Table IX. Ionization Ratios of 2-Nitro-4-chloroaniline ($pK_{BH^+} = -1.07$) and H_0 Values Evaluated in Perchloric Acid (3.05 *M*) Containing Various Amounts of Sodium Chloride

[NaCl], mol/l.	log *I*	$-H_0$	$-\Delta H_0$
	0.23	1.30	
0.2	0.26	1.33	0.03
0.4	0.29	1.36	0.06
0.6	0.34	1.41	0.11
0.8	0.35	1.42	0.12
1.0	0.41	1.48	0.18
1.2	0.46	1.53	0.23

From the graphs described above the influence of sodium iodide and sodium bromide on the acidity functions was evaluated, assuming the effect of bromide and iodide ions is equal to that of chloride ion.[16]

Kinetic Procedures. Sulfoxide solutions were prepared by weighing out the sulfoxide in a 50-ml volumetric flask which was filled to the mark with perchloric acid stock solution.

The perchloric acid solutions were prepared by dilution of concentrated perchloric acid with distilled water, previously refluxed while passing a stream of nitrogen. They were titrated with standard NaOH.

Sodium halide solutions were prepared by dissolving the desired amount of salt with deoxygenated distilled water in a volumetric flask. The solutions were kept under nitrogen and thermostated at 25 ± 0.05°.

At zero time 10 ml of the salt solution was added to the sulfoxide solution. Aliquots were withdrawn under nitrogen at various time and analyzed as follow.

Reduction. The aliquots were poured in an ice-cold aqueous solution containing a known amount of sodium thiosulfate, to destroy the iodine formed. The residual sodium thiosulfate was back titrated with standard iodine. From the analytical data and the stoichiometric equation (eq 7) the concentration of the sulfoxide at any time was calculated.

The pseudo-first-order rate constants (all the experiments were run with large excess of acid and halide ion) were obtained by plotting log [R_2SO] *vs.* time and determining the slope of the line from the graphs and from a least-squares analysis. An Olivetti Programma 101 desk computer was used.

A typical example is in Table X.

Table X. Reduction of *m*-Chlorophenyl Methyl Sulfoxide (0.005 *M*) with Sodium Iodide (0.5 *M*)[a]

t, sec		30	159	305	503	730	1009	1385	1792	2275
[R_2SO] × 10^3 *M*	5.00	4.90	4.65	4.38	4.04	3.72	3.44	2.85	2.41	1.87

[a] In aqueous perchloric acid (4.56 *M*) at 25°; $k_{obsd} = -2.303 \times \text{slope} = 4.11 \times 10^{-4}\ \text{sec}^{-1}$.

Since the H_A of the solution is -2.12 and the pK_a of *m*-chlorophenyl methyl sulfoxide is -2.99 on the H_A scale (see Table VIII), the ratio $h_A/(h_A + K_a) = 0.0711$, and therefore the values of k_1 ($5.78 \times 10^{-3}\ \text{sec}^{-1}$) and of k_1/[NaI] ($1.15 \times 10^{-2}\ \text{sec}^{-1}\ \text{mol}^{-1}$ l.) can be easily evaluated.

Racemization. The aliquots, withdrawn from the reaction of the optical active sulfoxide with sodium chloride or sodium bromide, were transferred in a thermostated cell of a Perkin-Elmer P22 spectropolarimeter. The optical activity was measured in the range 280–300 nm. From plots of log [α] *vs.* time, the pseudo-first-order constants were evaluated. The calculation has been described in detail in the previous paragraph.

Acknowledgments. We wish to thank Professors J. F. Bunnett and K. Yates for helpful discussions and the Consiglio Nazionale delle Ricerche, Rome, for financial support.

Organic Oxalates. IV. Pyrolysis of Diallyl, Disubstituted-Allyl, and Related Oxalates[1]

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Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. *Received May 12, 1970*

Abstract: Products from the low-pressure gas-phase pyrolysis of diallyl, dicrotyl, dicinnamyl, and related oxalates are reported. The results indicate that these oxalates are a convenient source of substituted allyl radicals. The main products from allyl and crotyl radicals are coupling products, but no coupling products are observed from cinnamyl radicals. The main product from the pyrolysis of di-*trans*-cinnamyl oxalate is indene which must result from an intramolecular cyclization of the cinnamyl radical. An isotope effect, k_H/k_D, of 2.92 is reported for the cyclization of *o*-deuteriocinnamyl radical to indene which suggests that formation of the intermediate cyclic radical from the cinnamyl radical is a reversible step. Several radicals generated from the appropriate oxalates that are similar to cinnamyl radicals also undergo cyclizations giving rise to cyclic products.

In part II[2] of this series we reported that the low-pressure gas-phase pyrolysis of ring-substituted dibenzyl oxalates produces benzyl radicals which couple to form bibenzyls in good yield. In part I[3] of this

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(1) (a) Part III: W. S. Trahanovsky and C. C. Ong, *Tetrahedron Lett.*, 3627 (1968). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences and Grant No. 3219-A from the Petroleum Research Fund, administered by the American Chemical Society. The mass spectrometer was purchased with funds from National Science Foundation Grant No. GP 1715 and a grant from the Iowa State Alumni Research Fund. We thank these organizations for their support. (c) Based on work by C. C. O. in partial fulfillment of the requirements for the Ph.D. Degree at Iowa State University. (d) Preliminary communications: ref 1a and footnote 10 of ref 2. (e) Alfred P. Sloan Research Fellow, 1970–1972.

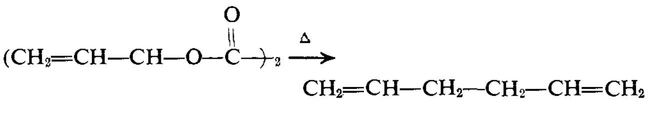
(2) W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, *J. Amer. Chem. Soc.*, **90**, 2839 (1968).

(3) W. S. Trahanovsky, J. A. Lawson, and D. E. Zabel, *J. Org. Chem.*, **32**, 2287 (1967).

series it was shown that the thermal decomposition of oxalates involves two-bond cleavage to produce the appropriate alkyl- and alkoxycarbonyl radicals and the rate of thermal decomposition of an oxalate increases as the stability of the alkyl radical increases. From these results it is apparent that diallyl oxalates should form allyl radicals under conditions similar to those used to generate benzyl radicals from dibenzyl oxalates since the stabilities of the two types of radicals are similar.[4] In this publication we report the study of the low-pressure gas-phase pyrolysis of diallyl, disubstituted-allyl, and related oxalates.

Results

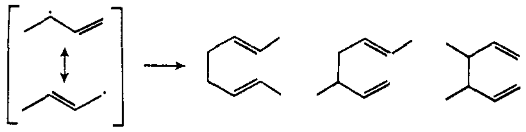
Biallyl in yields of 40–60% was obtained from the



$$(CH_2{=}CH{-}CH{-}O{-}\overset{\overset{O}{\|}}{C}{-})_2 \xrightarrow{\Delta} CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$$

pyrolysis of diallyl oxalate.[1d,4b,c] The low volatility of the oxalate led to recovery of *ca.* 20% oxalate when the pyrolysis was carried out under <3 mm pressure. A yield of 63% biallyl and only 1% recovered oxalate was obtained when the pyrolysis was carried out at 660° and 8 mm of pressure with the head heated to 80°.

Pyrolysis of di-*trans*-crotyl oxalate should lead to the crotyl radical which can couple at either position to form three structurally different olefins. Pyrolysis

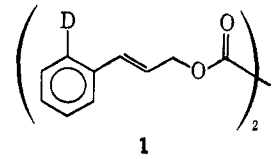


of di-*trans*-crotyl oxalate at 535° gave several products including 2,6-octadiene and 3-methyl-1,5-heptadiene which were obtained in a ratio of 52/48. Interconversion of these dienes was considered negligible since under similar pyrolytic conditions only 6% 3-methyl-1,5-heptadiene was converted to 2,6-octadiene. None of the third diene, 3,4-dimethyl-1,5-hexadiene, was obtained.

The characteristic nmr spectrum of indene was the main feature of the nmr spectrum of the pyrolysate of di-*trans*-cinnamyl oxalate at 570°. Nmr and glpc analysis using an internal standard showed per mole of oxalate 0.82 mol of indene, 0.19 mol of styrene, 0.11 mol of *trans*-β-methylstyrene, 0.098 mol of allylbenzene, 0.014 mol of toluene; small amounts of two unknown products, a trace of *cis*-β-methylstyrene, and no indan were produced. Pyrolysis of the oxalate at 650° gave very similar yields of products with the amount of indene being 0.86 per mole of oxalate.

Pyrolyses of *trans*-cinnamyl formate and acetate at 650° gave, respectively, 0.82 and 0.72 mol of indene and in both cases minor products similar to those obtained from the oxalate.

Di-*trans*-*o*-deuteriocinnamyl oxalate (**1**), which contained 9.2% of the undeuterated cinnamyl moiety, was pyrolyzed at 570° to give indene which was found to be 32.4% d_0 and 67.6% d_1 by mass spectral analysis.



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Correction for the 9.2% undeuterated cinnamyl moiety showed that cyclization to form the deuterated indene was 2.92 times faster than cyclization to form light indene.

Three related radical systems which could cyclize in a fashion similar to the cinnamyl radical were produced from the appropriate oxalate. Pyrolysis of di-*o*-phenylbenzyl, di-*o*-phenoxybenzyl, and di-*o*-benzylbenzyl oxalates at 570–650° gave 1.44 mol of fluorene, 0.25 mol of xanthene, and 0.12 mol of 9,10-dihydroanthracene, respectively, per mol of oxalate pyrolyzed. As minor products 0.05 mol of *o*-phenyltoluene was obtained from di-*o*-phenylbenzyl oxalate, 0.05 mol of *o*-phenoxytoluene and 0.05 mol of *o*-phenoxybenzyl alcohol were obtained from di-*o*-phenoxybenzyl oxalate, and 0.12 mol of anthracene was obtained from di-*o*-benzylbenzyl oxalate per mol of oxalate pyrolyzed.

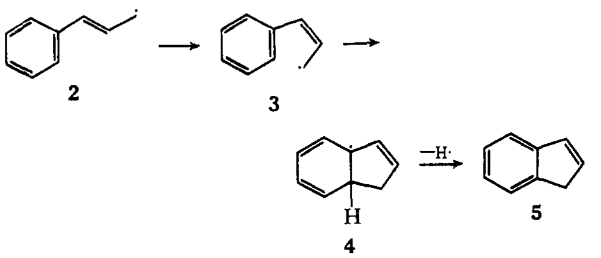
Dipropargyl oxalate was pyrolyzed in an effort to obtain 1,5-hexadiyne. However, benzene was the predominant product from pyrolyses at 600–660° and complex mixtures of products which were not analyzed resulted from pyrolyses run at 350–500° under pressures of 3–10 mm.

Discussion

From the above results it is clear the pyrolysis of disubstituted-allyl oxalates is a convenient means of generating the substituted allyl radicals. Two other groups of workers have also shown that the pyrolysis of diallyl oxalate leads to allyl radicals.[4b,c] The main products from allyl[4b,c] and crotyl radicals are coupling products, but no coupling products were observed from cinnamyl radicals.

The fact that no 3,4-dimethyl-1,5-hexadiene was obtained from the pyrolysis of the dicrotyl oxalate suggests that it is converted by a Cope rearrangement to the more stable 2,6-octadiene.[5] Thus the approximately equal amounts of 2,6-octadiene and 3-methyl-1,5-heptadiene imply that the crotyl radicals couple statistically to give the three olefins in a 1:2:1 ratio and the hexadiene rearranges to the octadiene.

The large amount of indene obtained from the pyrolysis of di-*trans*-cinnamyl oxalate indicates that intramolecular cyclization of the cinnamyl radical is a favorable process. Since no indan was found, the



(1)

cyclized radical, **4**, must not disproportionate but must lose a hydrogen atom possibly to organic material that is deposited on the pyrolysis column. The minor

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[4] (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1950; (b) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969), and references cited therein; (c) D. G. L. James and S. M. Kambanis, *Trans. Faraday Soc.*, **65**, 1350 (1969).

[5] F. F. Rust and D. O. Collamer, *J. Amer. Chem. Soc.*, **76**, 1055 (1954).

Table I. Yields, Melting and Boiling Points, Elemental Analyses, Nmr Signals, and Ir Absorption Bands of Symmetrical Oxalates ($R-CH_2-O-CO\!\!\rightarrow_2$)

R	Yield, %	Mp[a] or bp, °C	Anal, %[b]				Chem shifts, δ, ppm[c]			Ir frequency, cm^{-1} [d] >C=O
			Found		Calcd		Aromatic H	-CH$_2$-	Other	
			C	H	C	H				
$CH_2{=}CH-$	75	Bp 215–216 (lit.[e] 215)						4.7 (d, J = 5.5 Hz)	6.38-5.23 (m, $-CH{=}CH_2$)	1775 1740
trans-$CH_3CH{=}CH-$	82	Bp 100–102 (2 mm)	60.51	6.98	60.57	7.12		4.81 (d, J = 5.5 Hz)	5.25–6.22 (m, $-CH{=}CH-$) 1.72 (d, J = 5.5 Hz, $-CH_3$)	1770 1740
trans-$PhCH{=}CH-$	70	Mp 102–104	74.51	5.44	74.50	5.63	7.27 (m)	4.88 (d, J = 6 Hz)	6.4 (m, $CH{=}CH$)	1770 1740
o-$PhC_6H_{14}-$	73	Mp 108–110	79.55	5.22	79.59	5.25	7.31 (s)	5.2 (s)		1775 1752
o-$PhOC_6H_4-$	45	Mp 94–96	74.02	4.86	73.98	4.88	7.15 (m)	5.41 (s)		1770 1740
o-$PhCH_2C_6H_4-$	55	Mp 117–119[f]	79.80	5.78	79.91	5.82	7.2 (m)	5.22 (s)	4.05 (s, $-CH_2-$)	1770 1740

[a] Recrystallized from 95% ethanol unless otherwise specified. [b] Analyzed by Spang Microanalytical Lab., Ann Arbor, Mich. [c] Solvent was $CDCl_3$. [d] Solvent was $CHCl_3$. [e] C. Lespagnol, *Bull. Soc. Chim. Fr.*, 110 (1960). [f] Recrystallized from chloroform–hexane mixture.

products allylbenzene and β-methylstryene no doubt come from hydrogen abstraction by the cinnamyl radical. The formation of the minor product styrene is difficult to rationalize.

The cinnamyl radical has been generated by other routes but in most cases the formation of indene has not been reported. The Grignard reaction of cinnamyl chloride,[6,7] the decomposition of acetyl peroxide in allylbenzene,[7] and the thermal decomposition of *t*-butyl peroxy-2-phenyl-3-butenoate and *t*-butyl peroxy-4-phenyl-3-butenoate in chlorobenzene[8] gave only products from the coupling of cinnamyl radicals and allylbenzene but no indene. In the latter two cases, it is quite likely that if indene formed it would have been destroyed by reaction with the relatively unstable alkoxy radicals that were present. Large amounts of polymeric material were reported in both cases. Jones and Schmeltz recently reported that the pyrolysis of *trans*-cinnamic acid leads to 72% styrene and many other products including 2.5% indene.[9] These workers proposed that the cinnamyl radical was the precursor of the indene. The pyrolysis of *trans*-cinnamyl formate at 332–342° in a static system has been reported to form carbon dioxide and allylbenzene, presumably by a nonradical process.[10] These results are in contrast to ours since we obtained a high yield of indene from the formate. The difference is probably due to the different conditions used for the pyrolysis.

A question that exists concerning the mechanism of indene formation from the cinnamyl radical as depicted in eq 1 is whether or not the cyclization step, **3**–**4**, is reversible. If formation of the cyclic radical from the cinnamyl radical is reversible and the hydrogen abstraction step is rate determining, then one would expect an isotope effect for indene formation from *o*-deuteriocinnamyl radical. Our results from the pyrolysate of di-*trans*-*o*-deuteriocinnamyl oxalate at 570° indicate an isotope effect, k_H/k_D, of 2.92. This relatively large isotope effect suggests that formation of the cyclic radical intermediate from the cinnamyl radical is reversible and that the carbon–hydrogen bond breakage step is rate determining. These results are similar to those reported by Denney and Klemchuk.[11] These workers report an isotope effect of 1.38 at 143° for the formation of fluorenone from 2-(*o*-deuteriophenyl)benzaldehyde and an isotope effect of 1.32 for the formation of the lactone of 2-carboxy-2′-hydroxybiphenyl from the decomposition of 2-(*o*-deuteriophenyl)benzoyl peroxide. They also concluded that the formation of the intermediate cyclic radical is reversible.

The cyclic products obtained from the pyrolysis of di-*o*-phenylbenzyl, di-*o*-phenoxybenzyl, and di-*o*-benzylbenzyl oxalates indicate that the *ortho*-substituted benzyl radicals generated from the oxalates also undergo free-radical cyclizations similar to the cyclization of the cinnamyl radical. The high yield (72%) of fluorene from the *o*-phenylbenzyl radical indicates that the free-radical cyclization is indeed a facile reaction. The relatively low yields of xanthene and 9,10-dihydroanthracene may result from the fact that these compounds have active benzylic positions that should be readily attacked by radicals.

The failure of dipropargyl oxalate to produce 1,5-hexadiyne is probably a result of the thermal instability of the diyne[12] under our conditions.

Experimental Section

Materials and Methods. Equipment, some materials, and methods have been previously described.[1a,1d,2] Allyl alcohol, *trans*-crotyl alcohol, propargyl alcohol, 3-methyl-1,5-heptadiene, *trans*-cinnamyl alcohol and formate, *o*-dibromobenzene, and *o*-phenylbenzoic acid were obtained from Aldrich. *o*-Phenoxybenzoic and *o*-benzylbenzoic acids were obtained from K & K. Acrolein and dimethyl oxalate were obtained from Eastman. 2,6-Octadiene was obtained from Chemical Samples. Indene was obtained from Columbia.

o-Phenylbenzyl, *o*-phenoxybenzyl, and *o*-benzylbenzyl alcohols were prepared by lithium aluminum hydride reduction of the ap-

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(6) W. G. Young, J. D. Roberts, and H. Wax, *J. Amer. Chem. Soc.*, 67, 841 (1945).

(7) H. P. Koch, *J. Chem. Soc.*, 1111 (1948).

(8) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, 80, 1398 (1958).

(9) T. C. Jones and I. Schmeltz, *J. Org. Chem.*, 34, 645 (1969).

(10) J. M. Vernon and D. J. Waddington, *Chem. Commun.*, 623 (1969).

(11) D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.*, 80, 3289 (1958).

(12) (a) W. D. Huntsman and H. J. Wristers, *ibid.*, **85**, 3308 (1963); (b) W. D. Huntsman and H. J. Wristers, *ibid.*, 89, 342 (1967); (c) M. L. Heffernan and A. J. Jones, *Chem. Commun.*, 120 (1966).

propriate benzoic acid and converted to the oxalates without further purification.

1-*o*-Deuteriophenylpropen-1-ol. *o*-Deuteriobromobenzene was prepared by treating the Grignard reagent of *o*-dibromobenzene with deuterium oxide. The Grignard reagent of the distilled *o*-deuteriobromobenzene was prepared and converted to 1-*o*-deuteriophenylpropen-1-ol following the procedure of Ouellette, Robins, and South:[13] yield 55%; bp 80–85° (8 mm) (lit.[13] bp 76–77° (18 mm)).

Preparation of Symmetrical Oxalates. In Table I are presented pertinent data for each new symmetrical oxalate. The first two oxalates were prepared by method I,[1a] the third by method II,[1a] and the last three by method III. Method III was similar to method II except that after the reaction, water was added, the ether layer was separated, washed, dried (MgSO$_4$), and concentrated, and the crude oxalate was recrystallized from a suitable solvent.

Di-*trans*-*o*-**deuteriocinnamyl Oxalate.** Di-1-*o*-deuteriophenylpropenyl oxalate was prepared by method III: nmr (CDCl$_3$) δ 7.35 (s, 4.1), 5.84–6.4 (m, 2), and 5.15–5.55 (m, 2). Upon standing for a few days, the crude product solidified and was recrystallized from 95% ethanol: yield 55%; mp 102–104°. Mass spectral analysis showed the oxalate to be 1.4% d_0, 15.7% d_1, and 83.0% d_2.

Dipropargyl oxalate was prepared by method I: yield 20%; mp 96–98° (recrystallized from 95% EtOH) (lit.[14] mp 97–98°); ir (CHCl$_3$) 3340, 1788, and 1755 cm^{-1}; nmr (CDCl$_3$) δ 4.87 (d, J = 0 Hz, 2) and 2.56 (t, 4, J = 2 Hz).

trans-Cinnamyl acetate was prepared by acetylating *trans*-cinnamyl alcohol with acetyl chloride in triethylamine: yield 68%; bp 117–120° (11 mm) (lit.[15] bp 141° (18 mm)).

The procedure for pyrolysis of oxalates at high temperatures under vacuum has been illustrated by that of dibenzyl oxalate.[2] The following procedures give the main features of a typical run for the compound named.

Pyrolysis of Diallyl Oxalate. A 1-g sample of the oxalate was pyrolyzed at 635° in the usual manner except that a glass boat was used to contain the sample and the head of the apparatus was initially cooled to −78° and then heated to 75°. Nmr analysis of the pyrolysate using naphthalene as an internal standard showed that 63% biallyl was produced and 8.1% biallyl oxalate was recovered.

A 5-g sample of the oxalate was pyrolyzed at 660° using the standard apparatus except that the head was replaced with a 25-ml round-bottomed flask heated by a heating mantle and a larger trap was used. Distillation of the pyrolysate gave a 51% yield of biallyl, bp 58–60° (lit.[16] 59–60°).

Pyrolysis of di-*trans*-crotyl oxalate was carried out at 535°. Glpc analysis of the pyrolysate (6 ft × $^1/_4$ in. DC 550 silicone oil column) showed the presence of several products including 3-methyl-1,5-heptadiene and 2,6-octadiene. The presence of these two dienes was confirmed by glpc peak enhancement using authentic samples and analysis of the nmr spectrum of the pyrolysate.

Pyrolysis of di-*trans*-cinnamyl oxalate was carried out at 570° with a head temperature of 135–155°. Indene was found to be the main product by nmr and glpc analysis using dimethyl oxalate as a standard. Minor products were identified and their yields determined by glpc analysis.

Pyrolyses of *trans*-cinnamyl formate and acetate were carried out at 650° and the yields of indene were determined by nmr analysis using bibenzyl as an internal standard. The glpc chromatograms of both pyrolysates were very similar to that of the di-*trans*-cinnamyl oxalate pyrolysate. Significant amounts of starting material was recovered when the pyrolyses were carried out at lower temperatures.

Pyrolysis of di-*trans*-*o*-deuteriocinnamyl oxalate was carried out at 570°. The indene that was produced was purified by glpc and analyzed by mass spectrometry.

Pyrolysis of di-*o*-phenylbenzyl oxalate was carried out at 640° with a head temperature of 160–165°. The pyrolysate was analyzed by glpc (8 ft × $^1/_4$ in. 20% SE 30 column at 175°) using bibenzyl as an internal standard. The yield of fluorene was also confirmed by nmr analysis using dibenzyl sulfide as an internal standard.

Pyrolysis of di-*o*-phenoxybenzyl oxalate was carried out at 650° with a head temperature of 165–170°. The pyrolysate was analyzed by nmr using bibenzyl as an internal standard. The identity of xanthene was also confirmed by glpc analysis.

Pyrolysis of di-*o*-benzylbenzyl oxalate was carried out at 570° with a head temperature of 175–180°. The pyrolysate was analyzed by glpc and nmr using bibenzyl as an internal standard.

Pyrolysis of dipropargyl oxalate was carried out at 660° with a head temperature at 70°. An nmr spectrum of the pyrolysate (CCl$_4$) showed a large sharp peak at δ 7.25 which was assigned to benzene and other minor peaks scattered from δ 7.3 to 1.8.

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(13) R. J. Ouellette, R. D. Robins, and A. South, Jr., *J. Amer. Chem. Soc.*, **90**, 1619 (1968).

(14) C. Lespagnol, *Bull. Soc. Chim. Fr.*, 110 (1960).

(15) K. Hess and W. Wustrow, *Justus Liebigs Ann. Chem.*, **437**, 273 (1924).

(16) F. Cortese, *J. Amer. Chem. Soc.*, **51**, 2266 (1929).