reaction mixture was stirred for 4.5 hr. under a Dry Ice–acetone condenser. The liquid ammonia was then allowed to evaporate on the steam-bath while 300 ml. of ether was being added. The resulting ether suspension was refluxed for 15 min., and 300 ml. of water was added. The two layers were separated. The aqueous layer (to which was added a 5% sodium hydroxide extract of the ether layer) was made strongly acidic and the resulting mixture extracted with methylene chloride. The methylene chloride layer was dried over Drierite and the solvent removed. The residue was dissolved in ether and the solution concentrated. Approximately 80 ml. of hexane was added and the solution cooled to precipitate 25.8 g. (85%) of α,α,β-triphenylpropionic acid (IV), m.p. 128–130°. One recrystallization from a mixture of ether and hexane gave 25.2 g. (83%) of IV, m.p. 130–131.5°; reported m.p. 130–132°,[19] 125–127°.[23]

α,α,β-Triphenylbutyric Acid (V).—This acid, m.p. 146–147°, was obtained in an 89% yield by the alkylation of diphenylacetic acid with α-phenylethyl chloride essentially as described for the benzylation. One recrystallization from methanol containing a small amount of water gave 27.5 g. (87%) of V, m.p. 148–148.5°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.47; H, 6.26.

Admixture of this acid with diphenylacetic acid (m.p. 147.5–148°) lowered the melting point to 118–123°.

A sample of this acid was converted to the acid chloride by means of thionyl chloride. To the crude acid chloride was carefully added excess liquid ammonia[24] (vigorous reaction) and the liquid ammonia allowed to evaporate. After washing with water, the solid was collected on a funnel and recrystallized from methanol to give α,α,β-triphenylbutyramide, m.p. 147–147.5°.

Anal. Calcd. for $C_{22}H_{21}ON$: C, 83.77; H, 6.71; N, 4.44. Found: C, 84.05; H, 6.88; N, 4.28.

$\alpha,\alpha,\beta,\beta$-Tetraphenylpropionic Acid (VI).—This acid, m.p. 189–192°, was obtained in a 42% yield by the alkylation of 0.051 mole of diphenylacetic acid with 0.05 mole of benzhydryl bromide in 600 ml. of liquid ammonia essentially as described for the benzylation. One recrystallization from glacial acetic acid gave 7.8 g. (41%) of VI, m.p. 192–193.5° dec.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.68; H, 5.86. Found: C, 85.53; H, 6.03.

There was also obtained 4.1 g. (49%) of tetraphenylethylene, m.p. and mixed m.p. 221–222°. This product was isolated by removing the solvent from the ethereal layer. The crude product was recrystallized from methanol.

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(23) See Schlenk and co-workers, reference 15.

(24) A preliminary attempt to prepare the amide from the acid chloride and concentrated ammonium hydroxide in the usual manner gave a product that was difficult to purify.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

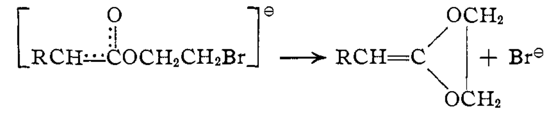
Oxygen Alkylation of Negatively Substituted Esters[1]

BY CHARLES O. PARKER

RECEIVED MAY 24, 1956

The anions of the mono-β-bromoethyl esters of cyanoacetic, malonic, acetoacetic and p-nitrophenylacetic acids undergo intramolecular displacement of bromide ion to yield substituted ketene ethylene acetals. From the β-bromoethyl esters of acetic, isobutyric, phenylacetic and diphenylacetic acids under the same conditions, no evidence of intramolecular alkylation could be found. The latter group of esters gave a mixture of products apparently derived from intermolecular interaction.

In connection with other work, reactions of certain negatively substituted β-bromoethyl esters were observed wherein intramolecular displacement of halide ion was apparently performed by the ester enolate ion to give oxygen alkylation products as



Identification of the products as substituted ketene ethylene acetals rests upon agreement between analytical data, infrared and ultraviolet absorption spectra. These data are presented in Table I.

Esters which have been studied in this investigation fall into two groups. Those bearing an α-substituent contributing to a resonance-stabilized anion underwent intramolecular oxygen alkylation as described. Bromoethyl cyanoacetate (I), (mono)-malonate (II), p-nitrophenylacetate (III) and acetoacetate (IV) comprise this group. Choice of base necessary to promote reaction of these esters was not critical. Cyanoketene-ethylene acetal could be isolated from I by reaction with alcoholic potassium hydroxide, with sodium methoxide or with potassium carbonate in water. These experiments confirmed the previously reported[2] relative resistance to attack by base of negatively substituted ketene acetals besides illustrating that oxygen alkylation occurred even in hydroxylic media. In order to avoid accompanying direct displacement of halide ion by base, reactions generally were performed using sodium hydride suspended in tetrahydrofuran. Under these conditions reaction was rapid, exothermic and its completeness measurable by observing hydrogen evolution. Isolation of product was accomplished simply by evaporating the filtrate from the precipitated sodium bromide. The yields of crude, solid products were greater than 90% from all esters except III. However, the fact that the products as initially isolated were not completely pure and required considerable purification (especially the p-nitrophenylketene ethylene acetal) suggests that other products were formed in the reaction in varying amounts. The possibility that p-nitrophenylketene ethylene acetal was being lost in gross amounts due to decomposition by adventitious moisture or by solubility in recrystallization solvents was checked and rejected. It proved to be stable toward water and hot alcohol and to be sparingly soluble in most solvents in the cold.

The second group of esters examined included bromoethyl acetate (V), isobutyrate (VI), phenylacetate (VII) and diphenylacetate (VIII). None of these gave products which appeared to include a ketene ethylene acetal structure. Neither was

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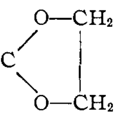
(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) S. M. McElvain and J. P. Schroeder, THIS JOURNAL, **71**, 47 (1949).

TABLE I

KETENE ETHYLENE ACETALS, R—CH=C



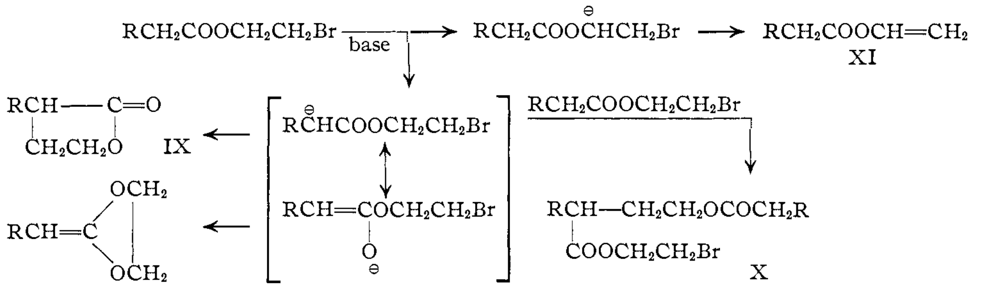
R	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	λmax, mμ[a]	ε × 10^{-4}	Infrared ν, cm.$^{-1}$
-CN[b]	83-86	54.05	4.50	12.61	54.03	4.23	12.00	226	1.43	2195(CN); 1656(C=C)
-COOEt	48.5-50.5	53.16	6.33		53.00	5.60		236	1.44	1692(C=O); 1621(C=C)[c]
p-O_2N-C_6H_4	185-186	57.97	4.35	6.76	57.56	4.47	6.71	355 238	1.79 1.04	1655(C=C); 1590(NO_2)
MeCO-	66.5-69	56.25	6.25		56.02	6.38		250	2.36	1674, 1643, 1619, 1584[d]

[a] Tetrahydrofuran solution. [b] NC—CH=C$(OMe)_2$, m.p. 41.5–42°, *cf.* ref.[1] [c] Melted capillary layer. [d] CH_2Cl_2 solution.

there evidence of intramolecular carbon alkylation (IX). Except for unreacted starting material the products consisted of much higher-boiling liquids, still containing bromine, which from the positions of the carbonyl bands in their infrared spectra, were adjudged to be intermolecular carbon-alkylation products (X). This group of esters was further distinguished from the first group by the sluggishness of their reactions with sodium hydride. At room temperature the rates of reaction were extremely slow. At the reflux temperatures of dioxane, di-*n*-butyl ether and at 150° in diphenyl ether the reactions proceeded enough to determine the nature of the products.

Discussion

Four possible reaction sequences which may occur on treatment of β-bromoethyl esters with base and involving bromide ion displacement may be outlined as



The α-substituted butyrolactones (IX) are known compounds[3,4] differing markedly in physical properties from the isomeric products actually isolated. The only other alternative isomeric structures, the corresponding vinyl esters (XI), were given statutory consideration. A representative member of this group, vinyl cyanoacetate, was characterized by extremely facile aqueous hydrolysis, giving cyanoacetic acid and acetaldehyde. Identification of the product derived from β-bromoethyl cyanoacetate as cyanoketene ethylene acetal was indicated clearly by inspection of its infrared spectrum. This showed complete disappearance of the carbonyl ester group and the presence of a cyano group and a carbon–carbon double bond (see Table I).

Whereas oxygen alkylation products of esters have never been isolated previously as the result of nucleophilic displacement by the ester enolate ion, participation of the ester carbonyl oxygen atom in reactions of this sort is of course well known.[5] However, what appears to be involved in the present situation is competition between two centers of electron density of an ambidentate ion.[6a] The ester anion, with its charge distributed between the α-carbon and carbonyl oxygen atoms, can displace bromide ion irreversibly in either case with formation of a sterically favorable five-membered ring. Consideration[6b] of the geometry of the resonance-stabilized ester anion shows that of structures sterically arranged for displacement of halide ion the one involving attack by the carbanion requires a *cis* relationship of the carbonyl and electronegative α-substituent groups and therefore less separation of negative charges in the transition state than would be required for attack by the oxygen anion.

Comparison of the ultraviolet absorption spectrum of carbethoxyketene ethylene acetal with that of ethyl β,β-diethoxyacrylate[7] shows very close correspondence in both the positions and intensities of absorption maxima. Compared with the spectra of ethyl crotonate[8] and ethyl β-ethoxycrotonate,[9] it is apparent that in both of the ketene acetals and the enol ether the alkoxyl substituents enhance conjugation of the double bond with the carbonyl group, *i.e.*, the absorption maxima are shifted to longer wave lengths. This implies a greater diminution of double-bond character of both the carbon–carbon double bond and of the

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(3) V. V. Feofilaktov and A. S. Onischenko, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 304 (1939); *C. A.*, **34**, 378 (1940).

(4) See S. A. Glickman and A. C. Cope, THIS JOURNAL, **67**, 1012 (1945), for previous references.

(5) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780 (1942).

(6) (a) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *ibid.*, **77**, 6269 (1955); (b) suggestion contributed by the referee.

(7) S. A. Glickman and A. C. Cope, *ibid.*, **67**, 1017 (1945); in cyclohexane solution λmax 234 mμ, ε 1.45 × 10^4.

(8) "International Critical Tables," Vol. V, 1929, p. 368; λmax (hex.) 198 mμ, log ε 4.25.

(9) *Ibid.*, λmax (EtOH) 227 mμ, log ε 425.

TABLE II

BROMOETHYL ESTERS, $RCH_2COOCH_2CH_2Br$

R	B.p., °C.	Mm.	$n^{20}D$	Analyses, % Calcd. C	H	Found C	H	Infrared γ, cm.$^{-1}$
I, -CN	93–94	0.15	1.4845	31.25	3.13[d]	31.57	3.08[d]	2235(CN); 1747(C=O)
II, -COOEt	74–80	0.005–0.02	1.4610	35.15	4.60	35.50	4.45	1757, 1739(C=O)[a]
III, *p*-O_2N-C_6H_4-	45–47[b]			41.66	3.47[e]	42.05	3.43[e]	1739(C=O); 1512(NO_2)
IV, MeCO-	80–81	0.05-0.06	1.4765	34.45	4.31	34.62	4.04	1737, 1710(C=O); 1645, 1623
VI. Me_2CH	80	20.4	1.4484	36.92	5.64	36.76	5.41	1733(C=O)[c]
VII, C_6H_5-	89–90	0.15	1.5372	49.38	4.53	49.52	4.34	1737(C=O)
VIII, $(C_6H_5)_2$	146–148	0.02	1.5793	60.19	4.70	60.23	4.65	1737(C=O)

[a] 1% soln. in CCl_4, 0.1-mm. cell. [b] M. p. [c] R = H (V) 1732 cm.$^{-1}$. [d] Nitrogen, calcd. 7.29, found 9.52. [e] Nitrogen, calcd. 4.86, found 4.71.

carbon–oxygen double bond in the ketene acetals over that observed in ordinary conjugated esters. In the infrared spectrum of carbethoxyketene ethylene acetal, the positions of the carbonyl and carbon–carbon double bond bands are indeed found at frequencies lower than usual for conjugated esters (1692 *vs.* 1718 cm.$^{-1}$ and 1621 *vs.* 1637 cm.$^{-1}$). The position of the carbon–carbon double bond band reported for ethyl β,β-diethoxyacrylate[10] is consistent with these data (1613 cm.$^{-1}$) but the position of the carbonyl band as reported (1736 cm.$^{-1}$) appears anomalous.

Experimental

β-Bromoethyl acetate was Eastman Kodak Co. reagent grade, used as such.

β-Bromoethyl cyanoacetate (I), *p*-nitrophenyl acetate (III), phenyl acetate (VII) and diphenyl acetate (VIII) were prepared by direct esterification of bromoethanol with the appropriate acid in benzene solution catalyzed with *p*-toluenesulfonic acid. The theoretical amount of water was removed by azeotropic distillation in two to three hours. I and III in benzene solution were washed only with water before working up. III was recrystallized from ethanol and from carbon tetrachloride. VII and VIII in benzene solution were washed with water and with sodium bicarbonate solution before drying and distilling.

β-Bromoethyl isobutyrate (VI) was prepared by reaction of bromoethanol with excess isobutyryl chloride without a solvent.

Ethyl β-bromoethylmalonate (II) was prepared in low yield by reaction of ethyl potassium malonate with 1,2-dibromoethane. A suspension of 289 g. (1.7 moles) of dried ethyl potassium malonate in one liter of 1,2-dibromoethane was stirred and heated under reflux for 16 hours. The mixture was cooled, extracted twice with water and the organic portion dried. Excess dibromoethane was recovered by distillation. The residue was distilled under vacuum through a short unpacked column, giving: (1) a forerun of 15 g., b.p. 52–56° (0.075 mm.), $n^{20}D$ 1.4181, and (2) a main fraction of 73 g., b.p. 84–86° (0.04 mm.), $n^{20}D$ 1.4568.[11] Fraction 2 was dissolved in ether and anhydrous hydrogen bromide was bubbled into the solution for ten minutes. After standing for two hours, the solution was washed free of acid with water, dried, solvent evaporated and the residue redistilled. A small forerun, b.p. 42–50° (0.025 mm.), and main fraction were collected; yield 50 g. (10.4%), see Table II.

β-Bromoethyl acetoacetate was prepared from diketene-acetone adduct[12] with bromoethanol[13] according to the general procedure for preparation of acetoacetic esters.[14] A solution of 35.9 g. (0.25 mole) of diketene–acetone adduct and 39.0 g. (0.31 mole) of bromoethanol containing a trace of *p*-toluenesulfonic acid was stirred and heated gradually in a flask equipped with a distillation head. When the reaction temperature reached 80–85°, the mixture darkened appreciably and evolved heat briefly. During three hours of heating at 90–100°, 10.5 ml. (18.3 ml. theor.) of acetone was collected by distillation. The reaction mixture was extracted several times with water, with 3 *N* hydrochloric acid and with benzene. The benzene solution was washed with water, dried, solvent evaporated, and the residue distilled through a Holtzmann column. Unreacted and undecomposed diketene–acetone adduct came over at room temperature at 0.1 mm. and was collected in an ice-chilled receiver. Thereafter the pressure dropped and product was collected in three fractions at 0.05–0.06 mm.: (1) 1.6 g., b.p. 75–80°, $n^{20}D$ 1.4789; (2) 12.1 g., 80–81°, 1.4765; (3) 5.4 g., 81°, 1.4773. Fractions 2 and 3 were combined; yield 33.5%.

Ketene Ethylene Acetals from I, II and IV.—A 250-ml. 3-neck flask equipped with a Trubore stirrer, pressure-equalized dropping funnel and condenser connected at the top to a wet-test meter saturated with hydrogen, was used for all reactions. To a stirred suspension of 0.1 mole of sodium hydride in 100 ml. of tetrahydrofuran,[15] 0.1 mole of bromoethyl ester was added slowly dropwise. Additions required one to two hours. Hydrogen evolved amounted to 2.0–2.2 l. by the end of the addition. Because of remaining larger particles of hydride, mixtures were then stirred overnight. The suspensions of sodium bromide were filtered and the filtrates evaporated. All residues solidified, were scraped out and evacuated over solid potassium hydroxide.

From I, 11.0 g. (99% yield); recrystallization from benzene gave 5.3 g. of white crystals, m.p. 79–82.5°. Evaporation of the filtrate gave a lower melting second crop. Sublimation at 70° (0.05 mm.) gave an analytical sample of cyanoketene ethylene acetal (Table I).

From II, 15.4 g. (97.5% yield); recrystallization from ether–petroleum ether gave 12.6 g., m.p. 48.5–50.5°. Distillation onto a cold finger at 90° (0.03 mm.) gave an analytical sample of carbethoxyketene ethylene acetal (Table I).

From IV (0.05 mole ester), 6.0 g. (93.8% yield); recrystallization from methylene chloride–ether at −75° gave 4.8 g. low melting. Distillation onto a cold finger at 70° (0.05 mm.) gave an analytical sample of acetylketene ethylene acetal (Table I).

***p*-Nitrophenylketene Ethylene Acetal.**—A solution of 28.8 g. (0.1 mole) of β-bromoethyl *p*-nitrophenylacetate in 50 ml. of tetrahydrofuran was added dropwise to a stirred suspension of 2.4 g. (0.1 mole) of sodium hydride in 150 ml. of tetrahydrofuran. Addition was completed in one hour when 2.02 l. of hydrogen had been evolved. During this time the reaction mixture developed a deep red color. The mixture was stirred and heated under reflux overnight, and during this time the color lightened to a deep yellow. The solution was cooled, filtered and the filtrate evaporated to dryness, leaving a sticky orange solid. The product was washed onto a filter with anhydrous ether and was dried *in vacuo*, giving 13.1 g. (63.4% yield) of low melting yellow solid. After two recrystallizations from ethylene dichloride there remained 4.4 g. of analytically pure product, m.p. 185–186°.

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[10] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

[11] Since the infrared spectrum of 2 contained an appreciable band at 1637 cm.$^{-1}$ which was not present in 1 and which might be due to some dehydrobromination product, fraction 2 was subjected to the further treatment described.

[12] Commercially available from Aldrich Chem. Co.

[13] Freshly distilled twice from anhydrous copper sulfate, leaving it white the second time.

[14] M. F. Carroll and A. R. Bader, THIS JOURNAL, **75**, 5400 (1953).

[15] Commercial tetrahydrofuran was stirred over solid potash for 4–5 hours, decanted and refluxed over calcium hydride overnight; distilled from calcium hydride.

Vinyl cyanoacetate,[16] b.p. 49–50° (0.45 mm.), $n^{20}\mathrm{D}$ 1.4410; infrared bands at 2240 (CN), 1754 (C=O), 1644 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_5H_5O_2N$: C, 54.05; H, 4.50; N, 12.61. Found: C, 54.36; H, 4.41; N, 12.56.

[16] Prepared by the method of R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

Acknowledgment.—The writer wishes to acknowledge gratefully helpful discussions with Drs. G. S. Hammond, W. D. Emmons, M. F. Hawthorne and K. S. McCallum.

HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH LABORATORY]

The Reaction of Carbalkoxycarbene with Saturated Hydrocarbons[1]

BY W. VON E. DOERING[2] AND L. H. KNOX

RECEIVED APRIL 27, 1956

In a previously unknown reaction, the photochemical decomposition of diazoacetic ester in saturated hydrocarbons R–H leads to the formation of saturated esters, RCH_2COOR', in yields of 30–50% of theory based on diazoacetic ester. Cyclopentane and cyclohexane give the esters of cyclopentane- and cyclohexaneacetic acids, respectively. The reaction of *n*-pentane and methyl diazoacetate gives the methyl esters of 3-ethylpentanoic, 3-methylhexanoic and heptanoic acids; 2,3-dimethylbutane and methyl diazoacetate give the methyl esters of 4,5-dimethylhexanoic and 3,3,4-trimethylpentanoic acids. A slight preference for the more highly substituted C–H bonds can be detected.

In our study of the photochemically induced reactions of aliphatic diazo compounds with various classes of organic molecules, this paper is a report on some of the results obtained with diazoacetic ester and saturated hydrocarbons. Although reactions of ethyl diazoacetate with a variety of unsaturated compounds are widely recorded in the literature,[3] there are no instances of reaction with saturated hydrocarbons and few that appear to have involved the carbon–hydrogen bond. In the thermally induced reaction of *p*-xylene,[4] mesitylene[5] and durene[6] with diazoacetic ester, 4-methyl-, 3,5-dimethyl- and 2,4,5-trimethylhydrocinnamic ester, respectively, have been isolated. In a pioneering study of the photolysis of diazomethane in organic solvents, Meerwein, Rathjen and Werner[7] isolated ethyl *n*-propyl and ethyl isopropyl ether from ethyl ether, *α*- and *β*-methyltetrahydrofuran from tetrahydrofuran and methyl isopropyl ether and *sec*- and *t*-butyl alcohols from isopropyl alcohol. From the photolysis of diazomethane in benzene, Doering and Knox[8] obtained toluene in addition to tropilidene.

In each of these examples, the structure of the product is consistent with direct attack on the carbon–hydrogen bond, but the presence of unsaturation or an oxygen atom in the examples cited obliges one to consider more involved mechanisms. Indeed, Huisgen[3] proposed the initial formation of an "ylid" intermediate to explain the ethyl ether–diazomethane reaction.

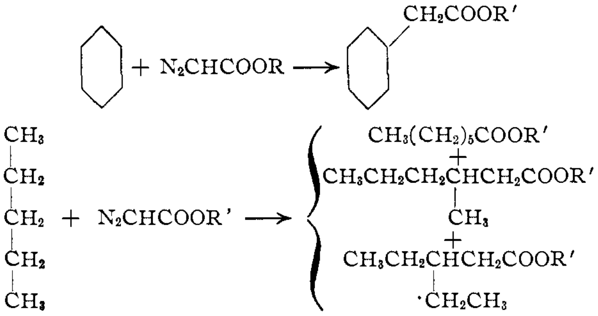
Reaction with saturated hydrocarbons offers no possibility for initial complex formation nor for reaction with unshared electrons or unsaturated bonds. Both its apparent simplicity and novelty encouraged the present study.

When dilute solutions of ethyl diazoacetate in saturated hydrocarbon solvent are irradiated, upwards of 80% of the nitrogen is smoothly evolved at a rate (measured semiquantitatively) which is independent of the temperature, the nature of the hydrocarbon and the dilutions employed. With a molar ratio of ethyl diazoacetate to hydrocarbon of 1:100 the rates of nitrogen evolution in cyclohexane at 12 and 80° and in 2,3-dimethylbutane at 12° were identical.

The reaction of cyclopentane and cyclohexane with ethyl diazoacetate afforded cyclopentaneacetic acid ethyl ester and cyclohexaneacetic acid ethyl ester in 48 and 42% yields, respectively. Ethyl cyclohexaneacetate was also obtained in comparable yield by heating cyclohexane and ethyl diazoacetate in a sealed tube at 150° for 8 hr. In the presence of copper powder, however, addition of ethyl diazoacetate to refluxing cyclohexane afforded only ethyl fumarate.

$$\mathrm{N_2CHCOOR'} \xrightarrow[\text{or heat}]{\text{light}} \mathrm{N_2 + H{-}\ddot{C}{-}COOR'}$$

$$\mathrm{H{-}\ddot{C}{-}COOR' + RH \longrightarrow RCH_2COOR'}$$



$$\mathrm{CH_3CH_2CH_2CH_2CH_3 + N_2CHCOOR' \longrightarrow CH_3(CH_2)_5COOR' + CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2COOR' + CH_3CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2COOR'}$$

In a consistent reaction scheme ethyl diazoacetate absorbs energy with elimination of nitrogen and formation of the highly reactive, neutral car-

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[1] Presented at the 119th Meeting of the American Chemical Society, Boston, Mass., April 2, 1951, "Abstracts of Papers," p. 2M.

[2] Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[3] R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

[4] E. Buchner and P. Schulze, *Ann.*, **377**, 259 (1910).

[5] E. Buchner and K. Scholtenhammer, *Ber.*, **53**, 865 (1920).

[6] L. I. Smith and P. O. Tawney, THIS JOURNAL, **56**, 2167 (1934).

[7] H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942).

[8] W. von E. Doering and L. H. Knox, *ibid.*, **72**, 2305 (1950); **73**, 828 (1951); **75**, 297 (1953).