Tetrahedron. Vol. 27, pp. 4777 to 4785. Pergamon Press 1971. Printed in Great Britain

REACTIVITY OF AMBIDENT ANIONS

HARDNESS OF ALKYL GROUPS AND SYMBIOTIC EFFECT IN ALKYLATION OF AMBIDENT ANIONS

A. L. KURTS, N. K. GENKINA, A. MACIAS, I. P. BELETSKAYA and O. A. REUTOV

Department of Chemistry, Moscow State University, Moscow, USSR

(*Received in the UK* 20 *April* 1971; *Accepted for publication* 13 *May* 1971)

Abstract—Effect of the alkylating agent nature in the case of O- and C-alkylation of both ethyl acetoacetate and acetylacetonate anions is reported. The value of the O/C-ratio depends on three factors: the polar effect of the alkyl substituents in the alkylating agents, the steric effect of the alkyl groups and the symbiotic effect of the leaving groups. The relative contributions of the first two effects depends on the leaving group nature. The steric effect predominates when the leaving group is a soft base (iodide, bromide, chloride) and the O/C-ratio decreases in the order sec. Bu > iPr > Et > Me. The alkyl group sequence opposite to the order given above is the case for the hard leaving group, tosylate, this is opposite to Pearson's order of alkyl group hardnesses. The influence of the leaving group nature on the O/C-ratio is also reported. A strong symbiotic effect of a leaving group was found for the methylation of the both enolate ions. In ethylation, the leaving group effect was less detectable; for the both secondary alkyl groups the O/C-ratio was almost non-susceptible to the nature of the leaving group.

IN THE present paper we report our results on leaving group and alkyl group effects on yields of O- and C-alkylation products (O/C-ratio)* in the alkylation of acetylacetonate and ethyl acetoacetate anions in hexamethylphosphotriamide (HMPT).

The data obtained are given in Tables 1 and 2.

For any leaving group, the O/C-ratio increases when the size of the alkyl group is increased. First we consider polar effects of alkyl groups in the series of alkyl halides and tosylates.

It is well known[1,2], that for the alkylation of enolate ions by different alkyl halides the O/C-ratio increases in the series:

$$\text{Me} < \text{Et} < \text{i.Pr} \leqslant \text{sec.Bu}$$
$$\text{Me} < \text{Et} < \text{n.Pr} < \text{n.Bu}$$

In the present work we obtained a similar sequence (Table 3). Usually such influence of the alkyl group is ascribed to steric factors. Should one accept that the alkyl group at a reaction site has electronodonor character, the observed sequence of alkyl groups in the given series can be explained by the domination of steric effects over polar. However, there is an alternative explanation based on the conception of the electronoacceptor character of the alkyl group at the saturated carbon atom[3–9]. In this case both factors result in an increase in the O/C-ratio.

To enhance the role of polar factors and to estimate their influence on the direction of the ambident anion reactions we studied the alkylation, by alkyl tosylates, of ethyl

* O/C-denotes the ratio of yields of the O-isomer to the sum of the yields of C- and C,C-products.

TABLE 1. ALKYLATION OF SODIUM ACETYLACETONATE BY DIFFERENT ALKYLATING AGENTS IN HMPT c. = 0·5 MOLE/l

R	X	General yield	%O	%C	%C,C[a]	O/C	temp.
1	2	3	4	5	6	7	8
Me	OTs	77	97	3	—	32	20
	Br	59	12	88	<1	0·14	20
	I	54	3	96	1	0·03	20
Et	OTs	90	90	10	—	9	20
	Cl	—	62	33	5	1·73	20
	Br	73	42	41	17	0·72	20
	I	84	17	60	23	0·20	20
n-Pr	OTs	85	92	8	—	11	20
	Br	85	48	38	14	0·9	20
n-Bu	OTs	81	96	4	—	24	20
	Cl	65	87	12	1	7	20
	Br	—	62	23	15	1·6	20
	I	—	24	39	37	0·32	20
n-Am	OTs	66	99	1	—	99	60
	Cl	65	95	4	1	19	50
	Br	84	68	12	20	2·1	65
	I	87	46	16	38	0·85	60
i-Pr	OTs	80	86	14	—	6·1[b]	50
	Cl	—	79	21	—	3·5	50
	Br	79	70	30	—	2·3	50
	I	82	52	48	—	1·1	50
sec-Bu	OTs	53	85	15	—	5·7[b]	60
	Cl	—	83	17	—	4·9	50
	Br	43	81	19	—	4·3	50
	I	62	62	38	—	1·6	50
All	OTs	79	37	9	54	0·60	20
	Br	—	7	18	75	0·08	20
	I	86	—	22	78	—	20
neo-Am	OTs	65	100	—	—	—	70
CH_3OCH_2	Cl	32	100	—	—	—	50
	I	—	82	18	—	4·5	20

[a] Dialkylation products. When RI and AllOTs are used as alkylating agents only the C,C-alkylation products are isolated. For R Cl and RBr, a small quantity of the C,O-alkylation product (1–3%) is formed.

[b] This ratio is practically independent of temperature in the region 20–60°.

TABLE 2. ALKYLATION OF POTASSIUM ENOLATE OF ETHYL ACETOACETATE BY DIFFERENT ALKYLATING AGENTS IN HMPT, c. = 0·25 MOLE/l

R	X	General yield	%O–	%C–	%C.C–	O/C	temp.
1	2	3	4	5	6	7	8
Me	OTs	96	89	7	4	8·1	20
	Br	87	14	42	44	0·16	20
	I	93	5	31	64	0·05	20
Et	OTs	90	88	11	1	8	20
	Cl	65	60	32	8	1·5	20
	Br	92	39	38	23	0·64	20
	I	95	13	71	16	0·15	20
n-Bu	OTs	84	90	10	<1	9	20
	Cl	75	68	27	5	2·1	20
	Br	88	40	47	13	0·67	20
i-Pr	OTs	78	84	16	—	5·3	20
	Cl	70	81	19	—	4·3	20
	Br	90	69	31	—	2·2	20
	I	77	40	60	—	0·66	20
Sec-Bu	OTs	78	86	14	—	6·2	40
	Cl	75	86	14	—	6·2	40
	Br	70	78	22	—	3·6	40
	I	60	56	44	—	1·3	20
All	OTs	88	22	43	35	0·28	20
	Cl	88	17	45	38	0·21	20
	Br	92	—	48	52	0	20
	I	90	—	50	50	0	20
neo-Am	OTs	40	100	—	—	—	80
CH_3OCH_2	Cl	75	100	—	—	—	45

TABLE 3. $(O/C)_{RX}/(O/C)_{MeX}$ RATIO FOR SODIUM ACETYLACETONATE AND POTASSIUM ETHYL ACETOACETATE ALKYLATION REACTIONS

X	Me	Et	n-Pr	n-Bu	n-Am	i-Pr	sec-Bu
			acetylacetone				
I	1	7	—	10	25	35	57
Br	1	5	7	12	15	16	30
OTs	1	0·28	0·33	0·75	3	0·19	0·18
			ethyl acetoacetate				
I	1	3	—	—	—	13	26
Br	1	3·8	—	4	—	13	21
OTs	1	1	—	1·1	—	0·66	0·78

acetoacetate and acetylacetone alkali enolates. In this case the influence of the alkyl groups on the O/C-ratio was found to be opposite to that for halides: Me > Et > i-Pr ~ sec. Bu (Table 3). The conclusion is that both effects are opposed to each other but polar factors prevail in the alkyl tosylates. Because electrophilic attack on oxygen (as the site of the most negative charge in the ambident anion) is determined mainly by electrostatic interaction[10,11], the O/C-ratio decrease in the alkyl tosylate series Me, Et, sec alkyl (Table 3) indicates electronodonor properties of alkyl substituents at the reaction site. Thus, the alkyl group effects in alkylation reactions of enolate ions by alkyl tosylates are opposite to those deducted from Pearson's series of alkyl group hardness.[3] The qualitative identity, in the case of the alkyl halides, of the alkyl group sequences in enolate alkylation and in Pearson's series of hardness implies that the softer alkylating agents, e.g. alkyl halides, in contrast to hard alkyl tosylates, exhibit the steric effects which prevail over the polar.

TABLE 4. $(O/C)_{ROTs}/(O/C)_{RX}$ RATIO FOR SODIUM ACETYLACETONATE AND POTASSIUM ETHYL ACETOACETATE ALKYLATION REACTIONS

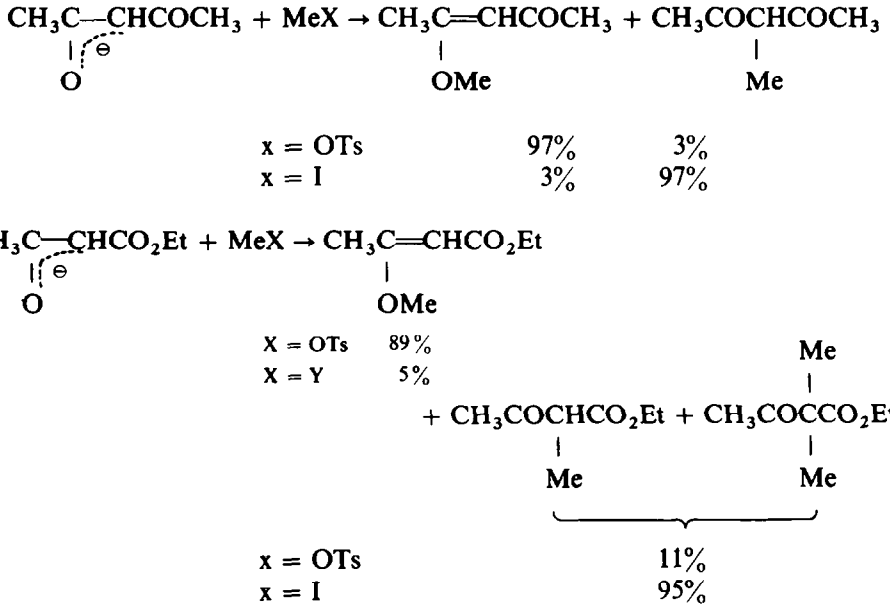
X	Me	Et	i-Pr	sec-Bu
		acetylacetone		
OTs	1	1	1	1
Cl	—	5·5	1·7	1·1
Br	230	12·5	2·6	1·3
I	~1000	45	6·1	3·6
		Ethyl acetoacetate		
OTs	1	1	1	1
Cl	—	5·3	1·2	1·0
Br	50	13	2·4	1·7
I	160	53	8	5

Nevertheless, even for alkyl tosylates, an increasing in alkyl group volume without an essential increase of inductive effect, e.g. for C_2-C_5 groups, results in a observed increasing in O/C-ratio (Table 3).

The steric effects are illustrated also by exclusive formation of O-isomer in the alkylation of enolate ions by neopentyl tosylate and neopentyl chloride.[2] The respective contribution of steric and polar effects, is determined by the hardness of the leaving groups. The significance of the polar effects increases as the leaving group becomes harder. In accord with this is the observation that the difference in O/C-ratio for chlorides and bromides becomes less in the series: Me, Et, and especially sec. alkyl (Table 4).

Now we consider in detail the leaving group effects. In accordance with the HSAB principle,[3] the leaving group effects can be explained in terms of the symbiotic stabilization of the transition state: the more essential stabilization must be expected when both the leaving group and nucleophile are soft (or hard) Lewis bases.[12] Because tosylate is a hard base and oxygen a hard center of enolate ions.[23] the O/C-ratio for tosylates must be greater than for softer bases such as bromides and iodides. In our case the variation in the O/C ratio in the methylation reaction from tosylate to iodide is the quantitative characteristic of the symbiotic effect. Table 4 shows that

in methylation the O/C-ratio undergoes practically full inversion from tosylate to iodide (O/C-ratio decreases by 10^2-10^3 for the both enolates)



The symbiotic effect of the leaving group is also easily noticeable in ethylation reactions. For both enolate ions the O/C-ratio is approximately 50 times lower for EtI as for ethyl tosylate (Table 4). The leaving group effect for the secondary alkyl groups is not so pronounced. Thus, changing sec-butyl tosylate for sec-butyl chloride or bromide has negligible effect on the composition of the alkylation products (for sec-BuI O/C > 1). Because i-Pr and sec-Bu groups are softer than Me and Et groups for the given reaction series, one would expect a less pronounced leaving group effect. But even taking into consideration the greater softness of the secondary alkyl groups one cannot explain the fact that when bromide or iodide are used instead of tosylate the O/C-ratio for sec-butyl decreases only 1·5 times for bromide and 3–5 times for iodide (Table 4). Thus, taking into consideration the symbiotic effect only, we cannot predict the direction of the enolate ion alkylation. We may only note that the quantity of O-isomer tends to increase when the softness of the leaving group decreases.

In the alkylation by ethyl, isopropyl and sec-butyl halides and tosylates there is doubtless another effect opposed to the symbiotic effect of the leaving group. It is difficult to be precise about the nature of this effect. One of the possible explanations is that the positive inductive effect (or hyperconjugation) of alkyl substituents at the reaction site of the alkylating agent depends on the nature of the leaving group and decreases in the order OTs > Cl > Br > J. The decrease of the O/C-ratio due to this effect must change, and in fact, does change in the same order.

Thus, normally, it is impossible to come to an unambiguous conclusion about which of the two effects, alkyl group softness, or the symbiotic effect of the leaving group, determines the main direction of the ambident anion reaction.

Sometimes, *e.g.* in the alkylation by n-alkyl halides or tosylates, the controlling

factor is the hardness of the leaving group. In the alkylation by sec-alkyl halides or sec-alkyl tosylates, the symbiotic effect of the leaving group is also important. However, in this case the softness of the sec-alkyl group is also clearly pronounced. In the other extreme case, when the alkylating agent is composed of a supersoft Lewis acid and a hard Lewis base (*e.g.* allyl tosylate) or when it is composed of a hard acid and soft base (*e.g.* chloro- and iodo-dimethyl ethers), the determining factor is the nature of the alkyl group (Tables 1 and 2).

EXPERIMENTAL

IR-Spectra were measured on a UR-10 instrument. NMR-spectra were determined on a Varian A-60 instrument (in CCl_4). Chemical shifts are given in δ using TMS as internal standard and coupling constant (J) in Hz. GLC data were obtained on Chrom-2 instrument using 2 m column filled with apiezon L (17%) on chromosorb W. The carrier gas was N_2. For ethylated derivatives the column temp. was 110°, the N_2 flow 100 ml/min. For other alkylated derivatives the temp. was 100–150°, N_2 : 100–180 ml/min.

"Schuchardt" HMPT was dried over 4Å Molecular sieves before use and distilled twice over CaH_2, b.p. 65°/1 mm. Sodium acetylacetonate and potassium ethyl acetoacetate were prepared according to the earlier described procedures.[13,14] Alkyl tosylates were obtained from the respective alcohols and *p*-toluenesulfochloride in dry Py.[15,16] and dried at 40–50°/1 mm. n-Alkyl tosylates were purified by distillation in vacuo.

Alcohol purity was controlled by chromatography.

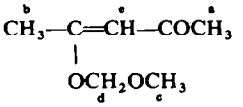
General procedure

A solution of the alkylating agent (0·022 M) in HMPT was added dropwise with stirring to the alkaline enolate (0·02 M) in HMPT. The mixture was left at a given temp. (see Tables 1 and 2) until it became neutral. The mixture was poured into an ice-water mixture (3-fold volume) and ether extracted. The ether solution was analysed (GLC) using the samples prepared as described below.

3-*Alkylacetylacetones* (R=Me, Et, iPr, nBu, sec Bu). These were obtained by the earlier described procedure.[1] Purity of samples obtained was controlled by GLC. Some characteristics of 3-alkylacetylacetones are shown in Table 5.

2-*Alkoxypent-2-ene-4-ones* (R=Me, Et, iPr, nBu, sec Bu). The mixture obtained by reaction of sodium acetylacetonate and the respective alkyl tosylate, containing 2-alkoxypent-2-ene-4-one and 5–15% 3-alkylacetylacetone were stirred for 2–3 hr. with conc. KOH aq. O-isomer was extracted ether and the ethereal solution washed several times with H_2O and dried ($MgSO_4$). Ether was evaporated and the substance distilled twice *in vacuo*. Some characteristics of 2-alkoxypent-2-ene-4-ones are listed in Table 5.

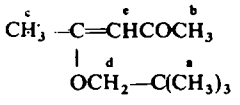
2-*Methoxymethyloxypent-2-ene-4-one*. (Calc.: C, 58·32; H, 8·39. Found: C, 58·51; H, 8·30%).



NMR: (a) −2·08 (3H, s), (b) −2·32 (3H, s), (c) −3·39 (3H, s), (d) −4·92 (2H, s), (e) −5·53 (1H, s).

2-*n-Butoxypent-2-ene-4-one*. B.p. 88–90°/6 mm (Calc.: C, 69·19; H, 10·32. Found: C, 69·74; H, 10·17%).

2-(2′,2′-*dimethyl*)-*n-propoxypent-2-ene-4-one*. B.p. 92–93°/3 mm. Calc.: C, 70·55; H, 10·65. Found: C, 70·43; H, 10·78%).



NMR: (a) −0·99 (9H, s), (b) −2·36 (3H, s), (c) −2·52 (3H, s), (d) −3·33 (2H, s), (e) −5·71 (1H, s).

The Ir of these compounds contain the following characteristic bands: ν(C=O) 1675–1685 cm^{-1}, ν(C=C) 1590–1595 cm^{-1} $\delta_{as}CH_3$ 1385–1400 cm^{-1}, δ_sCH_3 1350–1365 cm^{-1}, ν_{as}(C—O) 1275–1290 cm^{-1}, δ(=C—H) 810–825 cm^{-1}, ν_s (C—O) 1040–1070 cm^{-1}.

The NMR of these compounds show acetyl proton signals in the δ 2·33–2·40 ppm region, allyl proton signals in the δ 2·50–2·54 ppm region and vinyl proton signals δ 5·67–5·77 ppm. The NMR data confirm

the *trans*-structure for O-isomers. *Cis*- and *trans* isomerism marks *cis*- and *trans*-spatial position of two polar groups at the double band.

TABLE 5.

R	3-alkylacetylacetones		2-alkoxypent-2-ene-4-ones	
	Found n_D^{20}	Lit. n_D^{20}	Found n_D^{20}	Lit. n_D^{20}
Me	1·4416	1·4420	1·4671	1·4680
Et	1·4425	1·4419	1·4592	1·4600
n-Pr	1·4447	1·4450	—	—
i-Pr	1·4332	1·4325	1·4621	1·4615
n-Bu	1·4480	1·4470	1·4597	—
sec-Bu	1·4397	1·4402	1·4642	1·4648
neopentyl[a]	—	—	—	—
CH_3OCH_2	—	—	1·4612[b]	—

[a] m.p. 47°
[b] at 16°

Syntheses of 3,3-*dialkylacetylacetones*

3,3-*dimethylacetylacetone.* To 3-methylacetylacetone was added an equimolar amount of NaOMe in MeOH alcohol. Alcohol was evaporated and the resulting salt suspended in dimethylformamide—benzene (2:1) and a double excess of MeI added. The mixture was heated at 60° for two days, then washed with a conc KOH aq extracted with ether, dried over $MgSO_4$, ether evaporated, and the oil distilled *in vacuo.* (Calc.: C, 65·64; H, 9·37. Found: C, 65·37; H, 9·45%).

3,3-*diethyl- and* 3,3-*dibutylacetylacetones* were obtained by alkylation of acetylacetone with alkyl iodide in sulfolane at 60° (1 mole of acetylacetone, 3 mole RI and 1·5 mole K_2CO_3). The mixture was poured into water, ether extracted and stirred for 8 hr. with a 5% HCl aq., then with conc KOH aq. for 3 hr., washed with H_2O and dried over $MgSO_4$. Ether was evaporated and the substance distilled *in vacuo.*

3,3-*dibutylacetylacetone.* Calc.: C, 73·58; H, 11·32. Found: C, 73·54; H, 11·09%).

3,3-*diethylacetylacetone.* Calc.: C, 69·23; H, 10·25. Found: C, 69·39; H, 10·21%).

3,3-*diallylacetylacetone.* The mixture obtained by alkylation of sodium acetylacetonate with small excess of allyl bromide was subsequently treated with acid and alkali as described. Calc.: C, 73·34; H. 8·88. Found: C. 73·27; H. 8·89%).

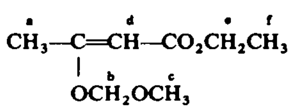
Ir of 3,3-dialkylacetylacetones show an intensive absorption band in the 1700–1705 cm^{-1} region (C═O).

Ethyl α-alkylacetoacetate and ethyl β-alkoxycrotonates. (R═nPr, iPr, nBu, sec-Bu.) were obtained from the mixtures resulting from reactions of potassium acetoacetic ester enolate with ROTs and RHal in HMPT by means of prep. GLC (chromatograph Tsvet-4, 5 m column with 5% of apiezon L on TND-TS-2M. t = 140–170°.

Ethyl α-ethylacetoacetate and ethyl β-ethoxycrotonate were obtained by the previously described method.[13]

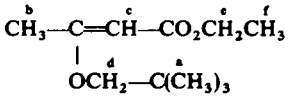
Ethyl α-allylacetoacetate was obtained from the reaction of potassium enolate of acetoacetic ester with AllI and AllBr, b.p. 74–75°/5 mm, lit[17] 96–97°/14 mm. n_D^{20} 1·4378 n_D^{25} 1·4365 Ir of all ethyl β-alkoxycrotonates show an intensive absorption band at 1632 cm^{-1} (C═C) and 1718 cm^{-1} (C═O) regions. Ir of all α-alkylacetoacetates show an absorption band at 1740–1745 cm^{-1} and 1717 cm^{-1}. In the NMR the vinyl proton signals are observed in the δ 4·8–4·85 region. Allyl proton signals for ethyl β-alkoxycrotonates and acetyl signals for α-alkylacetoacetates are observed at δ 2·15–2·25 and 2·15–2·05 regions respectively.

Ethyl β-methoxymethyloxycrotonate.



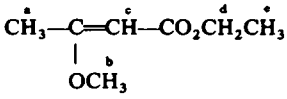
(Calc.: C, 55·16; H, 8·16. Found: C, 54·97; H, 8·28%). NMR: (a) 2·26 (3H, s), (b) 4·95 (2H, s), (c) 3·40 (3H, s), (d) 5·12 (1H, s), (e) 4·05 (2H, q), (f) 1·22 (3H, t) J_{fe} = 7 Hz.

Ethyl β-neopentyloxycrotonate.



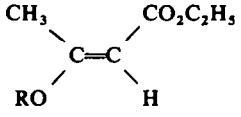
(Calc: C, 65·70; H, 9·95. Found: C, 65·58; H, 10·03%). NMR: (a) 0·98 (9H, s), (b) 2·23 (3H, s), (c) 4·80 (1H, s), (d) 3·31 (2H, s), (e) 3·99 (2H, q), (f) 1·16 (3H, t). $J_{fe} = 7$ Hz.

Ethyl β-methoxycrotonate.



(Calc: C, 58·31; H, 8·39. Found: C, 58·12; H, 8·35%). NMR: (a) 2·22 (3H, s), (b) 3·60 (3H, s), (c) 4·92 (1H, s), (d) 4·08 (2H, q), (e) 1·20 (3H, t). $J_{de} = 7$Hz.

The NMR data confirm the trans-structure for O-isomers[24, 25]



Enolate ions react in HMPT in their W-conformation[18, 19]

Syntheses of ethyl α,α-dialkylacetoacetates

α,α-Dimethyl was obtained by alkylation of sodium enolate of α-methylacetoacetate with MeI in MeOH. b.p. 78–80°/20 mm, lit.[20] 180–184° n_D^{20} 1·4180, n_D^{25} 1·4162; (Calc: C, 60·76; H, 8·86. Found: C, 61·02; H, 8·60%).

α,α-Diethyl was obtained by similar method, b.p. 75–77°/5 mm, lit.[20]: 210–213° n_D^{20} 1·4305, n_D^{25} 1·4300; (Calc: C, 64·51; H, 9·67. Found: C, 64·40; H, 9·60%).

Di-n-butyl was obtained by alkylation of sodium enolate of ethyl α-n-butylacetoacetate with n-butyl bromide in EtOH, b.p. 119–121°/5 mm, lit.[21] 143–147°/18–19 mm n_D^{20} 1·4393; (Calc: C, 69·42; H, 10·74. Found: C, 69·71; H, 10·52%).

TABLE 6.

R	C—		O—		C.C—	
	n_D^{20}		n_D^{20}		n_D^{20}	
	Found	Lit.	Found	Lit.	Found	Lit.
Me	1·4212	1·4205	1·4478[a]	1·4480[a 2]	1·4180	1·4162[a 20]
	—	—	—	—	1·4190	1·4215[b 17]
Et	1·4206	1·4212[a 2]	m.p. 30°	m.p. 30·2°[1]	1·4305	1·4300[a 20]
n-Pr	1·4250	1·4255[1]	1·4515	1·4498[a 2]	1·4370	1·4356[a 2]
n-Bu	1·4290	1·4302[1]	1·4525	—	1·4393	—
i-Pr	1·4247	1·4252[1]	1·4523	1·4515[1]		
sec-Bu	1·4315	1·4315[1]	1·4540	1·4535[1]		
neoC_5H_{11}	—	—	1·4470	1·4456[a 2]		
All	1·4378	1·4356[a 22]	—	—	1·4581	1·4572[c 17]

[a] at 25°

[b] For methyl α,α-dimethylacetoacetate

[c] at 17·4°

α,α-*Diallyl* was isolated from the reaction of potassium enolate of acetoacetate with allyl bromide and iodide in HMPT, b.p. 94–96°/ 5 mm, lit.[17] 124°/13 mm n_D^{20} 1·4561, $n_D^{17.5}$ 1·4572; (Calc: C, 66·66; H, 9·09. Found: C, 66·38; H, 9·02%).

Methyl α,α-dimethylacetoacetate. To a solution of sodium methylate in MeOH was added an equimolar amount of methyl acetoacetate. Alcohol was evaporated and the residue diluted with C_6H_6—DMF mixture (2:1) and a double excess of MeI added.

After a few min the C_6H_6 mixture was poured in H_2O and extracted with C_6H_6, dried over $MgSO_4$ and evaporated. The residue was repeatedly worked up with sodium methylate and MeI as above. After C_6H_6 evaporation the product was distilled *in vacuo*. b.p. 81–82/93 mm, lit.[17]: 172–173° n_D^{20} 1·4190, $n_D^{18.5}$ 1·4215; (Calc: C, 58·33; H, 8·33. Found: C, 58·36; H, 8·16%). The n_D^{20} of the obtained compounds are shown in Table 6.

REFERENCES

[1] S. T. Joffe, K. V. Vatsuro, E. E. Kugutcheva and M. I. Kabachnik, *Tetrahedron Letters* 593 (1965)
[2] W. J. Le Noble and H. F. Morris, *J. Org. Chem.* **34**, 1969 (1969)
[3] R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.* **89**, 1827 (1967)
[4] V. W. Laurie and J. S. Muenter, *Ibid.* **88**, 2883 (1966)
[5] R. C. Fort and P. von R. Schleyer, *Ibid.* **86**, 4194 (1964)
[6] W. M. Schubert, R. B. Murphy and J. Robins, *Tetrahedron* **17**, 199 (1962)
[7] F. W. Baker, R. C. Parish and L. M. Stock, *J. Am. Chem. Soc.* **89**, 5677 (1967)
[8] J. I. Brauman and L. K. Blair, *Ibid.* **90**, 6561 (1968)
[9] J. I. Brauman and L. K. Blair, *Ibid.* **91**, 2126 (1969)
[10] G. Klopman, *Ibid.* **90**, 223 (1968)
[11] R. Gompper, *Angew. Chem.* **76**, 412 (1964)
[12] R. G. Pearson and J. Songstad, *J. Org. Chem.* **32**, 2899 (1967)
[13] A. L. Kurts, I. P. Beletskaya, A. Macias and O. A. Reutov, *Tetrahedron Letters* 3679 (1968)
[14] R. G. Charles and M. A. Pawlikowsky, *J. Phys. Chem.* **62**, 440 (1958)
[15] R. S. Tipson, *J. Org. Chem.* **9**, 235 (1944)
[16] F. Drahwsal and D. Klamann, *Monatsh.* **82**, 457 (1951)
[17] J. W. Bruhl, *J. Prakt. Chem.* **50**, 119 (1894)
[18] H. E. Zaugg and A. D. Schaefer, *J. Am. Chem. Soc.* **87**, 1857 (1965)
[19] S. J. Rhoads and R. W. Holder, *Tetrahedron* **25**, 5443 (1969)
[20] J. Marshal and W. Cannon, *J. Org. Chem.* **21**, 245 (1956)
[21] W. B. Renfrow, *J. Am. Chem. Soc.* **66**, 144 (1944)
[22] M. S. Schechter, N. Green and F. B. La Forge, *J. Am. Chem. Soc.* **71**, 3165 (1949)
[23] R. E. Davis, *Tetrahedron Letters* 5021 (1966)
[24] D. V. Gardner and D. E. McGreer, *Canad. J. Chem.* **48**, 2110 (1970)
[25] J. S. Pizey and W. E. Truce, *J. Chem. Soc.* 865 (1964)