (Found: C, 64·35; H, 5·9; N, 13·7. $C_{11}H_{12}N_2O_2$ requires C, 64·65; H, 5·95; N, 13·7%). The *benzylidene derivative* of this was obtained as octagonal plates, m. p. 157°, from ethanol (Found: C, 73·8; H, 5·5; N, 9·5. $C_{18}H_{16}N_2O_2$ requires C, 73·9; H, 5·5; N, 9·6%).

Conversion of Inden-1(?3)-ylglycollic Acid into Inden-1-ylideneacetic Acid.—An ethanolic 0·034% solution (5 ml.) of the hydroxy-acid was mixed with 10N-sodium hydroxide (0·5 ml.) at 22°. Immediately on mixing, and after periods of 10 and 30 min., aliquot parts (1·62 ml.) were diluted (to 50 ml.) with ethanol and values of $E_{1\,cm.}^{1\%}$ were determined and compared with the values at $\lambda_{max.}$ for inden-1(?3)-ylglycollic acid (*Y*) and inden-1-ylideneacetic acid (*Z*). Results were as follows:

Time after mixing (min.) \ Frequency (mμ):	250	260	327
0	460	350	0·0
10	660 (25)	610 (20)	82 (18)
30	840 (48)	860 (41)	169 (38)
Y	450	350	0·0
Z	1250	1600	450

At these concentrations no purple colour is visible to the naked eye, but the inconsistent calculated percentage conversions (in parentheses) indicate that some other absorbing material must be present.

Inden-1(?3)-ylethylene Glycol.—Treatment of ethyl inden-1(?3)-ylglycollate (from indene) with lithium aluminium hydride in ether gave (76%) the olefinic *glycol*, m. p. 116°, $\lambda_{max.}$ 250 mμ (3·99), leaflets from chloroform. The same glycol (m. p. and mixed m. p. 116°) was obtained from the ester (*A*) by similar treatment (4·6 g. from 10·5 g.) (Found: C, 75·1; H, 6·9; active H, 1·09. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9; active 2H, 1·16%). The *monotrityl ether* was obtained as hexagonal prisms, m. p. 153—154°, from ethanol (Found: C, 85·9; H, 6·3. $C_{30}H_{26}O_2$ requires C, 86·1; H, 6·3%).

Indan-1-ylethylene Glycol.—Catalytic hydrogenation (palladium, at room temperature and

[17] Tiffenea and Orékhoff, *Bull. Soc. chim. France*, 1920, **27**, 789.

30 atm.) of the foregoing glycol in ethanol gave indan-1-ylethylene glycol as a syrup which gave a *di*-p-*nitrobenzoate*, m. p. 154°, rhombic plates (from pyridine–water) (Found: C, 62·75; H, 4·4; N, 5·75. $C_{25}H_{20}N_2O_8$ requires C, 63·0; H, 4·25; N, 5·9%).

Periodic acid (H_5IO_6; 1·4 g.) in water (2·5 ml.) was added with cooling to the indanylethylene glycol (1·1 g.) in ethanol (3·5 ml.). After occasional shaking during 40 min. the mixture was diluted with water and extracted with ether, to yield 1-formylindane (0·9 ml.). This gave a semicarbazone, m. p. and mixed m. p. 169°.

5-Methoxyindan-1-one.—Prepared from β-*m*-methoxyphenylpropionic acid by Uhlig's method,[18] a ketonic product was obtained contaminated with 30% of unchanged acid. Optimum conditions for the cyclodehydration were found to be the use of 20 g. of polyphosphoric acid per gram of β-*m*-methoxyphenylpropionic acid, at 80°, with a heating time of 60 min. This gave a mixture, m. p. 98—106°, of 5- and 7-methoxyindan-1-one (25 g., 85%). Recrystallisation from aqueous ethanol and then from di-isopropyl ether gave 5-methoxyindan-1-one as needles, m. p. 111°, in an overall yield of 61%. This method was found to give less darkening during the dehydration than an alternative procedure [19] (giving a 65% yield of the 5-methoxy-ketone, m. p. 108°) in which the same phosphoric acid mixture is used at 130° for 15 min.

Condensation with 5-Methoxyindan-1-one.—From the ketone (23·5 g.) in ether (40 ml.), ethyl chloroacetate (19 ml.), and potassium t-butoxide from potassium (7·15 g.) in t-butyl alcohol (190 ml.), by the procedure described [13] for acetophenone, there was obtained partly crystalline material by ether-extraction of the product. Recrystallisation from ethanol gave pale yellow platelets (3·5 g.), m. p. 125—135°, and the mother-liquors yielded a viscous brown oil (11·6 g.). Repeated crystallisation of the solid gave *ethyl 5-methoxyindan-1-ylglyoxylate* (0·6 g.) as off-white platelets, m. p. 140° if placed in a bath at this temperature [otherwise m. p. 137—139° (decomp.)], $\lambda_{max.}$ 235 (3·85) and 322 mμ (4·31) (Found: C, 67·5; H, 6·3. $C_{14}H_{16}O_4$ requires C, 67·5; H, 6·5%).

The ester gave an intense purple colour with ferric chloride in ethanol; it reduced Fehling's solution and Tollens's reagent, and darkened slowly in air. It yielded a semicarbazone and a 2,4-dinitrophenylhydrazone, neither of which could be purified. After Claisen hydrolysis, etc., the derived acid gave a p-*bromophenacyl ester*, m. p. 196°, as needles from ethanol (Found: C, 57·6; H, 4·1; Br, 19·55. $C_{20}H_{17}BrO_5$ requires C, 57·6; H, 4·1; Br, 19·15%).

Claisen hydrolysis of the viscous oil (above) gave a sodium salt (6·0 g.) as an amorphous precipitate. Fractional precipitation of the free acid, from the aqueous solution of the salt, with dilute sulphuric acid gave only one large fraction (3·5 g., yellow). Crystallisation from chloroform, then from aqueous ethanol and from acetone, gave *5-methoxyinden-1-ylideneacetic acid*, m. p. 205° (decomp.) if placed in a bath at this temperature (otherwise slow darkening only), as orange trigonal pyramids, $\lambda_{max.}$ 275 (4·48) and 345 mμ (4·04) (Found: C, 71·3; H, 5·0%; equiv., 202 ± 1. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%; equiv., 202). The p-*bromophenacyl ester*, yellow flattened needles from ethanol, had m. p. 145° (Found: C, 60·15; H, 4·0; Br, 19·8. $C_{20}H_{15}BrO_4$ requires C, 60·2; H, 3·8; Br, 20·0%).

Catalytic hydrogenation (Raney nickel) in ethanol at 100°/100 atm. gave the saturated acid, which after crystallisation from light petroleum had m. p. 82—83°, undepressed on admixture with 5-methoxyindan-1-ylacetic acid.

5-Methoxyindan-1-ylacetic Acid.—After a Reformatzky reaction with ethyl bromoacetate (14·0 g.), zinc (5·2 g.), and 5-methoxyindan-1-one (12·9 g.) in benzene, there was obtained a distillate, b. p. 140—167°/0·6 mm. (8·4 g.), which solidified and after crystallisation from light petroleum had m. p. 53—55°. Catalytic hydrogenation as for the acid above, then hydrolysis, gave 5-methoxyindan-1-ylacetic acid, m. p. 83—84°, as needles from light petroleum (lit.,[20] m. p. 79°) (Found: C, 69·9; H, 6·8. Calc. for $C_{12}H_{14}O_3$: C, 69·9; H, 6·85%). The p-*bromophenacyl ester*, m. p. 98—99°, formed needles from ethanol (Found: C, 59·6; H, 4·8; Br, 20·0. $C_{20}H_{19}BrO_4$ requires C, 59·6; H, 4·75; Br, 19·8%).

6-Methoxyindan-1-one.—Intramolecular Friedel–Crafts reaction with β-*p*-methoxyphenylpropionyl chloride as described [21] by Johnson and Glenn, even with resublimed aluminium trichloride, gave low yields of a product very difficult to purify; cyclodehydration of the acid

[18] Uhlig, *Angew. Chem.*, 1954, **66**, 435; Diss., Univ. Leipzig, 1954.
[19] Birch, Quartey, and Smith, *J.*, 1952, 1768.
[20] Novak and Protiva, *Chem. Listy*, 1956, **50**, 1995.
[21] Johnson and Glenn, *J. Amer. Chem. Soc.*, 1949, **71**, 1092.

gave better yields (cf. ref. 18). Optimum conditions were found to be polyphosphoric acid (500 g.) at 120° (*i.e.*, above the m. p. of the organic acid) and β-*p*-methoxyphenylpropionic acid (10 g.), with stirring for 6 min. After cooling and dilution with ice–water, the ketone was extracted with benzene. Washing with aqueous ammonia, potassium hydrogen carbonate, and saturated sodium chloride solution, and sublimation at 120°/0·25 mm. gave 6-methoxyindan-1-one, m. p. 105—108° (2·7 g., 30%). One recrystallisation from light petroleum gave the pure ketone, m. p. 108—109° (2·6 g.).

Condensation with 6-Methoxyindan-1-one.—With reaction conditions as for the 5-methoxy-isomer, the ketone (17·8 g.) gave by ether-extraction of the reaction mixture an orange viscous liquid. On distillation at 1·0 mm. some decomposition occurred, and the product (b. p. 140—180°) partly crystallised. Separation furnished a solid (7·2 g.), m. p. 46—49°, which after crystallisation from aqueous methanol, toluene–light petroleum, and aqueous acetone gave needles (0·2 g.) of *ethyl 5-methoxyinden-3-ylglycollate* (or ethyl 6-methoxyinden-1-ylglycollate), m. p. 75—76°, as cream-coloured plates, $\lambda_{max.}$ 220 (4·32) and 295 mμ (3·45) (Found: C, 67·75; H, 6·5. $C_{14}H_{16}O_4$ requires C, 67·55; H, 6·45%). The ester gave neither a colour with ferric chloride in ethanol nor a precipitate with Brady's reagent, and it absorbed bromine from carbon tetrachloride solution without evolution of hydrogen bromide.

After separation of the solid (above), the residue (4·8 g.) was hydrolysed by Claisen's method. Fractional precipitation gave one free acid only (1·5 g.). Crystallisation from benzene–light petroleum gave *6-methoxyinden-1-ylideneacetic acid* as orange needles, m. p. 180° if placed in a bath at this temperature (otherwise slow decomposition), $\lambda_{max.}$ 270 (4·58) and 325 mμ (3·72) (Found: C, 71·4; H, 5·4. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%). The p-*bromophenacyl ester*, m. p. 153—154°, separated as red flattened needles from ethanol (Found: C, 60·3; H, 4·0; Br, 19·6. $C_{20}H_{15}BrO_4$ requires C, 60·2; H, 3·8; Br, 20·0%). The corresponding ester (m. p. 145°) from 5-methoxyinden-1-ylideneacetic acid depressed the m. p. on admixture (to 134—139°).

Darzens Glycidic Ester Condensation with 2,2-Dimethylindan-1-one.—The ketone (m. p. 46—47°) was prepared as directed by Mousseron, Jacquier, and Cristol.[22] Under conditions as for the condensation of ethyl chloroacetate with 5-methoxyindan-1-one (in the presence of 1·25 mol. of potassium t-butoxide), there was 70% recovery of 2,2-dimethylindan-1-one. When the alkoxide was increased to five mol. the product (from 19·5 g. of ketone) furnished on repeated distillation two major fractions: (i) b. p. 163—164°/761 mm. (8 ml.), and (ii) b. p. 130—150°/1·5 mm. (4·2 g.). The first of these was ethyl ethoxyacetate: after hydrolysis it yielded ethanol (m. p. and mixed m. p. of the 3,5-dinitrobenzoate 94°) and ethoxyacetic acid [m. p. and mixed m. p. of the *p*-bromophenacyl ester 105° (Found: C, 48·2; H, 4·1; Br, 26·7. Calc. for $C_{12}H_{13}BrO_4$: C, 47·9; H, 4·3; Br, 26·5%)]. Fraction (ii) gave an intense transient violet colour with ferric chloride in ethanol. After Claisen hydrolysis, the sodium salt (3·5 g.) yielded p-*bromophenacyl 2,2-dimethylindane-1-spiro-2′-oxiran-3′-carboxylate*, as plates, m. p. 92°, from ethanol (Found: C, 60·5; H, 4·9; Br, 19·45. $C_{21}H_{19}BrO_4$ requires C, 60·7; H, 4·65; Br, 19·25%) This ester gave no colour with ferric chloride in ethanol and showed no immediate reaction with Brady's reagent.

The free acid, obtained from the sodium salt, showed no significant absorption above 225 mμ and gave a 2,4-dinitrophenylhydrazone, m. p. 170° (decomp., with sintering at 160°), as yellow needles from aqueous acetic acid (Found: C, 56·1; H, 4·7; N, 13·3. $C_{19}H_{18}N_4O_6$ requires C, 57·3; H, 4·55; N, 14·1%). This is probably the derivative of 2,2-dimethylindan-1-ylglyoxylic acid; when first prepared it was completely soluble in aqueous potassium hydrogen carbonate but on storage it soon became insoluble.

Darzens Glycidic Ester Condensation with Phenethyl Phenyl Ketone.—The ketone (m. p. 71—73°) was prepared according to Adams, Kern, and Shriner's directions.[23] A solution of potassium t-butoxide from potassium (4·87 g.) in t-butyl alcohol (125 ml.) was added dropwise during 1·5 hr. to a stirred suspension of the ketone (21 g.) in ethyl chloroacetate (13·4 ml.) and t-butyl alcohol (20 ml.) under nitrogen, at 8—10°. Benzene (10 ml.) was added and stirring continued for a further 1·5 hr., the temperature being allowed to attain 20°. After partial evaporation ether-extraction removed only one large fraction, b. p. 167—170°/0·6 mm. (24·8 g.). Neither the crude nor the redistilled product gave any intense colour with ethanolic sodium hydroxide, nor was there any colour with ferric chloride.

Claisen hydrolysis of this ester (12 g.) gave an ethanol-soluble salt precipitated by ether as

[22] Mousseron, Jacquier, and Cristol, *Bull. Soc. chim. France*, 1957, 346.
[23] Adams, Kern, and Shriner, *Org. Synth.*, 1928, **8**, 36.

a gel. After separation by centrifugation, the solid salt was washed with ether. A solution in water was acidified with dilute sulphuric acid; then ether-extraction furnished αβ-*epoxy*-βδ-*diphenylvaleric acid* (4·3 g.), needles (from carbon tetrachloride), m. p. 114° (decomp.) (Found: C, 76·3; H, 5·9%; equiv., 268 ± 1. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%; equiv., 268). The acid showed no significant absorption above 215 mμ, gave no colour with ferric chloride and did not absorb bromine from carbon tetrachloride solution. The p-*bromophenacyl ester* separated from ethanol as needles, m. p. 109—110° [mixed with the reagent (m. p. 109—110°) m. p. <90°] (Found: C, 64·55; H, 4·5; Br, 17·25. $C_{25}H_{21}BrO_4$ requires C, 64·5; H, 4·55; Br, 17·2%).

The acid (0·5 g.) was heated in the presence of soft-glass powder at 120—200°/4 mm. (bath-temperature) for 20 min., and held at 200° for 10 min. The distillate (0·3 g.), 2,4-diphenylbutan-1-al, gave a *semicarbazone*, m. p. 133—134°, needles from ethanol (Found: C, 72·7; H, 6·7; N, 14·65. $C_{17}H_{19}N_3O$ requires C, 72·6; H, 6·8; N, 14·95%).

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BATTERSEA COLLEGE OF TECHNOLOGY, LONDON, S.W.11. [*Received, October* 31*st*, 1961.]