(15) Kindly supplied by Dr. R. M. Forbis, Biochemicals Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Del.

(16) All melting points are uncorrected; ir spectra were determined on Perkin-Elmer 21, 221, and 621 instruments, uv spectra on a Carey 14 instrument, NMR spectra on a Varian Associates A-60 instrument, and mass spectra on Consolidated 103 and 110B (high-resolution) instruments.

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Conjugate Addition Reactions of Alkali Diphenylmethides to Acrylic Esters

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In contrast to previous failure to obtain conjugate addition products from the reaction of alkali diphenylmethides to acrylic esters, reaction conditions can be selected to afford adducts even from methyl acrylate. Yields of addition products are increased as alkyl substituents are introduced into the acrylate. Certain highly substituted cinnamates do not undergo conjugate addition but instead undergo carbonyl addition to give low yields of ketones.

The addition of anions to conjugated carbonyl compounds has been the object of much study and ranks among the most useful of organic synthetic reactions. The mechanism for the reversible addition of weaker bases (conjugate bases of carbon acids strong enough to be deprotonated by Grignard reagents[1]) to conjugated systems is generally accepted as involving direct addition to the β carbon to produce an enolate (eq 1).[2] Recently the importance of a second mechanism, an electron transfer from the nucleophile to the enone, has been demonstrated (eq 2).[3]

$$\mathrm{N}{:}^- + \mathrm{C{=}C{-}C{=}O} \longrightarrow \mathrm{N{-}C{-}C{=}C{-}O}{:}^- \tag{1}$$

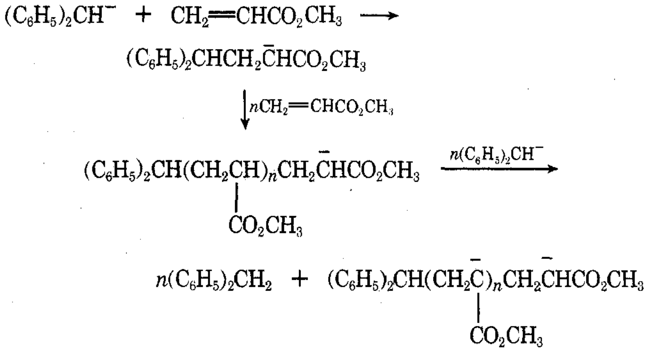
$$\begin{array}{c} \mathrm{N}{:}^- + \mathrm{C{=}C{-}C{=}O} \longrightarrow \mathrm{N}\cdot + \overbrace{\mathrm{C{\cdots}C{\cdots}C{\cdots}O^-}}^{5e} \\ \downarrow \\ \mathrm{N{-}C{-}C{=}C{-}O^-} \end{array} \tag{2}$$

Strongly basic nucleophiles, for example, diphenylmethide ion, are less commonly encountered as Michael donors. The reaction with ethyl cinnamate to give ethyl 3,4,4-triphenylbutyrate[4] and with ethyl α-phenylacrylate to give ethyl 2,4,4-triphenylbutyrate[5] and addition to several 1,1-diarylethylenes[6] have been reported, but an attempt to synthesize ethyl 4,4-diphenylbutyrate from potassium diphenylmethide and ethyl acrylate gave no adduct, although the color of the anion was discharged. Instead, polymerization of the ethyl acrylate apparently took place, and diphenylmethane was recovered.

We now find that sodium or potassium diphenylmethide will react with acrylates and substituted acrylates, and that the ease of reaction is remarkably affected by the structure of the acrylate, in a manner not predicted by a consideration of the usual addition mechanism of eq 1.

When sodium diphenylmethide in liquid ammonia was treated with 1 molar equiv of methyl acrylate, 80% of the diphenylmethane was recovered, 8% of a high-boiling ester was obtained along with a large amount of nonvolatile residue, and none of the Michael adduct, methyl 4,4-diphenylbutyrate, was detected. The reaction was interpreted as a polymerization of the methyl acrylate initiated by diphenylmethide ion, and neutralization of the unreacted diphenylmethide ion by the relatively acidic α hydrogens of the polyester (Scheme I). The small amount of distillable ester presumably corresponded to short chains of self-addition. Since the anionic polymerization of methyl acrylate is itself a series of conjugate additions reactions, it seemed possible to manipulate conditions so that mono adduct **1** could be obtained. Accordingly, a very dilute ethereal solution of methyl acrylate was added very slowly (2 hr) to sodium diphenylmethide. Work-up of this reaction afforded the mono adduct **1** in 10% yield, 60% of the diphenylmethane, and much nonvolatile material. Polymerization was further minimized by an increase in the mole ratio of sodium diphenylmethide to methyl acrylate to four. From this reaction the mono adduct **1** was obtained in 40% yield, the diadduct dimethyl 2-(2′,2′-diphenylethyl)glutarate **2** was isolated in 10% yield, and 83% (3.3 molar equiv) of the diphenylmethane was recovered. These results can be interpreted as indicating that the affinity of methyl acrylate for

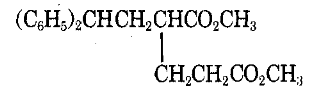
Scheme I



$$\begin{array}{l} (\mathrm{C_6H_5})_2\mathrm{CH}^- + \mathrm{CH_2{=}CHCO_2CH_3} \longrightarrow \\ \quad (\mathrm{C_6H_5})_2\mathrm{CHCH_2\bar{C}HCO_2CH_3} \\ \quad \downarrow n\mathrm{CH_2{=}CHCO_2CH_3} \\ (\mathrm{C_6H_5})_2\mathrm{CH(CH_2CH)}_n\mathrm{CH_2\bar{C}HCO_2CH_3} \ (\mathrm{CO_2CH_3}) \xrightarrow{n(\mathrm{C_6H_5})_2\mathrm{CH}^-} \\ \quad n(\mathrm{C_6H_5})_2\mathrm{CH_2} + (\mathrm{C_6H_5})_2\mathrm{CH(CH_2\bar{C})}_n\mathrm{CH_2\bar{C}HCO_2CH_3} \ (\mathrm{CO_2CH_3}) \end{array}$$

$(\mathrm{C_6H_5})_2\mathrm{CHCH_2CH_2CO_2CH_3}$

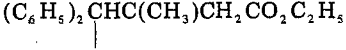
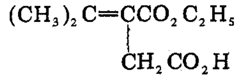
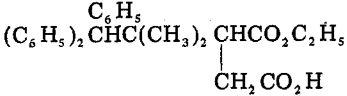
1



$(\mathrm{C_6H_5})_2\mathrm{CHCH_2CH(CH_2CH_2CO_2CH_3)CO_2CH_3}$

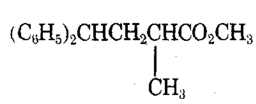
2

Table I
Reactions of Sodium Diphenylmethide with Acrylates

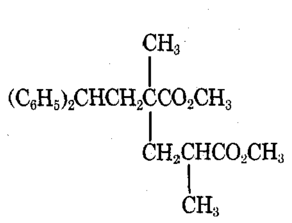
Registry no.	Acrylate	Product	Yield, %	Bp (mp), °C (mm)	Registry no.
96-33-3	$CH_2{=}CHCO_2CH_3$	1	40[a]	150–155 (0.8)[b]	10347-50-9
80-62-6	$CH_2{=}C(CH_3)CO_2CH_3$	3	40[c]	155–160 (0.8)[d]	57090-69-4
18707-60-3	$CH_3CH{=}CHCO_2CH_3$	$(C_6H_5)_2CHCH(CH_3)CH_2CO_2CH_3$	87[f]	155 (0.5)[g]	57090-72-9
41725-90-0	$CH_3CH{=}C(CH_3)CO_2CH_3$	$(C_6H_5)_2CHCH(CH_3)CH(CH_3)CO_2CH_3$	85	165 (0.5)[e]	57090-73-0
924-50-5	$(CH_3)_2C{=}CHCO_2CH_3$	$(C_6H_5)_2CHC(CH_3)_2CH_2CO_2CH_3$	90	160 (0.5)[h]	57090-74-1
49714-66-1	$(CH_3)_2C{=}(CH_3)CO_2CH_3$	$(C_6H_5)_2CHC(CH_3)_2CH(CH_3)CO_2CH_3$	80	170 (0.8)[e,i,j]	57090-75-2
25692-59-5	$C_6H_5CH{=}C(CH_3)CO_2CH_3$	$(C_6H_5)_2CHCH(C_6H_5)CH(CH_3)CO_2CH_3$	75	(116)[e]	57090-76-3
945-93-7	$C_6H_5C(CH_3){=}CHCO_2C_2H_5$	 $(C_6H_5)_2\underset{\mid\atop C_6H_5}{C}HC(CH_3)CH_2CO_2C_2H_5$	76	210 (0.8)[e]	57090-77-4
57090-70-7	 $(CH_3)_2C{=}\underset{\mid\atop CH_2CO_2H}{C}CO_2C_2H_5$	 $(C_6H_5)_2CHC(CH_3)_2\underset{\mid\atop CH_2CO_2H}{C}HCO_2C_2H_5$	55	(161)[e,k]	57090-78-5
3461-34-5	$(C_6H_5)_2C{=}CHCO_2CH_3$	$(C_6H_5)_2C{=}CHCOCH(C_6H_5)_2$	25	(98)[e]	57090-79-6
57090-71-8	$C_6H_5C(CH_3){=}C(CH_3)CO_2CH_3$	$C_6H_5C(CH_3){=}C(CH_3)COCH(C_6H_5)_2$	16	185–190 (0.5)[e]	57090-80-9
22035-53-6	$(CH_3)_2C{=}C(CO_2CH_3)_2$	$(C_6H_5)_2CHC(CH_3)_2CH(CO_2CH_3)_2$	75	(109)[e]	57090-81-0

[a] 4:1 ratio of sodium diphenylmethide, slow addition of dilute ethereal solution of methyl acrylate. [b] Hydrolyzed to 4,4-diphenylbutyric acid, mp and mmp 105°. [c] 2:1 ratio of sodium diphenylmethide, slow addition of dilute ester. [d] Hydrolyzed to 2-methyl-4,4-diphenylbutyric acid,[e] mp 95°. [e] Satisfactory CH analysis was obtained for this compound and was submitted for review. [f] When potassium diphenylmethide was used the yield was 60%. [g] Hydrolyzed to 3-methyl-4,4-diphenylbutyric acid,[e] mp 113° (reported[7] 113°). [h] Hydrolyzed to 3,3-dimethyl-4,4-diphenylbutanoic acid,[e] mp 129°. [i] The ester was not hydrolyzed with base or aqueous acid. The ester was cyclized with concentrated sulfuric acid to 2,3,3-trimethyl-4-phenyl-1-tetralone,[e] mp 137°. [j] The starting material was prepared by the condensation of acetone with diethyl 1-carbethoxyethanephosphonate.[8] [k] Because of the carboxyl proton a 2:1 ratio of sodium diphenylmethide was used.

an ester α anion is greater than for the diphenylmethide ion, but that dilution of the ester or an increase in the relative amount of diphenylmethide ion favored formation of the mono Michael adduct. To test the postulate of proton transfer from polyester to anion, an experiment was carried out with potassium diphenylmethide and methyl methacrylate. Here the polymeric ester has no α hydrogen, and as expected the color of the diphenylmethide ion was not discharged by 1 mol of ester. Work-up of this mixture gave 80% of the diphenylmethane, 12% of high-boiling ester, and a larger quantity of nonvolatile residue. Repetition of the experiment with sodium diphenylmethide gave 70% recovery of the diphenylmethane and 20% of high-boiling ester. Finally, slow addition of a dilute ethereal solution of methyl methacrylate to 1 mol of sodium diphenylmethide gave 60% recovery of diphenylmethane, 15% of the 1:1 adduct, methyl 2-methyl-4,4-diphenylbutyrate (**3**), and 5% of the 1:2 adduct, dimethyl 2,4-dimethyl-2-(2′,2′-diphenylethyl)glutarate (**4**). The yield of **3** reached a maximum at 40% when the ratio of diphenylmethide to methyl methacrylate was increased to 2:1.


$(C_6H_5)_2CHCH_2\underset{\mid\atop CH_3}{C}HCO_2CH_3$

3


$(C_6H_5)_2CHCH_2\overset{CH_3\atop\mid}{\underset{\mid\atop CH_2\underset{\mid\atop CH_3}{C}HCO_2CH_3}{C}}CO_2CH_3$

4

It was surprising that the presence of an α methyl group seemed to facilitate the conjugate addition, since the adduct is a tertiary anion. Further investigation with other substituted acrylates revealed that the normal (1:1) adduct can be obtained in good yield with methyl crotonate, methyl tiglate [methyl (*E*)-2-methyl-2-butenoate], ethyl trimethylacrylate, methyl isopropylidenemalonate, methyl α-methylcinnamate, and methyl β-methylcinnamate. No carbonyl addition was observed with these compounds; however, with ethyl 3,3-diphenylpropenoate and ethyl dimethylcinnamate the Michael adduct was not obtained and only carbonyl addition products were obtained. These results are summarized in Table I.

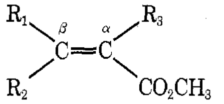
Possibly substituents on the acrylate moiety offer steric hindrance to addition, and this hindrance is overcome only by a very strong nucleophile (diphenylmethide), and not the less nucleophilic ester anion. This seems to be an unsatisfactory explanation, since it would be unlikely that the course of the reaction can be completely changed from polymerization of methyl acrylate (with a 1:1 mole ratio of reactants) to simple addition of methyl crotonate.[9]

An alternative explanation is that with very strong nucleophiles such as diphenylmethide ion, electron density at the β carbon in the transition state for addition is important. Calculation of the electron distribution in acrylates lends support to this idea, since increasing substitution on the double bond *decreases* the electron density at the β carbon, thus facilitating attack by the nucleophile; presumably electron distribution in the transition state is even more important than in the ground state. There may still be some steric effect, since diphenylmethide does not undergo conjugate addition to dimethylcinnamate and diphenylacrylate, only a small amount of carbonyl adduct being produced.

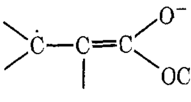
The electron density calculations are listed in Table II.

The stabilization introduced by substitution at the β carbon could also suggest the electron transfer mechanism, since the radical anion product of electron transfer (**5**) would also be stabilized by substitution. However, in view of the oxidation potential of diphenylmethide ion (−1.1 V[10]) and the reduction potential of acrylic esters (−1.78

Table II
Calculated Electron Densities in Acrylate Esters



R_1, R_2	R_3	α	β
H, H	H	4.0448	3.9498
H, H	CH_3	4.0408	3.9643
CH_3, H	H	4.0738	3.9163
CH_3, H	CH_3	4.0638	3.9319
CH_3, CH_3	H	4.1101	3.8973
CH_3, CH_3	CH_3	4.0910	3.9180



5

V[11]), electron transfer in this system appears to be highly unlikely.[10]

Experimental Section

The procedures for the reactions of acrylates with alkali diphenylmethides are so similar that only one is given in detail. Variations are indicated in the Discussion or in Table I, as are physical constants.[12]

Reactions of Acrylic Esters with Alkali Diphenylmethides. Methyl 2,3,3-Trimethyl-4,4-diphenylbutanoate. Sodium diphenylmethide was prepared by addition of 16.8 g (0.1 mol) of diphenylmethane in 50 ml of ether to 0.1 mol of sodium amide in liquid ammonia, prepared from 2.3 g (0.1 g-atom) of sodium and a small amount of anhydrous ferric chloride in 250 ml of liquid ammonia. The resulting deep orange solution was stirred for 10 min and 12.8 g (0.1 mol) of methyl trimethylacrylate in 25 ml of ether was added during 10 min. To the resulting green solution was added 6 g of ammonium chloride. The ammonia was replaced by ether and the mixture was stirred with 250 ml of 0.1 *N* hydrochloric acid. The aqueous layer was separated and extracted with 100 ml of ether, and the combined ether solutions were dried over sodium sulfate and concentrated to give 28 g of a pale yellow liquid. Distillation afforded 6 g of starting materials [bp 70–200°/(1 mm)] and 22 g of methyl 2,3,3-trimethyl-4,4-diphenylbutanoate, bp 170° (0.8 mm). A solution of 4 g of the ester was dissolved in 20 ml of cold concentrated sulfuric acid, and the orange solution was stirred for 5 min and poured onto ice. Recrystallization from petroleum ether afforded 1.5 g (40%) of 4-phenyl-2,3,3-trimethyl-1-tetralone, mp 137°.

Acknowledgement. The authors wish to thank Dr. H. A. Kuska, who provided the CNDO/2 programs from QCEP and assisted in their use.

Registry No.—Sodium diphenylmethide, 5152-68-1; 2-methyl-4,4-diphenylbutyric acid, 57090-82-1; 3,3-dimethyl-4,4-diphenylbutanoic acid, 57090-83-2; 2,3,3-trimethyl-4-phenyl-1-tetralone, 57090-84-3; diphenylmethane, 101-81-5; sodium amide, 7782-92-5.

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(9) See T. Tsuruta, *Prog. Polym. Sci. Jpn.*, **3**, 1 (1972).
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(11) L. Meites, P. Zuman, et al., "Electrochemical Data", Part I, Vol. A, Wiley, New York, N.Y., 1974.
(12) Analyses were by Micro-Tech Laboratories, Skokie, Ill.

Oxidative Addition of Sodium and Zinc Arenesulfinates to Derivatives of Diazenedicarboxylic Acid[1,2]

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1,2-Diazenedicarboxamide (DDA), a number of substituted diazenedicarboxamides, and diethyl diazenedicarboxylate react with the sodium and zinc salts of *p*-toluene- and benzenesulfinic acids in Me$_2$SO or DMF to give addition products (I) and/or addition–elimination products (II). With DDA and the N,N-disubstituted derivatives, the trisubstituted diazane (I) is unstable under alkaline conditions generated and undergoes elimination. The resulting products, sulfonyldiazanecarboxamides (II), are formed in high yield. DDA also undergoes oxidative addition with sodium arenesulfinates in aqueous media and subsequent elimination to give II in nearly quantitative yield. Symmetrically substituted diazenedicarboxamides, exemplified by *N,N*′-diethyl-1,2-diazenedicarboxamide and *N,N*′-diphenyl-1,2-diazenedicarboxamide, react with arenesulfinate salts in Me$_2$SO to yield a mixture of I and II. The latter may result from elimination of an isocyanate from I under alkaline conditions. Tetrasubstituted diazenedicarboxamides, such as *N,N,N*′*,N*′-tetramethyl-1,2-diazenedicarboxamide (TMDDA), and diazenedicarboxylates, such as diethyl diazenedicarboxylate (DEDD), afford only the trisubstituted product (I), the latter or its anion being stable under basic conditions.

α-Carbonyl diazenes may be characterized as oxidants by virtue of their tendency to act as strong electron acceptors. Oxidation may result in the formation of addition products involving a diazene and substrate.[3] The currently described reaction of α-carbonyl diazenes with salts of arenesulfinic acids to give products possessing the general structures I and II may be placed in this category. The oxidation of arenesulfinic acids by diphenyldiazene (azobenzene) and certain substituted analogues has been reported,[4,5] the reaction proceeding by addition of the acid across the diazene