TABLE II
ACONIC ACIDS (IV)

R	Yield, %	Mp, °C	λ_{max}^{EtOH}, mμ (ε)	C, % Calcd	C, % Found	H, % Calcd	H, % Found
C_3H_7	70	124–125[a]	216 (10,600)	...	...	...	...
C_5H_{11}	73	133–133.5	217 (10,300)	60.59	60.52	7.12	7.07
C_6H_{13}	75	125–126	218 (10,300)	62.25	62.41	7.60	7.69
C_8H_{17}	70	129–130	216 (12,500)	64.98	64.92	8.39	8.35

[a] See ref 5.

TABLE III
ALKYLIDENESUCCINIC ACIDS (I)

R	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found
C_3H_7	70	157.5–158[a]	...	...	...	...
C_5H_{11}	75	141–142	59.98	59.97	8.05	7.88
C_6H_{13}	82	130–131	61.66	61.65	8.47	8.49
C_8H_{17}	70	129–130	64.43	64.46	9.15	9.06

[a] Lit.[5] mp 159°.

TABLE IV
3,4-DIBROMO-3-CARBOXYALKANOIC ACIDS (II)

R	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found
C_3H_7	70	170–170.5	28.98	29.19	3.95	3.70
C_5H_{11}	90	140–141	33.46	33.75	4.48	4.56
C_6H_{13}	95	142–142.5	35.29	35.39	4.85	4.78
C_8H_{17}	90	124.5–125	38.82	39.09	5.51	5.49

identified by its infrared spectra. A number of the γ-keto acids prepared in this way are shown in Table I.

γ-Hexylaconic Acid (IV, R = C_6H_{13}).—A mixture of 11.5 g (0.03 mole) of 3-carboxy-3,4-dibromodecanoic acid and 90 ml (0.09 mole) of 1 *N* potassium hydroxide solution was stirred for 10 min at 20°. The alkaline solution was acidified with dilute sulfuric acid. The white precipitate was collected and recrystallized from *n*-hexane to give 4.9 g (75%) of white needles: mp 125–126°; λ_{max}^{EtOH} 218 mμ (ε 10300); infrared 1738, 1710 (carbonyl), 1630 cm^{-1} (C=C) (see Table II).

The aconic acid IV (R = C_6H_{13}) was also converted into the corresponding γ-keto acid III (R = C_6H_{13}) by treatment with excess 1 *N* alkaline solution at 70–90° for 1 hr in quantitative yield.

Methyl γ-Hexylaconate.—The esterification was carried out with diazomethane. Rapid distillation gave a fraction boiling at 116° (3 mm): $n^{20}D$ 1.4600; infrared 1755 (lactone carbonyl), 1715 (ester carbonyl), 1655 cm^{-1} (double bond).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 64.07; H, 8.37.

Decomposition of Ethyl Diazoacetate by a π-Allylic Palladium Chloride Complex

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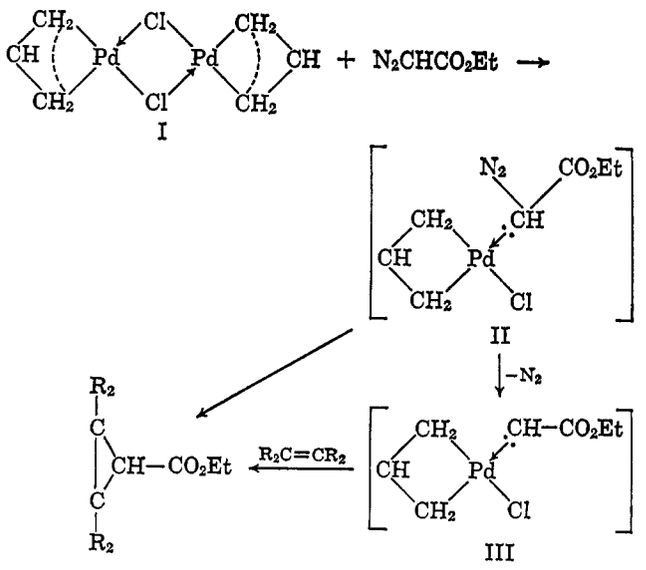
It is well known that diazo compounds are decomposed thermally, photochemically, and catalytically[1] with copper or copper salts. We have found that di-μ-chlorodi-π-allyldipalladium (I)[2] catalytically decomposes ethyl diazoacetate under very mild conditions. The products of this decomposition appear to arise from a carbene or related intermediate. A proposed mechanism is given in Scheme I. This mechanism is supported by the fact that bridged palladium complexes (I) are split by nucleophiles,[3] and ethyl diazoacetate may act in this fashion to give II. The complex II may then lose nitrogen to form III or may react directly with ethyl diazoacetate or the solvent.

SCHEME I



The results of these studies are summarized in Table I. It is of interest to note that palladium complex catalysis employed in the decomposition of ethyl diazoacetate gives virtually all diethyl fumarate, whereas the copper catalysis gives mainly diethyl maleate.[4]

The complex I is an efficient catalyst for the reaction of 2-butyne and ethyl diazoacetate at 0–10° to give ethyl 1,2-dimethyl-1-cyclopropene-3-carboxylate (IV); copper or copper salts are effective only at higher temperatures (65–120°). (See Scheme II.)

The cyclopropene IV did not react further even in the presence of a 5 molar excess of ethyl diazoacetate with the palladium complex even at 75°. On the other hand, the use of copper in refluxing benzene catalyzes the reaction of the cyclopropene IV and ethyl diazoacetate, and a small amount of the new compound, diethyl 1,3-dimethylbicyclo[1.1.0]butane-2,4-dicarboxylate (V), and two isomers of diethyl 3,4-dimethylmuconate were obtained.

(1) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 108–156.

(2) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

(3) S. D. Robinson and B. L. Shaw, *ibid.*, 4807 (1963).

(4) Control experiments with the palladium complex or copper with diethyl maleate or fumarate in refluxing benzene for 1.5 hr showed no isomerization.

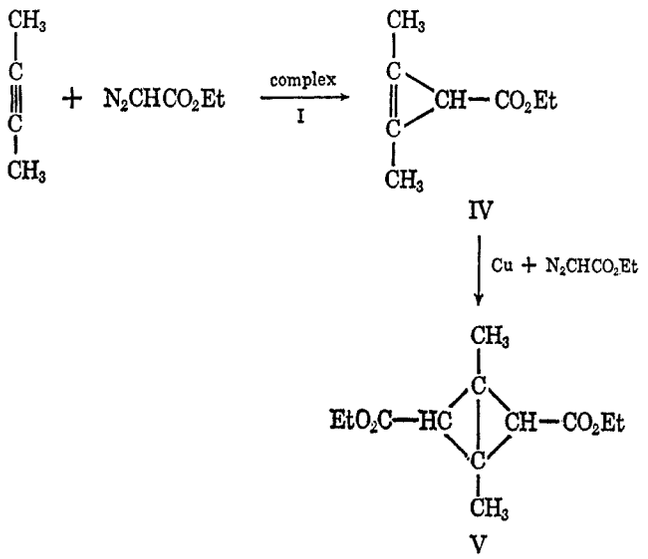
TABLE I

DECOMPOSITION OF ETHYL DIAZOACETATE IN VARIOUS SOLVENTS USING A PALLADIUM COMPLEX CATALYST

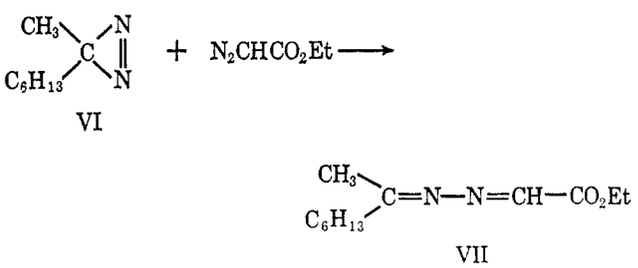
Solvent	Reaction conditions	Product	Yield, %[a]
Cyclohexene	5–10°, 5-hr addition time	Ethyl bicyclo[4.1.0]heptane-3-carboxylate[b]	47
Ethyl vinyl ether	0–5°, 10-hr addition time	1-Ethoxycyclopropane[c]	21
2-Butyne	0–10°, 6-hr addition time	Ethyl 1,2-dimethyl-1-cyclopropene-3-carboxylate	24.2
Ethyl 2,3-dimethyl-2-cyclopropene-1-carboxylate	0–10°, 5 molar excess of ethyl diazoacetate 25–30°, 5 molar excess of ethyl diazoacetate 65–75°, 5 molar excess of ethyl diazoacetate	Diethyl fumarate and starting material	
Acetonitrile	0–5°, 6.5-hr addition time	2-Methyl-5-ethoxyoxazole[d]	16.3
Methyl *n*-hexyldiazirine	0–10°, 1.5-hr addition time	Ethyl 5-methyl-3,4-diaza-2,4-undecadienenoate	

[a] Based on ethyl diazoacetate. [b] Fr. Abel, R. Brunner, and D. Mangelli, *Helv. Chim. Acta*, **12**, 19 (1929). [c] A. Dyakonov and N. A. Lugovtsova, *J. Gen. Chem. USSR*, **21**, 921 (1951). [d] R. Huisgen, H. Konig, G. Binsch, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961).

SCHEME II



SCHEME III



Methyl *n*-hexyldiazirine (VI),[5] which was inert to the palladium complex, and a 4 molar excess of ethyl diazoacetate reacted in chloroform in the presence of the palladium complex. Attempts to isolate the product by distillation, column chromatography, and crystallization failed. However, vapor phase chromatography showed the presence of a single high-boiling compound in addition to the diethyl fumarate. This compound was collected and identified as the azine VII. The reaction may have proceeded through ethyl 1-methyl-1-*n*-hexyl-2,4-diazabicyclo[1.1.0]butane-3-carboxylate, which subsequently rearranged to compound VII. (See Scheme III.)

Experimental Section

Ethyl Diazoacetate.[6]—Since large quantities of ethyl diazoacetate were prepared, extensive safety tests were performed. It was found that ethyl diazoacetate was insensitive to impact and static charge, and failed as a base charge in a blasting cap, but that it did decompose on a copper block heated to 130° in 6 min. During the course of this work, 5 lb of ethyl diazoacetate was distilled without incident in 100-g batches at 35° (5–6 mm).

Ethyl 1,2-Dimethyl-1-cyclopropene-3-carboxylate (IV).—A solution of 57 g of ethyl diazoacetate (0.5 mole) in 70 g of 2-butyne (1.3 moles) was added dropwise from a capillary dropping funnel over 6 hr to a cooled solution of 100 g of 2-butyne (1.85 moles), 5 g sodium bicarbonate, and 1.5 g of di-μ-chlorodi-π-allyldipalladium kept at 0–5° by means of an ice bath. Solvent was removed from the orange-red solution, and 130 g of 2-butyne was recovered. The residue was diluted with methylene chloride, filtered, and concentrated. Distillation through a 6-in. helices-packed column gave 17.1 g of IV, a colorless liquid, bp 35.5–36° (2.0 mm), yield 24.2%.

The infrared spectrum of the title compound showed important absorptions at 3020 (w), 1725 (s), 1645 (w), 1370 (m), 1175 (s), and 1050 (m) cm^{-1}. The nmr spectrum showed signals[7] at τ 8.77, 5.91, 8.0, and ~8.0 (>C*H*–CO_2Et, integration of the spectrum showed seven hydrogens in the methyl region). The mass spectrum showed significant peaks at mass numbers of 140 (mol wt), 95, and 67.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.56; H, 8.62; O, 22.82. Found: C, 68.40; H, 8.82; O, 22.88.

Diethyl 1,3-Dimethylbicyclo[1.1.0]butane-2,4-dicarboxylate (V).—A solution of 11.4 g of ethyl diazoacetate (0.1 mole) in 10 ml of benzene was added over 1.5 hr to a refluxing mixture of 3.8 g of ethyl 1,2-dimethyl-1-cyclopropene-3-carboxylate (0.02 mole), 0.2 g of powdered copper, and 10 ml of benzene. After the evolution of nitrogen had ceased, the mixture was filtered and concentrated. Gas chromatography was performed on a 2-ft column packed with XE-60 on Diatoport S and programmed from 75 to 250° at 11°/min. This showed the presence of 17% ethyl 1,2-dimethyl-1-cyclopropene-3-carboxylate, 19% diethyl fumarate, 26% diethyl maleate, 22% diethyl 1,3-dimethylbicyclo[1.1.0]butane-2,4-dicarboxylate, and 16% of two isomers of diethyl 3,4-dimethylmuconate. The percentages of products were determined from their areas.

The infrared spectrum (film) of the title compound showed important absorptions at 1740 (s), 1372 (m), 1165 (s), and 1035 (m) cm^{-1}. The nmr spectrum showed signals[7] at τ 8.75, 8.45, and 5.90. The mass spectrum showed significant peaks at mass numbers of 226 (mol wt), 181, 153, and 125.

(5) E. Schmitz and R. Ohme, *Angew. Chem.*, **73**, 115 (1961).

(6) N. Rabjohn, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, pp 424–426.

(7) Relative areas of nmr peaks were consistent with assignments.

The diethyl 3,4-dimethylmuconate isomers were isolated by gas chromatography and the structure was verified by infrared, nmr, and mass spectrometry.

Ethyl 5-Methyl-3,4-diaza-2,4-undecadienenoate (VII).—A solution of 22.8 g of ethyl diazoacetate (0.2 mole) in 20 ml of chloroform was added dropwise over 1.5 hr to a solution of 7.0 g of methyl *n*-hexyldiazirine (0.05 mole), 0.5 g of di-μ-chlorodi-π-allyldipalladium, and 10 ml of chloroform at 0–10°. After the evolution of nitrogen ceased, the orange solution was concentrated and analyzed by gas chromatography. The major peak was identified as diethyl fumarate, and the only other product was collected and identified as the title compound. The infrared spectrum (film) showed absorptions at 1755 (s), 1730 (s), 1640 (m), 1600 (w), 1375 (m), 1195 (s), 1040 (m), and 720 (w) cm^{-1}. The nmr spectrum showed signals at τ 8.65, 8.08, 5.66, and 2.63. The *n*-hexyl peaks in the nmr spectrum were complicated and not reported. The mass spectrum showed significant peaks at mass numbers of 183, 181, 169, and 153.

Reduction of Conjugated Double Bonds with Sodium Borohydride

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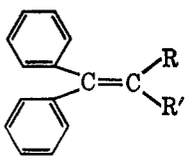
The use of sodium borohydride to effect the reduction of aldehydes and ketones is now a well-established and widely utilized procedure. More recently, its application in large excess to the preparation of alcohols from carboxylic acid esters has been reported.[1] The employment of sodium borohydride to reduce carbon–carbon double bonds, however, has not been widespread and there are but few references to such use. Shechter and co-workers[2] used this reagent to prepare a series of nitroalkanes starting with the corresponding α,β-unsaturated nitroalkenes; Le Moal and co-workers[3] employed potassium borohydride to reduce ethyl α-cyano-β-phenylcinnamate (Ia) to the appropriate hydrocinnamate; Adank and co-workers[4] converted a series of substituted 2,5-dioxo-5H-pyrrolo[2,1-*a*]-isoindoles to their dihydro derivatives using sodium borohydride; and, finally, Meschino and Bond[5] used the same reagent to reduce various ylidene cyanoacetates to their corresponding hydroxymethylpropionitriles, the carboethoxy group being attacked in addition to the double bond.



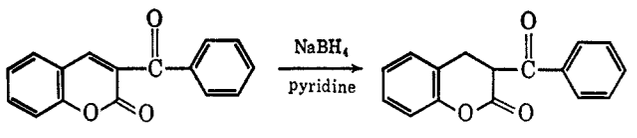
Ia, R = $COOC_2H_5$; R′ = CN
b, R = R′ = $COOC_2H_5$
c, R = R′ = CN

The application of sodium borohydride to the selective reduction of the ethylenic linkage of a number of simple organic compounds exhibiting α,β unsaturation is illustrated in Table I. These chemical reductions were carried out in a facile manner and within a short period of time. Equimolar quantities of the appropriate reactant and sodium borohydride in ethanol or 2-propanol were stirred for 3–4 hr in the cold and at room temperature, and the products were isolated by dilution of the reaction mixture with water, extraction of the aqueous mixture with ether or ethyl acetate, and distillation of the organic extracts. The yields of final material were generally good, although optimal conditions regarding temperature, reaction time, and solvent effects were not elucidated. The products thus prepared exhibited infrared spectra, refractive indices, and boiling points or melting points which were the same as those of materials obtained by independent means of synthesis. Physical properties are shown in Table II.

TABLE I
SODIUM BOROHYDRIDE REDUCTIONS

Reactant	Product	Yield, %
$CH_3CH{=}C(COOC_2H_5)_2$	$CH_3CH_2CH(COOC_2H_5)_2$	59
$(CH_3)_2C{=}C(COOC_2H_5)_2$	$(CH_3)_2CHCH(COOC_2H_5)_2$	74
$C_6H_5CH{=}C(COOC_2H_5)_2$	$C_6H_5CH_2CH(COOC_2H_5)_2$	69
$C_6H_5CH{=}C(CN)CONH_2$	$C_6H_5CH_2CH(CN)CONH_2$	81
$CH_2{=}C(COOC_2H_5)C_6H_5$	$CH_3CH(COOC_2H_5)C_6H_5$	80
$CH_2{=}CHCOOC_2H_5$	$CH_3CH_2COOC_2H_5$	25

In addition, 3-benzoylcoumarin (II) was converted to 3-benzoyl-3,4-dihydrocoumarin (III) by means of sodium borohydride in pyridine. The use of pyridine as a solvent to promote the preferential reduction of an ethylenic moiety over a ketone carbonyl group has been reported by Adank and co-workers.[4]



II III

The delocalization of the π-electrons of the ethylenic linkage, which occurs through conjugation of the carbon–carbon double bond with the ester, nitrile, phenyl, and/or amide groups present in the various reactants, results in the creation of an electrophilic center which is capable of being attacked by a nucleophile, in this case the borohydride anion. The failure[3] of diethyl diphenylmethylenemalonate (Ib) to undergo this type of reaction with potassium borohydride or other borohydrides is probably due to the lack of a relatively sufficiently strong and localized electro-

(1) M. S. Brown and H. Rapoport, *J. Org. Chem.*, **28**, 3261 (1963).
(2) H. Shechter, D. E. Ley, and E. B. Robertson, Jr., *J. Am. Chem. Soc.*, **78**, 4984 (1956).
(3) H. Le Moal, R. Carrie, and M. Bargain, *Compt. Rend.*, **251**, 2541 (1960).
(4) K. Adank, H. A. Pfenninger, W. G. Stoll, and M. Viscontini, *Helv. Chim. Acta*, **46**, 1030 (1963).
(5) J. A. Meschino and C. H. Bond, *J. Org. Chem.*, **28**, 3129 (1963).