anol, 12.5 g. (67%) of 1-phenyl-4-(diphenylhydroxymethyl)-1,3-hexanedione (XVI), m.p. 130–131°.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50. Found: C, 80.93; H, 6.70.

A solution of 1 g. of aldol XVI in 15 ml. of methanol and 5 ml. of concentrated hydrochloric acid was refluxed for 1 hr. The resulting mixture was cooled and filtered. The solid was recrystallized from 95% ethanol to afford 0.63 g. (68%) of 2,3-dihydro-3-ethyl-2,2,6-triphenylpyran-4-one (XVII), m.p. 165–166°.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.71; H, 6.26. Found: C, 84.60; H, 6.33.

Alkylations of Phenylacetic, α-Alkylphenylacetic, and Diphenylacetic Esters by Means of Sodamide and Sodium Hydride[1]

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Various alkylations of ethyl and *t*-butyl phenylacetates with alkyl halides and further alkylations of the resulting α-alkylphenylacetic esters were effected by means of sodamide in liquid ammonia. The method was successful even with *p*-chloro- and *p*-methoxyphenylacetic esters and with *p*-chlorobenzyl chloride. Typical alkylations were also effected by means of sodium hydride in refluxing monoglyme. Sodamide was preferable for monoalkylations of ethyl or *t*-butyl phenylacetates, but the two reagents were about equally effective for further alkylations of α-alkylphenylacetic esters. Sodium hydride was better for dialkylation of ethyl phenylacetate with the same halide in a single operation. The present methods were superior to earlier methods. Also the present methods appear useful for the synthesis of certain mono- and dialkylarylacetic acids, which were obtained on hydrolysis of the alkylated esters. Ethyl diphenylacetate was alkylated with certain halides by means of sodamide in liquid ammonia.

Alkylations of ethyl phenylacetate with alkyl halides have recently[2,3] been effected by means of sodamide in liquid ammonia in much better yields than had been obtained previously with other reagents.[4] The method, which was applicable also to *t*-butyl phenylacetate, involved addition of the ester to a molecular equivalent of the reagent, followed by a molecular equivalent of the halide (eq. 1, Y = H, R = ethyl or *t*-butyl).

$$\underset{\text{I}}{p\text{-YC}_6\text{H}_4\text{CH}_2\text{COOR}} \xrightarrow[\text{liq. NH}_3]{\text{NaNH}_2} \underset{\text{I}'}{p\text{-YC}_6\text{H}_4\overset{\text{Na}}{\overset{|}{\text{C}}}\text{HCOOR}} \xrightarrow{\text{R}'\text{X}} \underset{\text{II}}{p\text{-YC}_6\text{H}_4\text{CHR}'\text{COOR}} \quad (1)$$

The sodamide reagent has now been found suitable not only for other monoalkylations of I (eq. 1) but also for further alkylations of the resulting α-alkylphenylacetic esters II with the same or different halide to form III (eq. 2), none of which appear to have been reported previously with any reagent.[4]

$$\text{II} \xrightarrow[\text{liq. NH}_3]{\text{NaNH}_2} \underset{\text{II}'}{p\text{-YC}_6\text{H}_4\overset{\text{Na}}{\overset{|}{\text{C}}}\text{COOR}} \xrightarrow{\text{R}''\text{X}} \underset{\text{III}}{p\text{-YC}_6\text{H}_4\overset{\text{R}'}{\overset{|}{\text{C}}}\text{COOR}} \quad (2)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{R}''$$

The results are summarized in Tables I–III. The data in Tables I and II, including the yields, were based on distilled or recrystallized products, most of which were indicated to be pure by v.p.c. (single peak) or sharp melting point. The n.m.r. spectra presented in Table III are in agreement with the structures presented.

Table I shows that the yields of the five new monoalkylations (eq. 1) were 76–89%, which are comparable with those of 10 earlier cases.[2] Interestingly, the sodamide reagent was suitable with the *p*-chlorophenylacetic ester and with *p*-chlorobenzyl chloride, with which the benzyne type of reaction was possible. Also the reagent was a sufficiently strong base to produce the required intermediate I′ (see eq. 1) from the *p*-methoxyphenylacetic ester, which would presumably be less acidic than the unsubstituted ester.

Although the distilled or recrystallized products II were generally pure (see above), certain of the crude products were indicated by v.p.c. to be contaminated with small amounts (5–10%) of the corresponding dialkyl derivatives III (R′ = R″) and starting ethyl or *t*-butyl phenylacetate (I).[5] The two latter compounds presumably arose through equilibration of intermediate sodio salt I′ with sodio salt II′, which underwent further alkylation (eq. 3).

$$\text{I}' + \text{II} \rightleftharpoons \text{I} + \text{II}' \xrightarrow{\text{R}'\text{X}} \text{III (R}' = \text{R}'') \quad (3)$$

Actually, with the exception of three methylation products, the alkyl derivatives II reported previously[2] and in Table I contained an R′ group that had four or more carbon atoms so that they were separated readily from the dialkyl derivative III (R′ = R″) and starting ester I by distillation or recrystallization. Even the distilled methylation products of ethyl *p*-methoxyphenylacetate and *t*-butyl phenylacetate appeared to be essentially pure; the former was indicated to be pure by n.m.r. spectrum and analysis, and the latter by v.p.c. although the n.m.r. spectrum suggested a trace of impurity (see Table III). Moreover, the distilled monomethylation product of ethyl phenylacetate that was obtained recently[2] contaminated with 2–3% of

(1) This investigation was supported by the U. S. Army Research Office (Durham) and by Public Health Service Research Grant No. USPHS CA04455-06.

(2) W. G. Kenyon, R. B. Meyer, and C. R. Hauser, *J. Org. Chem.*, **28**, 3108 (1963).

(3) The alkylation of ethyl phenylacetate with β-phenylethyl bromide was then effected on a 0.05-mole scale in 87% yield in 10 hr. This reaction has now been accomplished on a 0.1-mole scale in yields of 77–82% in 3 hr.

(4) See A. C. Cope, H. L. Holmes, and H. O. House, *Org. Reactions*, **9**, 284 (1957); A. L. Mndzhoyan, O. L. Mndzhoyan, E. R. Bagdasaryan, and V. A. Mnatsakanyan, *Dokl. Akad. Nauk Arm. SSR*, **30**, 97 (1960); *Chem. Abstr.*, **55**, 3508*h* (1961).

(5) The molar ratios of II:III:I from the benzylations of ethyl phenylacetate and ethyl *p*-chlorophenylacetate and from *p*-chlorobenzylation of ethyl phenylacetate were 90:7:3, 83:13:4, and 83:8:9, respectively.

TABLE I

ALKYLATIONS OF PHENYLACETIC ESTERS I WITH ALKYL HALIDES TO FORM II BY SODAMIDE IN LIQUID AMMONIA (EQ. 1)

Ester I, p-$YC_6H_4CH_2CO_2R$ R	Y	Alkyl halide R'X	Mole scale	Reaction period, hr.	Ester II, p-$YC_6H_4CHR'CO_2R$ Yield, %	B.p. (mm.) or m.p., °C.	Formula	Calcd., % C	H	Cl	Found, % C	H	Cl
C_2H_5	H	p-$ClC_6H_4CH_2Cl$	0.2	3	79	152 (0.04)	$C_{17}H_{17}ClO_2$	70.70	5.94	12.28	70.53	5.90	12.46
C_2H_5[a]	CH_3O	CH_3I	0.1	1	86[b]	124 (3)	$C_{12}H_{16}O_3$	69.21	7.74	...	69.25	7.75	...
C_2H_5	Cl	$C_6H_5CH_2Cl$	0.1	1	89	62–64.5[c]	$C_{17}H_{17}ClO_2$	70.70	5.94	12.28	70.56	5.82	12.38
$C(CH_3)_3$	H	CH_3I	0.5[d]	1	83[b]	101–103 (10)[e]	...	...	...	...	...	...	...
$C(CH_3)_3$	H	$C_6H_5CH_2CH_2Br$	0.1	1	76[b]	114 (0.003)	$C_{20}H_{24}O_2$	81.04	8.16	...	80.95	8.10	...

[a] Prepared from p-methoxyphenylacetic acid; see R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, 69, 2325 (1947). [b] Indicated to be pure by v.p.c. [c] Recrystallized from methanol. [d] A 10% excess of sodamide was used. [e] W. W. Leake and R. Levine [*J. Am. Chem. Soc.*, 81, 1627 (1959)] reported b.p. 104–109° (10.6 mm.).

TABLE II

ALKYLATIONS OF α-ALKYLPHENYLACETIC ESTERS II WITH ALKYL HALIDES TO FORM III BY SODAMIDE IN LIQUID AMMONIA (EQ. 2)

Ester II,[b] p-$YC_6H_4CHR'CO_2R$ R	Y	R'	Alkyl halide R''X	Mole scale	Reaction period, hr.	Ester III,[a] p-$YC_6H_4CR'R''CO_2R$ Yield, %	B.p. (mm.) or m.p., °C.	Formula	Calcd., % C	H	Cl	Found, % C	H	Cl
C_2H_5	H	CH_3	CH_3I	0.3[c]	1.5	76[d]	119.5–120.5 (19)[d,e]	...	...	...	...	...	...	...
C_2H_5	H	n-C_4H_9	CH_3I	0.05	3.0	73[f,g]	122–125 (4.5)[g,h]	...	...	...	...	...	...	...
C_2H_5	H	n-C_4H_9	n-C_4H_9Br	0.01	4.0	92[i]	121–127 (1.1)[i,j]	...	...	...	...	...	...	...
C_2H_5	H	n-C_4H_9	$C_6H_5CH_2Cl$	0.05	5.0[k]	72[i]	125–130 (0.06)[i]	$C_{21}H_{26}O_2$	81.25	8.44	...	80.55	8.31	...
C_2H_5	H	$C_6H_5CH_2$	$C_6H_5CH_2Cl$	0.05	3.0	79[i]	160 (0.01)[i]	$C_{24}H_{24}O_2$	83.69	7.02	...	83.72	6.99	...
C_2H_5	H	p-$ClC_6H_4CH_2$	p-$ClC_6H_4CH_2Cl$	0.05	3.0	84 (99)[l]	88–90[m]	$C_{24}H_{22}Cl_2O_2$	69.74	5.37	17.16	69.90	5.31	17.31
C_2H_5	OCH_3	CH_3	CH_3I	0.05[c]	2.0	76[g]	132 (15)[g,n]	$C_{13}H_{18}O_3$	70.24	8.16	...	70.54	7.97	...
C_2H_5	Cl	$C_6H_5CH_2$	n-C_4H_9Br	0.05	2.0	87	139–144 (0.02)[o]	$C_{21}H_{25}ClO_2$	73.13[p]	7.31	10.28[p]	72.13	7.41	10.85
C_2H_5	Cl	$C_6H_5CH_2$	$C_6H_5CH_2Cl$	0.01	1.5	86 (97)[l]	97.5–100[q]	$C_{24}H_{23}ClO_2$	76.08	6.12	9.36	76.19	6.11	9.44
C_2H_5	H	$C_6H_5CH_2CH_2$	$C_6H_5CH_2CH_2Br$	0.05	1.0	17[r]	90.5–92[s]	$C_{26}H_{28}O_2$	83.83	7.58	...	83.92	7.63	...
C_2H_5	H	$C_6H_5CH_2CH_2$	n-C_4H_9Br	0.05	2.0	86	187–189 (2.5)	$C_{22}H_{28}O_2$	81.44	8.70	...	81.38	8.42	...
$C(CH_3)_3$	H	CH_3	CH_3I	0.1[c]	1.0	60	91 (3.3)	$C_{14}H_{20}O_2$	76.32	9.15	...	76.24	9.11	...
$C(CH_3)_3$	H	CH_3	$C_6H_5CH_2CH_2Br$	0.005	2.0	24[r]	122–130 (0.08)	$C_{21}H_{26}O_2$	81.25	8.44	...	80.20	8.42	...
$C(CH_3)_3$	H	$C_6H_5CH_2CH_2$	CH_3I	0.025	1.5	81	122–130 (0.08)	...	...	...	...	...	...	...

[a] Liquid ester products were indicated to be pure by v.p.c. [b] Starting esters were indicated to be pure by v.p.c. [c] A 10% excess of sodamide was employed. [d] Apiezon L column (5 ft.). [e] Lit.[7b] b.p. 107–108° (4.5 mm.). [f] Product contained 4.5% of starting ester. [g] Carbowax 20M column (5 ft.). [h] Lit.[7b] b.p. 122–123° (5 mm.). [i] Silicone gum rubber column (2 ft.). [j] Lit.[7b] b.p. 149° (1 mm.). [k] A Dry Ice–acetone condenser was employed. [l] Crude yield. [m] Recrystallized from ethanol; analytical sample melted at 89.5–91°. [n] E. Van Heyninger [*J. Am. Chem. Soc.*, 74, 4861 (1952)] reported b.p. 120° (10 mm.). [o] Recrystallized from methanol–water to give product, m.p. 52–53°. [p] Although this ester did not give an acceptable analysis, the values for the corresponding carboxylic acid were satisfactory (see Table VI). [q] Recrystallized from methanol; analytical sample melted at 98–101°. [r] Styrene was also obtained (see Experimental). [s] Recrystallized from 95% ethanol.

TABLE III

N.M.R. SPECTRA OF ESTERS OF TYPES II AND III[a,b]

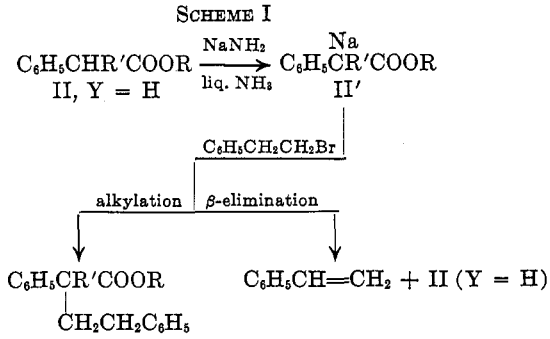
Ester	τ values
C_6H_5—$CH(CH_3)COO$-t-C_4H_9	2.77 (C_6H_5, singlet), 6.46 (>C*H*, quartet), 8.61 [–C(CH_3)$_3$ and >C*H*CH_3, doublet]
p-$ClC_6H_4CH(CH_2C_6H_5)COOC_2H_5$	6.06 (–CH_2CH_3, quartet), 6.74 (–CH_2C*H*, multiplet), 8.96 (–CH_2CH_3, triplet)
p-$CH_3OC_6H_4CH(CH_3)COOC_2H_5$	3.04 (C_6H_5, quartet), 5.99 (–OCH_2CH_3, quartet), 6.44 [–OCH_3 and –C*H*(CH_3)–, quartet], 8.62 [–CH(CH_3)–, doublet], 8.88 (–OCH_2CH_3, triplet)
$C_6H_5C(CH_3)_2COO$-t-C_4H_9	8.52 (CH_3—C—CH_3, singlet), 8.68 [–C(CH_3)$_3$, singlet]
$C_6H_5C(CH_2C_6H_5)_2COOC_2H_5$	3.18 (C_6H_5, complex), 6.06 (–CH_2CH_3, quartet), 6.74 (–$CH_2C_6H_5$, singlet), 9.02 (–CH_2CH_3, triplet)
p-$CH_3OC_6H_4C(CH_3)_2COOC_2H_5$	6.01 (–CH_2CH_3, quartet), 6.35 (p-OCH_3, singlet), 8.52 (CH_3—C—CH_3, singlet), 8.88 (–CH_2CH_3, triplet)
p-$ClC_6H_4CH(CH_2C_6H_5)COOC_2H_5$	5.94 (–CH_2CH_3, quartet), 6.71 (–$CH_2C_6H_5$, singlet), 8.91 (–CH_2CH_3, triplet)

[a] These spectra were obtained on a Varian Associates A-60 spectrometer. The internal standard was tetramethylsilane. [b] Chemical shifts are measured to the center of a singlet or multiplet. In each of the spectra listed in this table, the peak areas were quite consistent with the assignments indicated.

impurities has now been isolated apparently pure (indicated by v.p.c.).

Table II shows that the yields of the dialkyl derivatives III, including those from the p-chloro- and p-methoxyphenylacetic esters II and from p-chlorobenzyl chloride, were generally good to excellent (60–92%). The result with the p-methoxy ester II is noteworthy, as its α-hydrogen would presumably be deactivated not only by the p-methoxy group but also by the α-methyl group. However, the yields of the dialkyl derivative III from β-phenylethyl bromide were low (17–24%), the main product being styrene; evidently β-elimination predominated (Scheme I).

SCHEME I



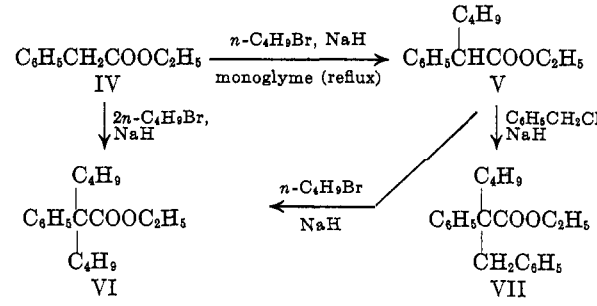
(R = ethyl or t-butyl, R′ = β-phenylethyl or methyl)

That the intermediate sodio ester was formed and effected the β-elimination was indicated by its alkylation with n-butyl and methyl halides to give the corresponding esters of type III in high yields (see Table II). Since appreciable β-elimination did not occur in the β-phenylethylations of ethyl and t-butyl phenylacetates under similar conditions (see Table I), the introduction of the β-phenylethyl group followed by the n-butyl or methyl group is to be recommended. The reason for the greater extent of β-elimination in the β-phenylethylations of the monoalkyl derivatives II than in those of the unalkylated phenylacetic esters I (see eq. 1 and 2, respectively) appears ascribable both to the presumably greater basicity of the carbanion II′ compared to carbanion I′ and to a steric factor which may hinder the rate of alkylation more than that of β-elimination.

Incidentally, an attempt to effect dialkylation of ethyl phenylacetate with excess n-butyl bromide and excess sodamide reagent in a single operation was unsatisfactory (see Experimental).

For comparison with the above results with sodamide, a typical monoalkylation of ethyl phenylacetate and typical further alkylations of the resulting α-alkylphenylacetate with the same and different halide were effected by means of sodium hydride in refluxing 1,2-dimethoxyethane (monoglyme). The reactions are illustrated in Scheme II, in which esters IV, V, and VI (or VII) represent specific examples of the general formulas I, II, and III, respectively (see eq. 1 and 2).

SCHEME II



When ester IV was added to the reagent followed by n-butyl bromide after 45 min., similar to the procedure with sodamide (see eq. 1), the yield of monobutylated ester V was only 8%, self-condensation of IV to form VIII occurred in 29% yield, and 28% of IV was recovered. Even when a mixture of I and the halide was added to the reagent, which was the procedure adopted, some of VIII was obtained. However, no self-condensation of t-butyl phenylacetate was observed when this ester was alkylated similarly, nor was self-condensation of ethyl ester V observed during its further alkylation (see Scheme II). The results are summarized in Table IV. The yields were based on distilled or recrystallized products, which were indicated to be pure by v.p.c. or sharp melting point.

$C_6H_5CH_2COCH(C_6H_5)COOC_2H_5$
VIII

Table IV shows that the yields of the mono-n-butyl derivative V (expt. 1 and 2) and of the corre-

TABLE IV

TYPICAL ALKYLATIONS BY MEANS OF SODIUM HYDRIDE IN REFLUXING MONOGLYME (SCHEME II)

Expt.	Starting ester (0.1 mole)	*n*-Butyl bromide, mole	Sodium hydride, mole	Main product	Yield, %	Starting ester and other products
1	IV	0.1	0.1[a]	V	56	IV (13%), VI (2%), VIII (6%)
2	IV	0.12	0.12[b,c]	V	56	IV (20%), VI (6%), VIII (5%)
3	IV[d]	0.1	0.1[e]	V[d]	66	VI[e] (<5%)
4	V	0.2	0.2	VI	93	...
5	IV	0.4	0.4	VI	83	...
6	V	0.2[f]	0.2	VII	82	...
7	V	0.1	0.1	VI	59	V (30%)
8	V	0.12	0.12	VI	61	V (29%)
9	V	0.1	0.1[g]	VI	44	V (42%)
10	V	0.1	0.1[h]	VI	21	V (70%)

[a] The reaction time was 40 min. [b] The solution of ethyl phenylacetate and *n*-butyl bromide was added over a period of 1.6 hr. [c] The reaction time was 4 hr. [d] *t*-Butyl ester instead of ethyl ester. [e] The reaction time was 2.5 hr. [f] Benzyl chloride was used instead of *n*-butyl bromide. [g] The solvent was tetrahydrofuran (refluxed). [h] The solvent was dimethylformamide (100°).

TABLE V

HYDROLYSIS OF ALKYLATION PRODUCTS II TO FORM CARBOXYLIC ACIDS IX

Ester II, *p*-$YC_6H_4CHR'CO_2R$				Acid IX, *p*-$YC_6H_4CHR'CO_2H$		
R	Y	R'	Method	Yield, %	M.p. or b.p. (mm.), °C.	Lit. m.p. or b.p. (mm.), °C.
C_2H_5	H	*p*-$ClC_6H_4CH_2$	Basic	79 (97)[a]	138–140.5[b]	140–140.5[c]
C_2H_5	CH_3O	CH_3	Basic	94	61–62.5[d]	55–57[e]
C_2H_5	Cl	$C_6H_5CH_2$	Basic	97	116–118[f]	140–150.5[g]
$C(CH_3)_3$	H	CH_3	Acidic	73	153–155 (21)	155 (21)[h]
$C(CH_3)_3$	H	$C_6H_5CH_2CH_2$	Acidic	98	70–73[d]	72–73[i]

[a] Crude yield. [b] Recrystallized from ethanol–water. [c] C. Vasilev, *Compt. rend. acad. bulgare sci.*, **10**, No. 1, 125 (1957); *Chem. Abstr.*, **52**, 5353*f* (1958). [d] Recrystallized from hexane. [e] V. N. Gupta and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **44A**, 223 (1956). [f] Recrystallized from methanol–water. [g] D. Ivanov, G. Vasilev, I. M. Panaiotov, C. Borisov, and N. Marekov, *Godishnik Sofiiskiya Univ. Fiz.-Mat. Fak.*, **52**, No. 3, 1 (1957/1958) (Pub. 1959); *Chem. Abstr.*, **55**, 1522*i* (1961). [h] S. P. Bakshi and E. E. Turner, *J. Chem. Soc.*, 171 (1961). [i] R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, **26**, 3696 (1961).

sponding mono-*n*-butyl derivative of the *t*-butyl phenylacetate (expt. 3) were 56 and 66%, respectively; these yields are appreciably lower than those (91 and 86%)[2] obtained with sodamide. However, the yields of the dialkyl derivatives VI and VII from V (see Scheme II) were 93 and 82%, respectively (expt. 4 and 6)[6]; these yields are comparable with those (83 and 72%) realized with sodamide. Moreover, di-*n*-butylation of I was accomplished in 83% yield in a single operation (expt. 5). The last four experiments listed in Table IV indicate that excess of both the halide and the reagent are desirable for the further alkylation of V, and that monoglyme is a better solvent for the reaction than tetrahydrofuran (expt. 9) or dimethylformamide (expt. 10).

At least in the cases studied with both reagents, sodamide is preferable to sodium hydride for monoalkylations of ethyl or *t*-butyl phenylacetate, and the two reagents are about equally suitable for further alkylations of the resulting α-alkylphenylacetate. However, only sodium hydride has been satisfactory for a dialkylation of ethyl phenylacetate with the same halide in a single operation which, obviously, is more convenient than the two-stage process.

The present direct method of alkylation of an α-alkylphenylacetic ester by means of sodamide or sodium hydride to form an ethyl dialkylphenylacetate

SCHEME III

$$RR''CHCOOH \xrightarrow[P\ (red)]{Br_2} R'R''CBrCOOH$$

$$R'R''CBrCOOH \xrightarrow[AlCl_3]{C_6H_6} C_6H_5CR'R''COOH$$

$$C_6H_5CR'R''COOH \xrightarrow[(acid)]{C_2H_5OH} III$$

III (or VI) appears superior to a recent indirect process involving a Friedel–Crafts reaction (Scheme III).[7] Thus our method afforded ester III (R' = *n*-C_4H_9; R'' = CH_3) with sodamide and ester III (R' = R'' = *n*-C_4H_9) with sodium hydride or sodamide in yields of 70–80%, whereas the earlier method produced these esters in over-all yields of only 19 and 29%, respectively. Moreover, not only could certain of the starting dialkylacetic acids required in Scheme III be prepared more conveniently through the present alkylations of the appropriate esters (see below), but the Friedel–Crafts method may not be suitable for certain ring-substituted products.

Hydrolysis of Alkylated Esters.—The alkylation products II and III (see eq. 1 and 2) were hydrolyzed to form the corresponding carboxylic acids IX and X, respectively. The ethyl esters were saponified, but the *t*-butyl esters were hydrolyzed with *p*-toluenesulfonic acid.

p-$YC_6H_4CHR'COOH$ IX *p*-$YC_6H_4CR'R''COOH$ X

(6) Recently, *n*-butylation of ethyl 2-methylbutanoate was effected with sodium hydride in diglyme to form the corresponding ethyl trialkylacetate in 38% yield: R. E. Pincock and J. H. Rolston, *J. Org. Chem.*, **29**, 2990 (1964). The much better yields of ethyl dialkylphenylacetates obtained by us (see Table IV) may be ascribed to the relatively greater activity of the α-hydrogen of the α-alkylphenylacetates.

(7) (a) A. L. Mndzhoyan, G. T. Tatevosyan, and S. G. Agbalyan, *Dokl. Akad. Nauk Arm. SSR*, **25**, No. 1, 11 (1957); *Chem. Abstr.*, **52**, 2798*g* (1958). (b) A. L. Mndzhoyan, G. T. Tatevosyan, and S. G. Agbalyan, *Dokl. Akad. Nauk Arm. SSR*, **29**, 235 (1959); *Chem. Abstr.*, **54**, 22475*i* (1960).

TABLE VI
HYDROLYSIS OF ALKYLATION PRODUCT III TO FORM CARBOXYLIC ACID X

Ester III, p-YC6H4CR'R''CO2R				Acid X, p-YC6H4CR'R''CO2H				Calcd., %			Found, %		
R	Y	R'	R''	Yield, %	M.p. or b.p. (mm.), °C.	Lit. m.p. or b.p. (mm.), °C.	Formula	C	H	Cl	C	H	Cl
C_2H_5	H	CH_3	CH_3	67	72–74[a]	80–81[b]	...	...	...	...	...	...	...
C_2H_5	H	CH_3	n-C_4H_9	33 (99)[c]	151–152 (2)	162–164 (7)[d]	...	...	...	...	...	...	...
C_2H_5	H	n-C_4H_9	n-C_4H_9	72 (87)[c]	133–135 (0.08)	170 (4)	...	...	...	...	...	...	...
C_2H_5	H	n-C_4H_9	$C_6H_5CH_2$	90	110–113[e]	...	$C_{19}H_{22}O_2$	80.81	7.85	...	80.75	7.92	...
C_2H_5	H	$C_6H_5CH_2$	$C_6H_5CH_2$	56 (95)[c]	153–155[f]	153–154 (β-form)[g]	...	...	...	...	...	...	...
C_2H_5	H	p-$ClC_6H_4CH_2$	p-$ClC_6H_4CH_2$	80 (96)[c]	198–200[e]	...	$C_{22}H_{18}Cl_2O_2$	68.58	4.71	18.40	68.36	4.90	18.47
C_2H_5	OCH_3	CH_3	CH_3	83 (95)[c]	88–89.5[h]	89–90[i]	$C_{11}H_{14}O_3$	68.02	7.27	...	67.88	7.27	...
C_2H_5	Cl	$C_6H_5CH_2$	n-C_4H_9	92	100–104	...	$C_{19}H_{21}ClO_2$	72.03	6.68	11.19	72.22	6.43	10.84
C_2H_5	Cl	$C_6H_5CH_2$	$C_6H_5CH_2$	56 (80)[c]	144–144.5[j]	...	$C_{22}H_{19}ClO_2$	75.31	5.46	10.11	75.28	5.28	10.21
C_2H_5	H	$C_6H_5CH_2CH_2$	n-C_4H_9	58 (92)[c]	116.5–117.5[h]		$C_{20}H_{24}O_2$	81.04	8.16	...	81.00	8.17	...
$C(CH_3)_3$	H	CH_3	CH_3	39 (92)[c]	72–74[a]	80–81[b]	...	...	...	...	...	...	...
$C(CH_3)_3$	H	CH_3	$C_6H_5CH_2CH_2$	90	103–105[h]	107–108[k]	$C_{17}H_{18}O_2$	80.28	7.13	...	80.52	7.34	...
$C(CH_3)_3$	H	CH_3	CH_3	44 (95)[c]	104.5–106.5[h]	107–108[k]	...	...	...	...	...	...	...

[a] Recrystallized from ethanol. [b] M.p. 80–81°: I. M. Heilbron, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 145. [c] Crude yield. [d] Ref. 7a. [e] Recrystallized from methanol–water; the analytical sample recrystallized from hexane melted at 112–113.5°. [f] Recrystallized from ethanol–water. [g] T. Ando and N. Tokura, *Bull. Chem. Soc. Japan*, **31**, 1026 (1958); *Chem. Abstr.*, **53**, 19966*e* (1959). [h] Recrystallized from hexane. [i] Recrystallized from water: Å. Jönsson, *Acta Chem. Scand.*, **8**, 1211 (1954); *Chem. Abstr.*, **49**, 12367*i* (1955). [j] Recrystallized from methanol. [k] Recrystallized from benzene–pentane: W. L. Benzce, Belgian Patent 615,312 (1962); *Chem. Abstr.*, **59**, P1558*b* (1963).

The results are summarized in Tables V and VI. These tables show that the yields of acids IX and X were generally good to excellent (56–98%). The present alkylation–hydrolysis methods appear useful for the synthesis of certain of these acids, a number of which are new (see Table VI).

Alkylations of Ethyl Diphenylacetate.—Alkylations of this ester have previously been effected in good yields with certain alkyl halides by means of sodium and potassium ethoxides in ethanol,[8,9] sodium hydride in dimethylformamide,[10] and potassium amide in benzene–ether.[8] We have accomplished n-butylation and benzylation of this ester by means of sodamide in liquid ammonia to form XIa and b in yields of 75 and 71%, respectively (eq. 4).

$$(C_6H_5)_2CHCOOC_2H_5 \xrightarrow[2.\ RX]{1.\ NaNH_2\ (NH_3)} (C_6H_5)_2\overset{R}{\overset{|}{C}}COOC_2H_5 \quad (4)$$

XIa, R = n-C_4H_9
b, R = $CH_2C_6H_5$

Alkylation product XIa appears not to have been reported previously, but product XIb has been obtained as a distillable oil[10]; we have isolated XIb as a solid.

Experimental[11]

Alkylations of Phenylacetic and α-Alkylphenylacetic Esters by Sodamide.—To a stirred suspension of 0.1–0.5 mole of sodamide[12] in 500–600 ml. of commercial anhydrous liquid ammonia was added 1 mol. equiv. of the appropriate ester in 15–50 ml. of anhydrous ether, followed after 10–15 min. by 1 mol. equiv. of the appropriate halide in 10–15 ml. of anhydrous ether. After stirring for the appropriate length of time, a slight excess of 1 mol. equiv. of ammonium chloride was added, and the ammonia was allowed to evaporate to dryness with stirring. The residue was taken up in ether and water and the layers were separated. The ethereal layer was washed with saturated sodium bicarbonate solution, followed by saturated sodium chloride solution,[13] and then combined with two ethereal washings of the original aqueous layer, treated in the same manner. The ethereal solution of the product was dried over anhydrous magnesium sulfate, and the solvent was removed. The residue was distilled *in vacuo* or recrystallized. The liquids were analyzed by v.p.c. employing an appropriate column. Data and results are summarized in Tables I and II. Certain of the products were analyzed by n.m.r. (Table III). Some special cases are considered below.

In the reaction of ethyl 2,4-diphenylbutanoate with β-phenylethyl bromide, the residue obtained after removing the solvent was fractionated to afford 3.15 g. (60.5%) of styrene, b.p. 66–67° (65 mm.), identified as its dibromide, m.p. and m.m.p. 72–73°.[14] Further fractionation yielded 7.82 g. (58.5%) of recovered ethyl 2,4-diphenylbutanoate, b.p. 157–159° (2.5 mm.). The pot residue was triturated with hexane, and the resulting solid was recrystallized from ethanol to give 3.1 g. (17%) of ester III, R' = R'' = β-phenylethyl (see Table II).

Similarly, in the reaction of t-butyl 2-phenylpropanoate with β-phenylethyl bromide, distillation of the crude product afforded

(8) H. Staudinger and P. Meyer, *Helv. Chim. Acta*, **5**, 656 (1922).
(9) A. C. Cope and S. M. McElvain, *J. Am. Chem. Soc.*, **54**, 4319 (1932).
(10) H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers, and R. W. DeNet, *J. Org. Chem.*, **26**, 644 (1961).
(11) Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Dr. I. Schoeller and Ilse Beetz, Kronach, West Germany. Melting points (Mel-Temp capillary melting point apparatus) and boiling points are uncorrected. An F and M Model 500 programmed temperature gas chromatograph equipped with a disk chart integrator was used to produce the vapor phase chromatograms. The carrier gas was helium.
(12) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 122 (1954).
(13) In the reactions with methyl iodide, the ethereal layers were washed also with saturated sodium bisulfite solution to remove the iodine color.
(14) See C. R. Hauser, J. C. Shivers, and P. S. Skell, *J. Am. Chem. Soc.*, **67**, 409 (1945).

styrene, isolated as the dibromide, m.p. 70.5–72.5°.[14] Further fractionation yielded 6.14 g. (60%) of recovered *t*-butyl 2-phenylpropanoate, b.p. 75–104° (10 mm.), and 3.78 g. (24%) of ester III (R′ = methyl; R″ = β-phenylethyl) (see Table II).

Treatment of Ethyl Phenylacetate with Excess Butyl Bromide and Sodamide.—To a stirred suspension of 0.225 mole of sodamide in 600 ml. of liquid ammonia was added a solution of 16.4 g. (0.1 mole) of ethyl phenylacetate and 30.8 g. (0.225 mole) of *n*-butyl bromide in 100 ml. of ether. After 4 hr., 12.0 g. (0.225 mole) of solid ammonium chloride was added, and the reaction was worked up as described above to give 10.39 g. (47%) of ethyl 2-phenylhexanoate (type II ester), b.p. 120–123° (4.5 mm.), and 7.13 g. (26%) of 5-carbethoxy-5-phenylnonane (type III ester), b.p. 144–145° (4.5 mm.). Each product showed a single v.p.c. peak (Apiezon L at 200°); their retention times were identical with those of authentic samples.

Alkylations by Means of Sodium Hydride.—To a stirred slurry of sodium hydride reagent[15] in 200 ml. of refluxing monoglyme, under dry nitrogen, was added a solution of the appropriate ester and alkyl halide in 100 ml. of monoglyme over a period of 20 min. Refluxing was continued for 3 hr., and most of the solvent was then removed under reduced pressure. The resulting paste was cooled in an ice bath, and 150 ml. of ether was added. After stirring the mixture, 100 ml. of water was added dropwise. The layers were separated, and the ethereal solution was extracted with two 100-ml. portions of water. The ethereal solution of the product was dried over anhydrous magnesium sulfate, and the solvent was removed. The residue was fractionally distilled *in vacuo* to give the mono- and dialkyl derivative; the pot residue was recrystallized to afford β-keto ester VIII. The mono- and dialkyl derivatives V and VI or VII, respectively, were indicated to be pure by v.p.c.; their retention times were identical with those of authentic samples. β-Keto ester VIII was identified by the mixture melting point method.

Hydrolysis of Alkylation Products II and III.—Esters of types II and III were hydrolyzed by appropriate methods to form carboxylic acids of types IX and X, respectively. The ethyl esters were refluxed for 24 hr. with ethanolic potassium hydroxide, and the *t*-butyl esters were refluxed with *p*-toluenesulfonic acid monohydrate in toluene until isobutylene ceased to be evolved. The resulting mixtures were worked up by common procedures (see ref. 2), and the carboxylic acids were distilled or recrystallized from appropriate solvents. The results are summarized in Tables V and VI.

Alkylations of Ethyl Diphenylacetate. A. With *n*-Butyl Bromide.—To a stirred suspension of 0.05 mole of sodamide in 250 ml. of liquid ammonia was added a solution of 12.02 g. (0.05 mole) of ethyl diphenylacetate[16] in 50 ml. of ether, followed after 15 min. by a solution of 6.85 g. (0.05 mole) of *n*-butyl bromide in 15 ml. of ether. After 2 hr. the reaction mixture was worked up as described above for the phenylacetic esters to give 11.17 g. (75%) of ethyl 2,2-diphenylhexanoate (XIa), b.p. 115–117° (0.1 mm.), which was indicated to be pure by v.p.c. using a 2-ft. silicone gum rubber column. A redistilled sample, b.p. 116–117° (0.07 mm.), was analyzed.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.00; H, 7.87.

This reaction was repeated employing a 10-hr. stirring period (Dry Ice condenser) to afford 11.46 g. (77%) of XIa, b.p. 122–125° (0.15 mm.).

A 1.48-g. sample of ester XIa was saponified with ethanolic potassium hydroxide (refluxed 24 hr.) to yield 1.24 g. (93%) of crude 2,2-diphenylhexanoic acid, m.p. 122–130°. Recrystallization from hexane afforded 1.09 g. (81%) of acid, m.p. 130–132°, lit.[17] m.p. 130–132°.

B. With Benzyl Chloride.—This alkylation was effected as described above for *n*-butyl bromide to give, after recrystallization from aqueous alcohol, 11.72 g. (71%) of ethyl 2,2,3-triphenylpropanoate (XIb), m.p. 62–63°, lit.[10] b.p. 180–190° (1.1–1.2 mm.).

A 1.51-g. sample of XIb was saponified with ethanolic potassium hydroxide (refluxed 24 hr.) to yield 1.34 g. (97%) of 2,2,3-triphenylpropanoic acid, m.p. and m.m.p. 131.5–133°, lit.[18] m.p. 130–131.5°.

(15) This reagent, obtained from Metal Hydrides, Inc., as an approximately 55% dispersion of sodium hydride in mineral oil, was used as received.

(16) R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).

(17) A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan, and R. Kh. Bostandzhyan, *Dokl. Akad. Nauk Arm. SSR*, **28**, No. 1, 11 (1959); *Chem. Abstr.*, **54**, 1412e (1960).

(18) C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 4942 (1956).

An Abnormal Dehydrogenation during the Preparation of 1,8-Diphenylnaphthalene[1]

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Dehydrogenation of 1,8-diphenyl-1-hydroxydecalin (9) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone yielded a mixture of 1,8-diphenylnaphthalene (1) and 1,6-diphenylnaphthalene (11), the latter product arising from rearrangement. Several improvements in the previously reported synthesis of 1,8-diphenylnaphthalene (1) and a new synthesis of 1,6-diphenylnaphthalene (11) are described.

In continuing our study[2] of 1,8-diphenylnaphthalene (**1**)[3] and its derivatives, we wished to improve our previous synthesis in order to make derivatives with substituents in the phenyl rings more readily accessible. Several modifications (detailed in the Experimental and summarized in Scheme I) in our previous procedures have resulted in an improved yield of the intermediate ketone **3** and the characterization of the intermediate alcohol **7**; the stereochemistry assigned this alcohol **7** is based on the assumption that phenyllithium will attack the ketone **5** from the less hindered side. Difficulty was encountered in repeating the previously described[2b] dehydrohalogenation of the bromo ketone **4** with lithium chloride in dimethylformamide to form the rearranged[4] ketone **5**. In subsequent experiments with lithium chloride in dimethylformamide, mixtures of the rearranged product **5** and the unrearranged ketone **6** were produced. As was to be anticipated from other

(1) This work has been supported by research grants from the National Science Foundation (Grant No. G-25214) and the National Institutes of Health (Grant No. GM-08761).

(2) (a) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963); (b) H. O. House and H. W. Thompson, *ibid.*, **28**, 360 (1963); (c) *ibid.*, **26**, 3729 (1961).

(3) For a second synthesis of this hydrocarbon and discussion of its properties, see (a) A. S. Bailey, G. A. Dale, A. J. Shuttleworth, and D. P. Weizmann, *J. Chem. Soc.*, 5110 (1964); (b) E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964).

(4) Analogous rearrangements during dehydrohalogenation of α-halo ketones with lithium chloride in dimethylformamide have been noted previously. For examples, see (a) W. G. Dauben, G. A. Boswell, and W. H. Templeton, *J. Am. Chem. Soc.*, **83**, 5006 (1961); (b) W. F. Johns, *J. Org. Chem.*, **28**, 1616 (1963).