THE JOURNAL OF Organic Chemistry®

VOLUME 30, NUMBER 5 MAY 12 1965

The Chemistry of Carbanions. IX. The Potassium and Lithium Enolates Derived from Cyclic Ketones[1]

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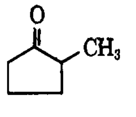
Received November 13, 1964

The compositions of the enolate anion mixtures derived from 2-methylcyclopentanone, 1-decalone, *trans*-2-decalone, and *cis*-2-decalone have been studied. Equilibration among the isomeric enolate anions derived from each ketone did not occur unless an excess of the free ketone was present. This was particularly true for the lithium enolate anions where a substantial excess of un-ionized ketone was required before rapid equilibration was observed. As a consequence, it is possible to prepare different enolate anion mixtures from an unsymmetrical ketone reflecting either kinetic or thermodynamic control by the appropriate choice of reaction conditions and quantities of reactants.

In our earlier studies of enolate anion equilibria,[3] methods were developed for the preparation and analysis of equilibrium mixtures of ketone enolate anions. For analysis of these mixtures, the solution of enolate anions was quenched either in buffered deuterium oxide to form mixtures of monodeuterated ketones or in acetic anhydride to form mixtures of enol acetates. The latter procedure has fewer analytical complications, particularly for cyclic ketones, and has been the method employed in our subsequent work. Since our previous studies dealt primarily with equilibrium mixtures of the potassium enolates of acyclic ketones, we have now extended these studies to include preparations and analyses of both the potassium and lithium enolates derived from cyclic ketones.

In other recent studies,[4] ketone enolate anions which have been generated in the absence of either a relatively acidic proton-donating solvent or an excess of the ketone appeared not to lead to equilibrium mixtures of enolate anions. This failure to equilibrate seemed to be especially true when lithium enolates were involved. To explore these phenomena further, we have examined the ease of equilibration of enolate anions formed under various conditions.

The cyclic ketones employed in this study are **1**–**4**. Each of these compounds was converted to a mixture of the corresponding enol acetates **5**–**13** by previously described procedures[3,5] and the enol acetates were separated and characterized. The n.m.r. spectra (see Experimental) of the pure enol acetates served to define their structures. The stereochemistry of enol acetates **8** and **9** was established by conversion of each ester to the corresponding *cis*- or *trans*-1-decalone. The various enol acetates were equilibrated at 100° in the presence of *p*-toluenesulfonic acid to give equilib-



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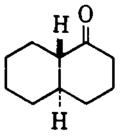

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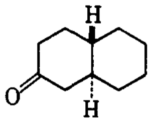

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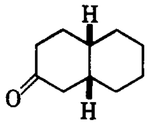
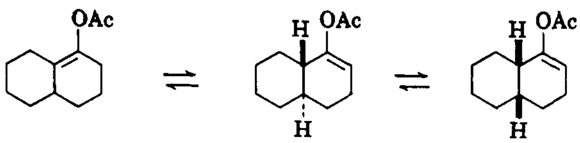
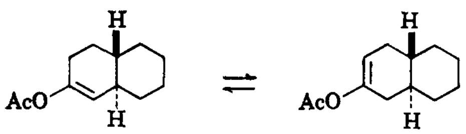


4

5 (98%) **6** (2%)



7 (93.8%) **8** (4.7%) **9** (1.5%)



10 (28%) **11** (72%)

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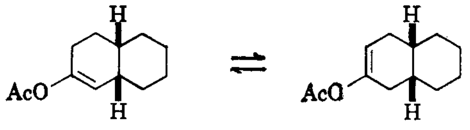
(1) This research has been supported by Grant No. AF-AFOSR-573-64 from the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(2) National Science Foundation Predoctoral Fellow, 1963–1965.

(3) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

(4) (a) G. Stork, P. Rosen, and N. L. Goldman, *J. Am. Chem. Soc.*, **83**, 2965 (1961); (b) R. E. Schaub and M. J. Weiss, *Chem. Ind.* (London), 2003 (1961); (c) M. J. Weiss, R. E. Schaub, J. F. Poletto, G. R. Allen, Jr., and C. J. Coscia, *ibid.*, 118 (1963); (d) M. J. Weiss, *et al.*, *Tetrahedron*, **20**, 357 (1964); (e) D. Caine, *J. Org. Chem.*, **29**, 1868 (1964).

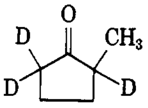
(5) (a) H. O. House and H. W. Thompson, *ibid.*, **26**, 3729 (1961); (b) M. Mousseron, F. Winternitz, R. Granger, J. Claret, and M. Trinquier, *Bull. soc. chim. France*, 598 (1947).



12 (60%) **13** (40%)

rium mixtures having the compositions indicated in the accompanying equations. The positions of equilibrium for the 2-decalone derivatives **10**–**13** are of interest since the preference for a 2,3 double bond in the *trans* series (*i.e.*, **11**) and a 1,2 double bond in the *cis* series (*i.e.*, **12**) is much less[6] than appears to be the case for enol derivatives of 3-keto steroids.[7]

Of initial concern in this study was the question of what conditions are required to achieve equilibration of the various enolate anions derivable from ketones **1**–**4**. To provide an unambiguous answer we chose to follow a previously described procedure[3] in which each ketone (**1**–**4**) was mixed with an equimolar portion of its polydeuterated analog (**15**–**18**); this mixture of nondeuterated and polydeuterated ketones was converted to the corresponding enolate anions by reaction with either triphenylmethyllithium or triphenylmethylpotassium in 1,2-dimethoxyethane. After the resulting mixture of enolate anions had been quenched in acetic anhydride or in an aqueous buffer, the products (enol acetates and/or ketones) were analyzed by mass spectrometry. If the products were mixtures of nondeuterated and polydeuterated material, no equilibration had occurred, whereas mixtures of partially deuterated material with an approximately statistical distribution of deuterium at the α-carbon atoms of the ketone (or corresponding positions of the enol acetates) indicated complete equilibration. The results of these experiments (see Experimental) indicated that little equilibration occurred over a period of 1 hr. at 25° with either potassium or lithium enolates when no free ketone was present in the reaction medium. In other words, both equilibria of the type illustrated in the following equation (1) and intramolecular 1,3 proton transfers must occur very slowly under the usual conditions employed in organic synthesis.[8] As found previously with the potassium enolates of several acyclic ketones,[3] the presence of only 2–10 mole % excess of the ketone (1) in solution with its potassium enolates permitted rapid equilibration among the enolates, the equilibration being complete in less than 30 min. at room temperature. Since the potassium enolates of all three decalones (**2**, **3**, and **4**) were only slightly soluble in 1,2-dimethoxyethane, we were able only to examine suspensions of these potassium enolates. As might be expected with these suspensions, equilibration of the enolate anions occurred very slowly even when excess ketone was present.



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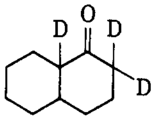

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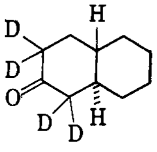

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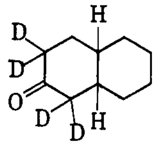

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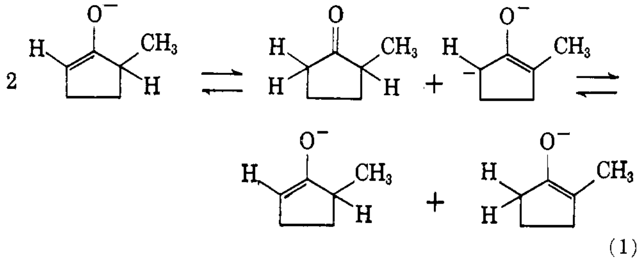

(1)

Solutions of the lithium enolates of all four ketones (**1**–**4**) were found to equilibrate very slowly when only a slight excess (5 mole % or less) of the free ketone was present in the solution and rapid equilibration among these lithium enolates was achieved only when a substantial excess (25–100 mole %) of the free ketone was present in the solution. Thus, it is clear that equilibration of potassium enolates is much more rapid than equilibration of lithium enolates in the presence of a small amount of excess ketone as previous product studies have suggested.[4] This rate difference is presumably a reflection of the fact that the lithium–oxygen bond is more nearly covalent (or is a much tighter ion pair) than the potassium–oxygen bond.

These data caused us to question the validity of our earlier, preliminary examination[3] of the equilibrium position of the lithium enolates derived from the acyclic ketones **19** and **20** since these measurements had been made with solutions of lithium enolates containing only a slight excess of the free ketone. Accordingly we have re-examined these two cases and found that the equilibrium values reported for ketone **19** are correct,

$(CH_3)_2CH{-}CO{-}CH_2CH_3$ **19** $n\text{-}C_4H_9{-}CH_2{-}COCH_3$ **20**

but the values reported for ketone **20** do not correspond to an equilibrium mixture but rather to the mixture of enolate anions formed in a kinetically controlled process.

The compositions of the mixtures of potassium and lithium enolate anions obtained in this study are summarized in Table I. The data include both enolate anion mixtures obtained from the ketones under conditions approaching kinetic control and mixtures obtained under thermodynamically controlled conditions. From reference to Table I, it is apparent that, *when equilibrium has been established*, the concentration of the more highly substituted enolate is usually slightly greater with the lithium enolate mixture than it is with the potassium enolate mixture. This conclusion, which is contrary to what our preliminary data[3] on lithium enolates had suggested, would appear to be explicable in terms of the greater covalent character of the lithium-oxygen bond. In other words, the negative charge of lithium enolates is more nearly localized on oxygen than is the negative charge of potassium enolates. As a result, the carbon–carbon double bond of the lith-

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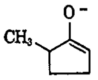
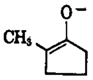
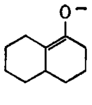
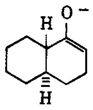
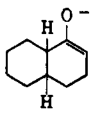
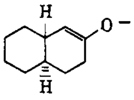
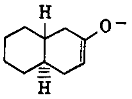
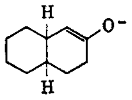
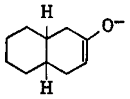
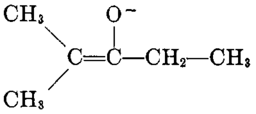
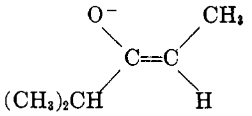
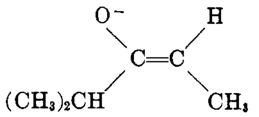
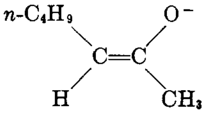
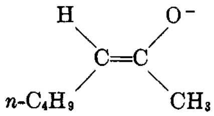
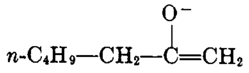
(6) *Cf.* H. Favre and A. J. Liston, *Can. J. Chem.*, **42**, 268 (1964).

(7) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp. 276–279.

(8) Presumably these considerations are applicable only to solutions of enolates in nonprotonic solvents since the presence of a proton-donating solvent would offer a mechanistic pathway for exchange which need not involve a dianion intermediate or an intramolecular proton transfer.

Table I

Composition of Mixtures of Enolate Anions Generated in 1,2-Dimethoxyethane

Ketone and reaction conditions	Enolate anion composition, %[a]		
1			
Ph_3CK (apparent kinetic control)[b]	55	45	
Ph_3CK (equilibrium)	78	22	
Ph_3CLi (kinetic control)	28	72	
Ph_3CLi (equilibrium)	94	6	
2			
Ph_3CK (apparent kinetic control, enolate not in solution)	29	58	13
Ph_3CLi (kinetic control)	10	68	22
Ph_3CLi (equilibrium)	66	21	13
3			
Ph_3CK (apparent kinetic control, enolate not in solution)[c]	52	48	
Ph_3CLi (kinetic control)	13	87	
Ph_3CLi (equilibrium)	53	47	
4			
Ph_3CK (apparent kinetic control, enolate not in solution)[c]	59	41	
Ph_3CLi (kinetic control)	68	32	
Ph_3CLi (equilibrium)	68	32	
19			
Ph_3CK (equilibrium)[d]	12	74	14
Ph_3CLi (equilibrium)[e]	<1	>98	<1
20			
Ph_3CK (apparent kinetic control)[c]	37	9	54
Ph_3CK (equilibrium)	46	12	42
Ph_3CLi (kinetic control)[e]	25 or less	5 or less	70–88
Ph_3CLi (equilibrium)[f]	*ca.* 65	*ca.* 22	*ca.* 13

[a] Unless otherwise noted, the compositions listed are average values from analyses of two or more different reactions; the individual values differed from these average values by ±3% or less except as noted in footnote *f*. [b] These values are based on a single reaction. The deuterium distribution obtained in this case (Table II) suggests that partial equilibration may have occurred. [c] Although the reaction conditions employed for these reactions (Table III) are expected to give kinetic control, the use of deuterium labeling to establish kinetic control was not done in this case. [d] Ref. 3. [e] Ref. 3 and this study. [f] The measurements of these enolate anions in the presence of a large excess of ketone was complicated by a competing aldol condensation and may not represent true equilibrium values (see Experimental).

ium enolate resembles more closely an olefinic carbon–carbon double bond. Although the reason is perhaps debatable, it is clear experimentally that an olefinic double bond is stabilized by alkyl substitution. This stabilizing effect may be seen from the equilibrium positions for various enol acetates such as **5–13** and earlier examples.[3]

Two features of importance in synthetic chemistry arise from these findings. First, it will be noted that the mixtures obtained by adding 1 equiv. of an unsymmetrical ketone to 1 equiv. of a strong base in the absence of a proton-donating solvent may not be equilibrium mixtures of enolate anions, especially in cases where a lithium cation is involved. Since there is a kinetic preference for abstracting a proton from the less highly substituted α-carbon atom,[3,4e] this kinetically controlled generation of enolate anions will usually lead to mixtures of enolate anions in which the less highly substituted enolate predominates. On the other hand, conversion of a ketone to its mixture of enolate anions under circumstances which permit equilibration (*e.g.*, the addition of 1.05 equiv. of a ketone to a solution containing 1.0 equiv. of triphenylmethylpotassium) may lead to an enolate anion mixture of rather different composition. This is especially true with five- and six-membered cyclic ketones where the more highly substituted enolate is favored at equilibrium. However, it will be noted that, irrespective of whether one employs reaction conditions permitting generation of enolate anions with kinetic control or thermodynamic control, many ketones still yield mixtures containing substantial amounts of both structurally isomeric enolates and, consequently, mixtures of products are to be expected from further reaction.

Of more importance is the demonstration that enolate anions produced in the absence of excess ketone and in the absence of proton-donating solvents do not undergo appreciable equilibration during periods of 1 hr. or longer. This finding clearly indicates that a single enolate anion could be generated and stored for at least limited periods of time. The generation of specific enolate anions by reduction[4] of α,β-unsaturated ketones, α-halo ketones, and α-chloromercuri ketones with metals illustrate the possibility. We have developed an alternative method for the production of a specific enolate anion which consists of reaction of 1 equiv. of the corresponding enol acetate with 2 equiv. of methyllithium in 1,2-dimethoxyethane solution. A description and discussion of this procedure will be presented in the next paper of this series.

Experimental[9]

Preparation of Starting Materials.—The sources or preparations of ketones **1**, **2**, **19**, and **20** have been cited previously.[3,5] The *trans*-1-decalone (**2**) employed was an equilibrium mixture containing about 95% of the *trans* isomer **2** and 5% of the *cis* isomer. Reaction of 1-(1-pyrrolidino)cyclohexene with methyl vinyl ketone as previously described[10] produced a mixture of unsaturated ketones[10,11] containing[12] $\Delta^{1,9}$-octal-2-one (*ca.* 90%, second eluted) and $\Delta^{9,10}$-octal-2-one (*ca.* 10%, first eluted). Catalytic hydrogenation of the octalone mixture over a 5% palladium-on-carbon catalyst in acidic ethanol[13] yielded a mixture[12] of *cis*-2-decalone (**4**, *ca.* 91%, second eluted) and *trans*-2-decalone (**3**, *ca.* 9%, first eluted) from which the pure *cis* isomer **4** was collected.[14] Reduction of the octalone mixture with lithium in liquid ammonia as previously described[13] gave a sample of *trans*-2-decalone (**3**, *ca.* 90%, first eluted) contaminated with about 10% of the starting 2-octalones (eluted second and third). The pure *trans*-**2**-decalone, b.p. 109–110° (8 mm.), $n^{14}\mathrm{D}$ 1.4855 [lit.[15] b.p. 100–102° (12 mm.), $n^{20}\mathrm{D}$ 1.4818], could be separated by fractional distillation of this mixture through a 40-cm. spinning-band column. A better separation procedure consisted of refluxing a solution of the crude reduction product (from 0.0611 mole) of the octalones in 90 ml. of ether with 4.5 g. (0.0635 mole) of pyrrolidine for 48 hr. The resulting solution was washed with aqueous hydrochloric acid to remove the pyrrolidine adduct of the unsaturated ketone and then washed with aqueous sodium chloride, dried, concentrated, and distilled. The distillate, b.p. 62–64° (0.4 mm.), $n^{26}\mathrm{D}$ 1.4812 [lit.[13] b.p. 127–128° (28 mm.), $n^{23}\mathrm{D}$ 1.4820], was the pure[12] *trans*-2-decalone.

The solutions of triphenylmethylpotassium in 1,2-dimethoxyethane were prepared and standardized as previously described.[3,16] Solutions which were approximately 1 *M* triphenylmethyllithium were prepared by the following procedure.[17] The solvent was removed from 15 ml. (15 mmoles) of a 1 *M* ethereal methyllithium solution under reduced pressure and the residual white solid was dissolved in 15 ml. of 1,2-dimethoxyethane. A 4.4760-g. (18.3-mmole) portion of triphenylmethane was added and the resulting solution was stirred under a nitrogen atmosphere until a negative Gilman color test for methyllithium was obtained (usually 2–3 hr.). A 0.50-ml. aliquot of the solution was titrated with pure 2-heptanone, 50.6 mg. (0.452 mole or 90% of the theoretical amount) of the ketone being required to just discharge the red color.

Preparation of the Polydeuterated Ketones.—The procedure illustrated by the following example was found most convenient for the preparation of samples of the polydeuterated ketones **15–18**. The previously described[3] samples of 2,4,4-trideuterio-2-methyl-3-pentanone (90% d_3 species, 10% d_2 species) and 1,1,1,-3,3-pentadeuterio-2-heptanone (86% d_5 species, 14% d_4 species) were used. A solution of 1.8908 g. (12.4 mmoles) of *trans*-2-decalone (**3**) and 38 mg. (0.36 mmole) of sodium carbonate in 6 ml. of deuterium oxide and 20 ml. of 1,2-dimethoxyethane was refluxed for 18 hr. and then concentrated under reduced pressure. The ketone was recovered by extraction with ether followed by drying and concentrating the ethereal extract. A total of seven such equilibrations were performed. The final recovered ketone **17** (403 mg. or 22%) was analyzed by mass spectrometry and found to contain 95% d_4 species and 5% d_3 species. The n.m.r. spectrum[18] of the sample lacks absorption present at δ 2.05–2.4 in the spectrum of the nondeuterated ketone **3** attributable to the protons α to the carbonyl group. The infrared spectrum[18] of the deuterated ketone **17** differs from the spectrum of the nondeuterated material in having additional peaks at 2140 (sh) and 2190 (C–D stretching), in lacking absorption at 1410–1420 cm.$^{-1}$ (CH_2–CO), and in several other bands in the fingerprint region.

Comparable exchange experiments with the *cis* ketone **4** gave a sample of the deuterated ketone **18** containing 99% d_4 species and 1% d_3 species. The sample lacks infrared (1410 cm.$^{-1}$) and n.m.r. absorption[18] attributable to protons α to the carbonyl group and has peaks at 2120, 2150, and 2220 cm.$^{-1}$ (C–D stretch). The deuterio ketone **16**,[19] obtained by exchange of 1-decalone with methanol-d_1 in the presence of sodium methoxide, contained 86% d_3 species and 14% d_2 species. This sample also lacks infrared absorption[18] at 1410 cm.$^{-1}$ attributable to a –CH_2–CO– grouping and has much diminished n.m.r. absorption[18] in the region δ 2.1–2.5 where the spectrum of *trans*-1-decalone (**2**) has a complex multiplet attributable to the protons α to the carbonyl function. The sample has infrared bands at 2110, 2150, 2200, and 2220 cm.$^{-1}$ (C–D stretching). The deuterated ketone **15**, obtained by exchange with sodium carbonate and deuterium oxide, contained 99% d_3 species and 1% d_2 species. The n.m.r. spectra[18] of the deuterated (**15**) and nondeuterated (**1**) ketones differ in the absence of absorption in the region δ 1.9–2.0 (protons α to the carbonyl function) for the deuterated ketone. Also the doublet ($J = 6.5$ c.p.s.) at δ 1.05 in the spectrum of ketone **1** is a triplet ($J = 1$ c.p.s. for deuterium–hydrogen coupling) in the spectrum of ketone **15**. The infrared spectrum[18] of the deuterated ketone **15** lacks absorption at 1410 (–CH_2–CO–) and has peaks at 2120 (sh), 2140, 2200 (sh), and 2230 cm.$^{-1}$ (C–D stretching).

Preparation of the Enol Acetates.—Reaction of 1-decalone with isopropenyl acetate and *p*-toluenesulfonic acid as previously described[5] produced (in 79% yield) a liquid, b.p. 56–58° (0.15 mm.), which contained[14] the enol acetate **7** (43%, first eluted), the enol acetate **8** (40%, second eluted), and the enol acetate **9**

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[9] All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated, magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer, Model 237, infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The n.m.r. spectra were determined at 60 Mc. with a Varian, Model A-60, n.m.r. spectrometer. The mass spectra were obtained with a CEC, Model 21-130, mass spectrometer. The microanalyses were performed by the Scandinavian Microanalytical Laboratory.

[10] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

[11] (a) R. L. Augustine and H. V. Cortez, *Chem. Ind.* (London), 490 (1963); (b) D. J. Baisted and J. S. Whitehurst, *J. Chem. Soc.*, 4089 (1961).

[12] A gas chromatography column packed with Ucon Polar suspended on Chromosorb P was employed.

[13] R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958); see also, E. E. van Tamelen and W. C. Proost, Jr., *J. Am Chem. Soc.*, **76**, 3632 (1954).

[14] A gas chromatography column packed with Carbowax 20M suspended on Chromosorb P was employed.

[15] W. Hückel, W. Egerer, and F. Mössner, *Ann.*, **645**, 162 (1961).

[16] H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962).

[17] A similar procedure has been described by H. Gilman and B. J. Gaj, *ibid.*, **28**, 1725 (1963).

[18] Determined as a solution in carbon tetrachloride.

[19] E. Lund, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 941 (1963).

TABLE II

THE PREPARATION OF ENOLATE ANIONS FROM MIXTURES OF NONDEUTERATED AND POLYDEUTERATED KETONES

Ketone (total mmoles of non- and polydeuterated ketone added)	Base (mmoles)	Solvent, ml.	Reaction time, hr.	Deuterium distribution in ketone from $HOAc-H_2O$ quenching, %						Composition of enol acetate mixture from Ac_2O quenching (%)
				d_0	d_1	d_2	d_3	d_4	d_5	
1 (1.03)	Ph_3CLi (1.26)	2.1	0.5	49	8	42	1	...	...	**5** (28), **6** (72)[a]
1 (3.04)	Ph_3CLi (2.4)	4.0	0.5	34	39	24	3	...	...	**5** (94), **6** (6)[b]
			1.0	32	44	22	2	...	...	**5** (94), **6** (6)[c]
1 (0.93)	Ph_3CK (0.98)	1.5	0.5	41	15	43	1	...	...	**5** (55), **6** (45)[d]
1 (1.35)	Ph_3CK (0.98)	1.5	0.5	27	47	25	1	...	...	**5** (78), **6** (22)[e]
1 (1.65)	Ph_3CK (1.63)	2.1	0.5	27	47	24	2	...	...	**5** (77), **6** (23)[f]
2 (1.65)	Ph_3CLi (1.59)	2.0	1.0	45	17	34	2	...	...	**7** (10), **8** (68), **9** (22)[g]
2 (1.14)	Ph_3CLi (1.05)	1.5	1.0	43	16	38	3	...	...	**7** (11), **8** (67), **9** (22)[h]
2 (1.17)	Ph_3CLi (0.58)	1.0	1.0	23	32	31	14	...	...	**7** (65), **8** (22), **9** (13)[i]
2 (0.92)	Ph_3CLi (0.45)	1.0	1.0	23	26	33	18	...	...	**7** (67), **8** (20), **9** (13)[j]
2 (1.10)	Ph_3CK (1.03)	1.5[k]	0.5	45	12	43	..	...	...	**7** (29), **8** (58), **9** (13)[l]
3 (1.14)	Ph_3CLi (1.10)	2.0	1.0	38	6	12	41	3	...	**10** (12), **11** (88)[m]
3 (1.03)	Ph_2CLi (0.50)	1.0	1.0	8	21	35	28	8	...	**10** (54), **11** (46)[n]
3 (0.91)[o]	Ph_3CLi (0.56)	1.0	1.0	15	32	33	16	4	...	**10** (52), **11** (48)[p]
4 (1.14)	Ph_3CLi (1.10)	2.0	1.0	42	5	9	43	1	...	**12** (67), **13** (33)[q]
4 (1.15)	Ph_3CLi (0.55)	1.0	1.0	8	23	36	26	7	...	**12** (67), **13** (33)[r]
4 (1.19)	Ph_3CLi (0.60)	1.0	1.0	11	25	33	24	7	...	**12** (68), **13** (32)[s]
19 (1.36)	Ph_3CLi (1.36)	2.0	0.5	32	45	21	2	...	...	**25** (>98)[t]
20 (1.03)	Ph_2CLi (0.92)	1.5	1.0	23	26	21	15	9	6	**26** (69), **27** (18), **28**(13)[u]

[a] The calculated yields were **1** (4%), **5** (12%), and **6** (31%). The deuterium contents of these products were **1**, 51% d_0, 10% d_1, 34% d_2, and 5% d_3; **5**, 53% d_0, 7% d_1, 39% d_2, and 1% d_3; **6**, 46% d_0, 9% d_1, 45% d_2, and 1% d_3. [b] The calculated yields were **1** (12%), **5** (40%), and **6** (3%). The deuterium contents of these products were **1**, 19% d_0, 36% d_1, 34% d_2, and 11% d_3; **5**, 36% d_0, 41% d_1, 23% d_2. [c] The calculated yields were **1** (13%), **5** (37%), and **6** (3%). The deuterium contents of these products were **1**, 22% d_0, 40% d_1, 30% d_2, and 8% d_3; **5**, 32% d_0, 46% d_1, and 22% d_2. [d] The calculated yields were **1** (2%), **5** (40%), and **6** (33%). The deuterium contents of these products were **5**, 42% d_0, 16% d_1, 40% d_2, and 2% d_3; **6**, 32% d_0, 12% d_1, 54% d_2, and 2% d_3. [e] The calculated yields were **1** (15%), **5** (63%), and **6** (18%). The deuterium contents of these products were **5**, 24% d_0, 49% d_1, 26% d_2, and 1% d_3; **6**, 24% d_0, 48% d_1, 26% d_2, and 2% d_3. [f] The calculated yields were **1** (15%), **5** (65%), and **6** (19%). The deuterium contents of these products were **5**, 29% d_0, 47% d_1, 23% d_2, and 1% d_3; **6**, 28% d_0, 48% d_1, 22% d_2, and 2% d_3. [g] The calculated yields were **2** (10%), **7** (5%), **8** (36%), and **9** (12%). [h] The calculated yields were **2** (33%), **7** (6%), **8** (36%), and **9** (12%). [i] The calculated yields of enol acetates were **7** (48%), **8** (16%), and **9** (10%). [j] The calculated yields of enol acetates were **7** (47%), **8** (14%), and **9** (9%). [k] Since this potassium enolate was only slightly soluble, the reaction mixture was a suspension. [l] The calculated yields were **2** (12%), **7** (21%), **8** (42%), and **9** (10%). [m] The calculated yields were **3** (18%), **10** (8%), and **11** (57%). [n] The calculated yields of enol acetates were **10** (29%) and **11** (26%). [o] In this experiment a 1.7:1 mole ratio of nondeuterated to polydeuterated ketone was employed. [p] The calculated yields of enol acetates were **10** (27%) and **11** (25%). [q] The calculated yields were **4** (6%), **12** (44%), and **13** (21%). [r] The calculated yields of enol acetates were **12** (34%) and **13** (17%). [s] The calculated yields of enol acetates were **12** (36%) and **13** (16%). [t] The calculated yields were **19** (12%) and **25** (43%). [u] The calculated yields were **20** (36%), **26** (35%), **27** (9%), and **28** (7%).

(17%, third eluted). The first two samples (**7** and **8**) were collected[14] and identified with the previously characterized samples by comparison of retention times and infrared spectra. A collected sample of the ester **9** was redistilled in a short-path still. This material has infrared absorption[18] at 1760 (ester C=O) and 1680 cm.$^{-1}$ (C=C) with n.m.r. peaks at δ 5.39 (1H triplet, J = 3.5 c.p.s., vinyl C-H) and at 2.13 (singlet, $CH_3-CO-O-$) as well as broad absorption in the regions δ 1.9-2.5 and 1.2-1.8.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; mol. wt., 194. Found: C, 74.31; H, 9.39; mol. wt., 194 (mass spectrum).

A sample (from 0.23 to 0.15 mmole) of each of the pure enol acetates **7**, **8**, and **9** was mixed with 0.5 mg. (0.003 mmole) of anhydrous *p*-toluenesulfonic acid and each of the mixtures was heated to 100° in a sealed tube for 96 hr. The resulting solutions were diluted with pentane and then washed with aqueous sodium bicarbonate, and dried, concentrated, and analyzed.[14] Each of the mixtures contained, in addition to a small amount of 1-decalone, a mixture of the three enol acetates the average composition of which was **7** (93.8%), **8** (4.7%), and **9** (1.5%). None of the values obtained in the individual runs differed from these average values by more than ±0.6%.

Since earlier reports[5,20] of the 1-decalone enol acetates had not provided rigorous evidence for the stereochemistry of pure compounds **8** and **9**, the following transformations were effected. To a solution of 0.6 mmole of methyllithium in 1 ml. of 1,2-dimethoxyethane containing a few milligrams of triphenylmethane (as an indicator) was added the *cis* enol acetate **9** (46.9 mg. or 0.242 mmole) at which point the solution still retained the red color of the triphenylmethyl anion. The solution was stirred for 1 hr. and then a 0.5-ml. aliquot was quenched in dilute, aqueous acetic acid. The remaining 0.5-ml. aliquot of the reaction solution was quenched in a mixture of deuterium oxide and deuterioacetic acid. After each of the resulting mixtures had been extracted with ether, the ethereal solutions were washed with aqueous sodium bicarbonate, dried, and concentrated. The nondeuterated sample exhibited two peaks on gas chromatography[14,21] corresponding to *trans*-1-decalone (22%, first eluted) and *cis*-1-decalone (78%, second eluted). A sample of the *cis* ketone was collected and shown to have infrared peaks characteristic[20] of *cis*-1-decalone. Treatment of the sample with dilute, aqueous acid isomerized the material to a mixture of decalones containing[14] more than 95% of *trans*-1-decalone. Because of the fact that the preheater (and/or columns) employed in our gas chromatographic separations caused partial isomerization of *cis*-1-decalone to *trans*-1-decalone, the degree of stereoselectivity in conversion of the *cis* enol acetate **9** to *cis*-1-decalone is probably a good deal better than the above analysis would indicate. The *cis*-1-decalone was collected[21] from the deuterated sample and found to contain 88% d_1 species and 12% d_0 species. This monodeuterated sample has infrared absorption[18] at 2150 and 2205 (more intense) cm.$^{-1}$ (C-D stretching).

The same procedure was used with 111.4 mg. (0.575 mmole) of the *trans* enol acetate **8** employing 1.2 mmoles of methyllithium and 1 ml. of 1,2-dimethoxyethane. The nondeuterated sample contained[14] 97% *trans*-1-decalone and 3% *cis*-1-decalone. The infrared spectrum of a collected sample of the major product was identical with the spectrum of an authentic sample of *trans*-1-decalone. The *trans*-1-decalone was collected from the deuterated sample and found to contain 91% d_1 species and 9% d_0 species. This material has infrared absorption at 2150 (more intense) and 2190 cm.$^{-1}$ (C-D stretching).

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(20) C. Djerassi and J. Staunton, *J. Am. Chem. Soc.*, **83**, 736 (1961).

(21) A gas chromatography column packed with Dow-Corning silicone fluid, no. 710, suspended on diatomaceous earth was employed.

Reaction of 2.0 g. (0.013 mole) of *cis*-2-decalone (**4**) with excess isopropenyl acetate in the presence of *p*-toluenesulfonic acid as previously described[3,5] yielded 2.24 g. (88%) of a mixture of enol acetates, b.p. 67° (0.2 mm.), containing[22] **12** (*ca.* 40% first eluted) and **13** (*ca.* 60%, second eluted). Each pure enol acetate was collected from the gas chromatograph. The enol acetate **12** has infrared absorption[18] at 1750 (ester C=O) and 1675 (C=C) cm.$^{-1}$ with an n.m.r. singlet[18] at δ 2.03 (3H, CH_3–CO–O–) as well as broad absorption within the region 1.2–2.4 and a doublet (J = 3.5 c.p.s.) of triplets (J = 1 c.p.s.) centered at 5.15 [1 vinyl CH in the environment >CH–CH=C(OAc)–CH_2–]. The isomeric enol acetate **13** has infrared absorption[18] at 1760 (ester C=O) and 1685 (C=C) cm.$^{-1}$ with an n.m.r.[18] singlet at δ 2.04 (3H, CH_3–CO–O–) as well as broad absorption in the region 1.2–2.4 and a broad, unresolved peak centered at 5.22 (1H, vinyl C–H).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; mol. wt., 194. Found for **12**: C, 74.08; H, 9.26; mol. wt., 194 (mass spectrum). Found for **13**: C, 74.02; H, 9.30; mol. wt., 194 (mass spectrum).

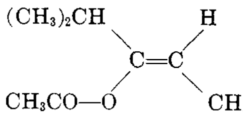
Samples (40 mg.) of each of the pure enol acetates **12** and **13** were equilibrated at 100° in the presence of 0.7 mg. of *p*-toluenesulfonic acid as previously described. In each case the equilibrated mixture contained[14] 60% acetate **12** and 40% acetate **13**.

A 2.0-g. (0.013-mole) sample of *trans*-2-decalone (**3**) was allowed to react with excess isopropenyl acetate in the presence of *p*-toluenesulfonic acid in the usual manner. The resulting product, 2.20 g. (86%), b.p. 68–69° (0.2 mm.) [lit.[5b] b.p. 110–112° (15 mm.), n^{25}_{D} 1.4825, for a mixture of **10** and **11**], contained[22] enol acetate **11** (*ca.* 40%, first eluted) and enol acetate **10** (*ca.* 60%, second eluted). Each pure ester was collected[22] from the gas chromatograph. The acetate **11** has infrared absorption[18] at 1755 (ester C=O) and 1685 (C=C) cm.$^{-1}$ with an n.m.r.[18] singlet at δ 2.02 (3H, CH_3–CO–O–) as well as broad absorption in the region 1.0–2.3 and a broad, unresolved peak at 5.07 (1H, vinyl C–H). The isomeric acetate **10** has infrared peaks[18] at 1760 (ester C=O) and 1685 (C=C) cm.$^{-1}$ with an n.m.r.[18] singlet at δ 2.01 (3H, CH_3–CO–O–), broad absorption in the region 1.0–2.3, and a doublet (J = 3.5 c.p.s.) of triplets (J = 1 c.p.s.) centered at 5.22 [1 vinyl C–H in the environment >CH–CH=C(OAc)–CH_2–].

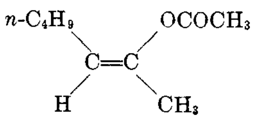
Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; mol. wt., 194. Found for **11**: C, 74.10; H, 9.29; mol. wt., 194 (mass spectrum). Found for **10**: C, 74.03; H, 9.32; mol. wt., 194 (mass spectrum).

Samples (40 mg.) of each of the pure enol acetates **10** and **11** were equilibrated at 100° in the presence of 0.5 mg. of *p*-toluenesulfonic acid as previously described. Each equilibrated mixture contained[14] 28% of the acetate **10** and 72% of the acetate **11**.

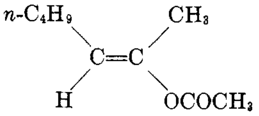
Experiments to Establish the Presence or Absence of Equilibration among Enolate Anions.—Unless otherwise noted, equimolar mixtures of the ketones **1–4**, **19**, and **20** and their previously described polydeuterated derivatives were added to standardized solutions of either triphenylmethyllithium or triphenylmethylpotassium in1,2-dimethoxyethane. The quantities employed are given in Table II. After the resulting solutions (or suspension in the case of the potassium enolate of ketone **2**) had been stirred for the specified times, aliquots were removed and quenched in acetic anhydride and in acetic acid–water mixtures of such concentration that the pH of the final solution was 5–6. As described previously,[3] the mixtures from the acetic anhydride quenching procedure were stirred with mixtures of pentane and aqueous sodium bicarbonate after which the pentane solution was dried and a weighed amount of an internal standard (*m*-diisopropylbenzene for ketone **1**, acenaphthene for ketones **2–4**, and anisole for ketones **19** and **20**) was added. The pentane solution was then concentrated and analyzed by gas chromatography,[14,22] response factors being determined from independent calibration curves. In certain cases, samples of enol acetates and ketones from these mixtures were collected and analyzed for deuterium content by mass spectrometry. The mixtures from the aqueous acetic acid quenching procedures were extracted with ether within 10 min. after quenching and the ethereal extracts were dried and concentrated. The pure ketone was collected from a gas chromatograph and analyzed for deuterium content by mass spectrometry. In all cases, appropriate control experiments were employed to demonstrate the lack of hydrogen–deuterium exchange either in the quenching medium or on the gas chromatography column used for collecting the samples. The results of these experiments are summarized in Table II. The enol acetates **25–28**, obtained from ketones **19** and **20**, were collected from quenching experiments employing nondeuterated samples of ketones **19** and **20** and shown to be identical with previously described samples[3] by comparison of retention times and infrared spectra.



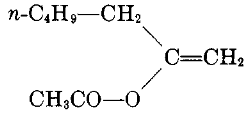
25



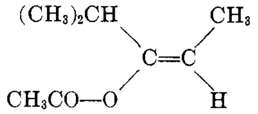
26



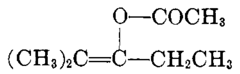
27



28



29



$$(CH_3)_2C{=}\overset{\overset{\displaystyle O{-}COCH_3}{|}}{C}{-}CH_2CH_3$$

30

Since the statistical deuterium distribution observed (Table II) in experiments with 2-methyl-3-pentanone (**19**) could be considered to indicate that exchange was occurring only between the C-4 positions of the deuterated and nondeuterated ketones **19** without concurrent exchange at the C-2 positions, the following additional experiment was performed. The ketone **19** was converted as previously described[3] to a mixture of enol acetates containing[14] 52% of **25**, 7% of **29**, and 41% of **30**. A mixture of 129.1 mg. (0.911 mmole) of this enol acetate mixture and 50 mg. (0.50 mmole) of the ketone **19** was added to a solution of 2.0 mmoles of methyllithium in 2 ml. of 1,2-dimethoxyethane. The addition served to consume all of the methyllithium (as judged from the disappearance of the color of the triphenylmethyl anion indicator) and provide about 0.3 mmole of excess ketone. The resulting solution was stirred for 1 hr. at room temperature and then quenched in excess acetic anhydride; the product was isolated and analyzed in the usual way. The enol acetate portion of the product contained[14] more than 98% enol acetate **25**, the calculated yield of which was approximately 90%. (The *t*-butyl acetate peak in the gas chromatogram interfered sufficiently to prevent a more accurate yield calculation.) A comparable experiment was done with 0.885 mmole of the enol acetate mixture and 2.0 mmoles of methyllithium so that no excess ketone **19** was present. After the resulting solution had been stirred for 1 hr. and then quenched in acetic anhydride, the recovered enol acetate mixture contained approximately 53% of **25**, 5% of **29**, and 42% of **30**. Thus, equilibration among all three enolates derivable from the ketone **19** occurs when excess ketone is present.

Formation and Analysis of Mixtures of Enolate Anions.—As in previous experiments, measured quantities of ketones **1–4**, **19**, and **20** were added to standardized solutions of triphenylmethylpotassium or triphenylmethyllithium in 1,2-dimethoxyethane under a nitrogen atmosphere. The resulting solutions (or suspensions with the potassium enolates of ketones **2–4**) were stirred for the specified period of time and then aliquots were quenched in acetic anhydride. The enol acetate mixtures were separated and analyzed[14,22] by previously described procedures. The internal standards and column calibrations described in the previous experiment were employed. The reaction products were shown to be identical with authentic samples by comparison of retention times and by comparison of the infrared spectra of collected samples. The experimental results are summarized in Table III. In the case of the ketone **20**, certain of the analyses of enolate anion mixtures were also obtained by quenching aliquots of the solutions in deuterium oxide containing sufficient deuterioacetic acid so that the pH of the final solution was 5 to 6. The resulting mixtures of monodeuterated ketones were isolated and analyzed by mass spectrometry as described previously.[3]

A solution of 25.5 mmoles of triphenylmethyllithium in 23 ml. of 1,2-dimethoxyethane was treated with a slight excess (2.565 g. or 26.2 mmoles) of 2-methylcyclopentanone (**1**) and then 1-ml. aliquots were removed from the reaction solution after 1, 5, and 40 min. Each of the aliquots was quenched in acetic anhydride and the enol acetate mixtures were separated and analyzed in the usual way. In each case a mixture of 33% of enol acetate **5** and 67% of enol acetate **6** was obtained. The reaction

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[22] A gas chromatography column packed with Dow-Corning silicone fluid, no. 550, suspended on Chromosorb P was employed.

TABLE III

THE PREPARATION AND COMPOSITION OF MIXTURES OF ENOLATE ANIONS

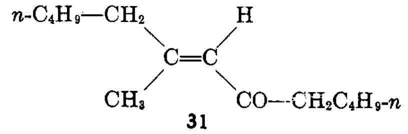
Ketone (mmoles)	Base (mmoles)	Solvent, ml.	Reaction time, hr.	Composition of enol acetate mixture (%)	Calculated yields from Ac_2O quenching experiment (%)
1 (2.36)	Ph_3CLi (2.36)	5.0	0.5	**5** (27), **6** (73)	**1** (9), **5** (13), **6** (34)
			1.0	**5** (29), **6** (71)	**1** (8), **5** (13), **6** (33)
1 (6.38)	Ph_3CK (6.38)	8.0	0.5	**5** (81), **6** (19)	**1** (16), **5** (57), **6** (14)
1 (3.22)	Ph_3CK (3.22)	10.0	0.5	**5** (78), **6** (22)	**1** (13), **5** (54), **6** (16)
1 (3.69)	Ph_3CK (3.69)	10.0	0.5	**5** (75), **6** (25)	**1** (15), **5** (56), **6** (19)
2 (4.70)	Ph_3CK (4.70)	7.5[a]	0.5	**7** (29), **8** (58), **9** (13)	**2** (15), **7** (20), **8** (40), **9** (9)
2 (4.90)	Ph_3CK (4.90)	7.8[a]	0.5	**7** (29), **8** (58), **9** (13)	**2** (12), **7** (21), **8** (41), **9** (9)
3 (1.06)	Ph_3CLi (1.06)	2.8	0.5	**10** (13), **11** (87)	**3** (18), **10** (8), **11** (55)
3 (1.10)	Ph_3CLi (1.10)	1.5	0.5	**10** (13), **11** (87)	**3** (14), **10** (9), **11** (56)
3 (1.84)	Ph_3CK (1.80)	4.5[a]	0.5	**10** (52), **11** (48)	**3** (7), **10** (39), **11** (36)
3 (1.94)	Ph_3CK (1.92)	4.8[a]	1.0	**10** (51), **11** (49)	**3** (8), **10** (39), **11** (38)
4 (1.07)	Ph_3CLi (1.07)	2.9	0.5	**12** (69), **13** (31)	**4** (16), **12** (49), **13** (22)
4 (1.13)	Ph_3CLi (1.11)	1.5	0.5	**12** (69), **13** (31)	**4** (16), **12** (52), **13** (24)
4 (3.58)[b]	Ph_3CK (2.04)	10.0[a]	0.5	**12** (60), **13** (40)	**4** (49), **12** (25), **13** (17)
4 (1.56)[b]	Ph_3CK (0.80)	4.0[a]	0.5	**12** (57), **13** (43)	**4** (47), **12** (18), **13** (14)
4 (1.60)[b]	Ph_3CK (0.80)	4.0[a]	1.0	**12** (61), **13** (39)	**4** (47), **12** (23), **13** (15)
19 (1.26)	Ph_3CLi (1.26)	2.0	0.5	**25** (>98)	**19** (3), **25** (57)
19 (2.45)	Ph_3CLi (1.26)	2.0	1.0	**25** (>98)	**25** (60)
20 (1.17)[c]	Ph_3CLi (1.16)	2.0	0.5	**26** (25), **27** (5), **28** (70)	**20** (38), **26** (9), **27** (2), **28** (25)
20 (1.45)	Ph_3CLi (1.19)	2.2	1.0	**26** (61), **27** (26), **28** (13)	**20** (48), **26** (34), **27** (15), **28** (7)
20 (0.97)	Ph_3CK (1.14)	1.5	0.5	**26** (37), **27** (11), **28** (52)	**20** (3), **26** (34), **27** (10), **28** (48)
20 (1.60)	Ph_3CK (1.90)	2.0	<0.02	**26** (37), **27** (10), **28** (53)	
			0.5	**26** (37), **27** (9), **28** (54)	
20 (0.81)	Ph_3CK (0.76)	1.0	0.5	**26** (46), **27** (12), **28** (42)	**20** (8), **26** (41), **27** (11), **28** (37)
20 (1.16)	Ph_3CK (1.14)	1.2	0.5	**26** (45), **27** (13), **28** (42)	

[a] Since the potassium enolate was only slightly soluble, the reaction mixture was a suspension. [b] In this titration, it was necessary to add excess *cis*-2-decalone in order to discharge the red color of the triphenylmethyl anion. Apparently, the precipitate of potassium enolate incorporates an additional equivalent of the ketone in this case. [c] In two comparable experiments, the solution of enolate anions was quenched in a mixture of deuterium oxide and deuterioacetic acid. From each reaction the recovered ketone contained 24% d_0, 70% d_1, and 6% d_2 species. The deuterium distribution in the monodeuterated ketones (see ref. 3) was approximately 26% $n\text{-}C_4H_9\text{-}CHD\text{-}CO\text{-}CH_3$ (corresponding to enol acetate **26** and **27**) and 74% $n\text{-}C_4H_9\text{-}CH_2\text{-}CO\text{-}CH_2D$ (corresponding to enol acetate **28**).

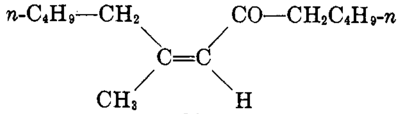
mixture remaining after 40 min. was added to 54 g. (0.51 mole) of acetic anhydride and then subjected to the usual isolation procedure. Distillation separated 1.57 g. (42.8%) of the mixture of enol acetates **5** and **6**. The residue from this distillation was separated into material soluble in cyclohexane, from which only triphenylmethane was isolated, and 0.43 g. of a cyclohexane-insoluble fraction which was identified as α-methylglutaric acid apparently formed by an oxidation of one of the enolate anions. The acid was identified by esterification with ethereal diazomethane to form dimethyl α-methylglutarate whose infrared and ultraviolet spectra were compared with the spectra of an authentic sample. Thus, no materials were isolated corresponding to aldol condensation products.

The α-methylglutaric acid was apparently formed in this experiment by the unintentional air oxidation of the enolate anion corresponding to enol acetate **6**. We believe it unlikely that unavoided air oxidation led to significant errors in quantitative experiments listed in Table I–III for two reasons. In all cases the reactions were conducted under a nitrogen atmosphere and all transfers were made with nitrogen-filled syringes inserted through "no-air" stoppers to minimize contact with oxygen and atmospheric moisture. However, more significant is the fact that all of the enol acetate composition data could be reproduced to within ±3% except when competing aldol condensation was occurring. In the case of reactions of 2-methylcyclopentanone (**1**) with triphenylmethyllithium under kinetically controlled conditions, at least 15 different quantitative runs have been made under various conditions, all of which gave enol acetate compositions corresponding to the values listed in Tables I–III. This reproducibility in the various quantitative runs leads us to believe that no serious errors were introduced either from adventitious air oxidation or from partial equilibration in the kinetically controlled runs.

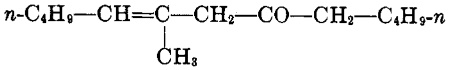
To a solution of 11.7 mmoles of triphenylmethyllithium in 20 ml. of 1,2-dimethoxyethane was added 1.686 g. (14.8 mmoles) of 2-heptanone. The resulting solution was stirred for 1 hr. and then poured into 50 ml. of aqueous 10% hydrochloric acid. The organic components, extracted with ether, were dried and distilled to separate 631 mg. (37%) of 2-heptanone, b.p. 145–150°. The residue was triturated with methanol and the methanol extract was concentrated and distilled to separate 701 mg. of liquid, b.p. 120–130° (0.05 mm.), $n^{20}D$ 1.4580, exhibiting two peaks by gas chromatography.[14] These two peaks, A (*ca.* 45%, first eluted) and B (*ca.* 55%, second eluted), were collected. The material in peak A has infrared absorption[18] [1720, 1690, 1645 (sh), and 1620 cm.$^{-1}$] suggestive of a mixture of conjugated and nonconjugated unsaturated ketones while the sample in peak B has infrared absorption[18] at 1690 (conjugated C═O) and 1620 (conjugated C═C) cm.$^{-1}$. The mass spectrum of material collected from each gas chromatographic peak has a molecular ion peak at *m/e* 210 with fragment peaks at *m/e* 154 [$C_5H_{11}\text{-}(CH_3)C{=}CH\text{-}C(OH){=}CH_2^+$], 139 [$C_5H_{11}\text{-}(CH_3)C{=}CH\text{-}C{\equiv}O^+$], and 99 [$C_5H_{11}\text{-}C{\equiv}O^+$]. These data suggest that the high-boiling products are aldol condensation products having structures such as **31**, **32**, or **33**. Since the rate of formation of these aldol products appears to be slower than the rate of equilibration of the lithium enolate anions derived from 2-heptanone (**20**), the compositions of the mixtures of enolate anions reported (Tables I–III) are believed to represent equilibrium concentrations. However, lacking accurate values for the relative rates of aldol condensation and enolate equilibration, we cannot exclude the possibility that the compositions reported are steady-state concentrations rather than equilibrium concentrations.



31



32



$$n\text{-}C_4H_9\text{—}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{—}CH_2\text{—}CO\text{—}CH_2\text{—}C_4H_9\text{-}n$$

33

Several experiments were performed to examine the use of lithium dimethylamide as a base for generating lithium enolate anions. The following procedure is illustrative. The ether was removed from 1 ml. of an approximately 1 *M* ethereal solution of methyllithium under reduced pressure and the residual lithium reagent, under a nitrogen atmosphere, was treated with 1.4 ml. of 1,2-dimethoxyethane containing 1.33 mmoles of dimethylamine. In other comparable experiments, it was shown that 1 mole of methane is rapidly evolved for each mole of methyllithium employed. Several milligrams of triphenylmethane (as an indicator) was added to the solution of lithium dimethylamide[23] and 2-methylcyclopentanone (105.4 mg. or 1.08 mmoles) was added until the red color of the triphenylmethyl anion was discharged. The resulting solution was concentrated under reduced pressure to remove dimethylamine and then diluted with 1 ml. of 1,2-dimethoxyethane; the concentration and dilution process was then repeated. At this time no dimethylamine could be detected (moist litmus paper) in a stream of nitrogen which had been passed through the solution. The solution was then added to 2.26 g. (22.2 mmoles) of acetic anhydride and the enol acetates were isolated from the mixture and analyzed in the usual way. The composition of the enol acetate mixture was 30% enol acetate **5** and 70% enol acetate **6** with the calculated yields being 28% of **1**, 12% of **5**, and 29% of **6**. Comparable yields and enol acetate compositions were obtained in two additional experiments. Thus, the conditions employed correspond to kinetically controlled enolate formation with triphenylmethyllithium.

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[23] Other experiments performed by Mr. Ben Tefertiller in our laboratories have demonstrated that lithium dimethylamide attacks the solvent, 1,2-dimethoxyethane, relatively rapidly so that it is not practical to store these solutions for more than 1 hr. Thus, these solutions are distinctly less stable than solutions of triphenylmethylpotassium.[16]

Electrolytic Reductive Coupling. VI.[1] Aromatically Substituted Ethylenes[2]

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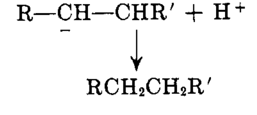
Received November 13, 1964

Illustrative examples (9-benzalfluorene and 2-phenyl-1,3-butadiene) are presented of the hydrodimerization of highly conjugated olefins upon electrolysis in relatively concentrated solution in quaternary ammonium electrolytes. When the ethylenic hydrogens are substituted by bulky groups, reduction occurs but hydrodimerization is blocked If the hydrocarbons are electrochemically reduced at a cathode voltage more positive than that of a given Michael acceptor, they may be reductively coupled with the acceptor. Thus 9-benzalfluorene couples with 1 mole of ethyl acrylate and with 2 moles of acrylonitrile; 8,8-diphenylbenzofulvene couples with 3 moles of acrylonitrile.

The polarographic reduction of conjugated olefins and the elucidation of the mechanism of the electrode process have been the subjects of extended studies.[3,4] When there is no intervention of proton donors, two rapid successive one-electron additions are indicated leading from the hydrocarbon (I) through the anion-free radical (II) to the dianion (III). The over-all

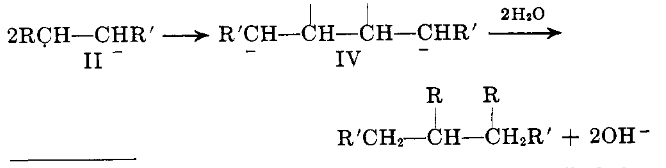
$$\underset{\text{I}}{\mathrm{RCH{=}CHR'}} \xrightarrow{e} \underset{\text{II}^-}{\mathrm{R\dot{C}H{-}CHR'}} \xrightarrow{e} \underset{^-\text{III}^-}{\mathrm{RCH{-}CHR'}}$$

effect is a two-electron uptake. When the intermediate II can react with a proton at the electrode surface, the sequence of events is modified as follows. The



$$\mathrm{I} + e \rightleftarrows \mathrm{II} + H^+ \longrightarrow \mathrm{R\dot{C}H{-}CH_2R'} + e \longrightarrow \mathrm{R{-}\underset{-}{C}H{-}CHR'} + H^+ \downarrow \mathrm{RCH_2CH_2R'}$$

formation of reduced dimers electrochemically has been ascribed in the case of stilbene[3] ($R = R' = C_6H_5$) to the coupling of two radicals (II) followed by the reaction of the dianion IV with water or other proton donor. It is considered that under polarographic conditions a dianion III reacts with water to form the dihydro compound,[5] whereas in the reduction of conjugated hydrocarbons (I) with sodium the intermediate III adds to another molecule of I to produce reduced dimer.[6] Reduction of stilbene in the presence of carbon dioxide has been reported to yield *meso*-diphenylsuccinic acid presumably by stepwise addition of electrons and carbon dioxide.[3]



$$\underset{\text{II}^-}{\mathrm{2R\dot{C}H{-}CHR'}} \longrightarrow \underset{\text{IV}}{\mathrm{R'\underset{-}{C}H{-}\overset{R}{C}H{-}\overset{R}{C}H{-}\underset{-}{C}HR'}} \xrightarrow{2H_2O} \mathrm{R'CH_2{-}\overset{R}{C}H{-}\overset{R}{C}H{-}CH_2R'} + 2OH^-$$

As part of our program on electrolytic reductive coupling of activated olefins in relatively *concentrated* aqueous solution,[7] we examined the behavior of 9-benzalfluorene, 2-phenyl-1,3-butadiene, and 8,8-diphenylbenzofulvene in hydrodimerizations and of the pairs 9-benzalfluorene–acrylonitrile, 8,8-diphenylbenzofulvene–acrylonitrile, and 9-benzalfluorene–ethyl acrylate in mixed reductive couplings. In the absence of mechanistic studies we have scrutinized the results for consistency with the proposal that carbanionic intermediates are involved.

Hydrodimerizations.—It is known that 9-benzalfluorene is a Michael acceptor.[8] Electrolysis of a solution of this hydrocarbon in aqueous methyltri-*n*-butylammonium *p*-toluenesulfonate containing dimethylformamide was carried to only partial conversion. A 66% yield (based on current) of the known hydro dimer 1,2-diphenyl-1,2-bis(9-fluorenyl)ethane was obtained. During the reaction the surface of the mercury cathode was red.[3]

2-Phenyl-1,3-butadiene in a similar experiment gave the known dihydro compound 2-phenyl-2-butene (V)

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[7] M. M. Baizer, *Tetrahedron Letters*, 973 (1963).

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