

oxidizing solution and stirred for 18 hr. The yellow solution was poured onto ice-water and stirred for an additional 3 hr, the resultant solid was filtered and dissolved in ether, the ether was dried (MgSO<sub>4</sub>), and the sample was concentrated under reduced pressure. The concentrated solution was chromatographed on 100 g of Florisil with hexane-ether (1:1) yielding 2.21 g (82%) of a yellow-white solid. The individual azoxybenzene isomers were partially separable *via* glpc (205°, the minor azoxyacetate preceding the major isomer), in this instance indicating that no fractionation of the mixture had occurred under the conditions of chromatography. Both glpc and Eu(fod)<sub>3</sub> pmr analysis indicated that the major isomer predominated by 9.3:1.

**2-Acetoxy-5-methylazoxybenzene.**—Two recrystallizations from hexane-ethanol of the oxidized 2-acetoxy-5-methylazoxybenzene mixture gave the major isomer, 2-acetoxy-5-methylazoxybenzene, as pale yellow needles: mp 76.5–77.0°; ir (KBr) 1760, 1225, 1193, 774, and 684 cm<sup>-1</sup>; uv max (methanol) 243 nm ( $\epsilon$  10,600) and 324 (11,200); nmr (CCl<sub>4</sub>)  $\delta$  ~6.50 and 5.57 (m, 8, aromatic protons), 2.38 (s, 3, C-5 -CH<sub>3</sub>), and 2.21 ppm (s, 3, -COCH<sub>3</sub>). *Anal.* Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 66.66; H, 5.22; N, 10.37. Found: C, 66.48; H, 5.26; N, 10.33.

**2-Hydroxyl-5-methylazoxybenzene.**—2-Acetoxy-5-methylazoxybenzene (2.70 g, 0.01 mol) was dissolved in 100 ml of ethanol-water (1:1), and 15 g of potassium hydroxide was added. The solution was refluxed for 30 min, acidified with 10% hydrochloric acid, and poured onto 300 ml of ice-water. After stirring overnight, the crude product was suction filtered and dissolved in ether, and the ether was dried (MgSO<sub>4</sub>) and removed under vacuum. Recrystallization from hexane-ethanol gave 1.8 g (79%) of yellow-orange needles, mp 72.5–73.0° (lit.<sup>23</sup> mp 74°).

**Oxidation of 2-Hydroxyl-5-methylazobenzene.**—2-Hydroxy-5-methylazobenzene<sup>21</sup> (2.12 g, 0.01 mol) was dissolved in 100 ml of the oxidizing solution and stirred for 24 hr. The yellow-orange solution was then poured onto ice-water and stirred for 3 hr at room temperature. The resultant crude solid was collected by suction filtration and dissolved in ether, and the ether was dried (MgSO<sub>4</sub>) and removed under vacuum, yielding 1.9 g (90%) of a yellow-orange solid. The individual azoxybenzene isomers were partially separable *via* glpc (195°, the major azoxyphenol preceding the minor isomer). Conversion of the crude azoxyphenols to the acetates by treatment with pyridine-acetic an-

hydride as detailed for 2'-acetoxy-5'-methylazoxybenzene, and glpc (205°, the major azoxyacetate preceding the minor isomer) coupled with Eu(fod)<sub>3</sub> pmr spectral clarification, indicated that the major azoxyphenol isomer predominated by 2.6:1.

**2'-Hydroxy-5'-methylazoxybenzene.**—Two recrystallizations from hexane-ethanol of the oxidized 2'-hydroxy-5'-methylazoxybenzene mixture gave the major isomer, 2'-hydroxy-5'-methylazoxybenzene, as yellow needles, mp 124.5–125.0° (lit.<sup>23</sup> mp 125°).

**2'-Acetoxy-5'-methylazoxybenzene.**—2'-Hydroxy-5'-methylazoxybenzene (1.06 g, 0.005 mol) was dissolved in 30 ml of pyridine, and 3 ml of acetic anhydride was added. The solution was stirred for 1 hr, poured onto 300 ml of hydrochloric acid (20%) at 0°, and extracted into ether, and the ether was dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The concentrated solution was chromatographed on 50 g of Florisil using pentane-ether (1:1) and the product corresponding to the yellow band was collected, yielding 0.9 g (67%) of a viscous yellow oil which resisted crystallization. Distillation in a microstill at 0.5 mm with a pot temperature of 165° gave a clear yellow oil: ir (neat) 1780, 1205, 769, and 688 cm<sup>-1</sup>; uv max (methanol) 230 nm ( $\epsilon$  10,500) and 310 (14,500); nmr (CCl<sub>4</sub>)  $\delta$  ~6.50 and 5.57 (m, 8, aromatic protons), 2.38 (s, 3, C-5 -CH<sub>3</sub>) and 2.16 ppm (s, 3, COCH<sub>3</sub>). *Anal.* Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 66.66; H, 5.22; N, 10.37. Found: C, 66.63; H, 5.25; N, 10.54. Glpc (205°) and Eu(fod)<sub>3</sub> treatment of this azoxyacetate revealed it to be isomerically pure and to possess glpc and Eu(fod)<sub>3</sub> behavior identical with those of the minor azoxyacetate formed from the oxidation of 2-acetoxy-5-methylazoxybenzene.

**Registry No.**—Eu(fod)<sub>3</sub>, 17631-68-4; 2'-methylazoxybenzene, 34810-71-4; 2-methylazoxybenzene, 34810-72-5; 2-chloro-4'-methylazobenzene, 34810-73-6; 2'-chloro-4-methylazoxybenzene, 34810-74-7; 2-chloro-4'-methylazoxybenzene, 34810-75-8; 4'-methylazobenzene-2-carboxylic acid, 13304-23-9; 4'-chloroazoxybenzene-2-carboxylic acid, 34810-77-0; 2-acetoxy-5-methylazoxybenzene, 34810-78-1; 2'-acetoxy-5'-methylazoxybenzene, 34810-79-2.

## Thermal Decomposition of Methyl and Phenyl Triphenylmethylazocarboxylates<sup>1a,b</sup>

DOUGLAS E. ZABEL AND WALTER S. TRAHANOVSKY\*<sup>1c</sup>

Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010

Received January 4, 1972

Products from the decomposition of methyl and phenyl triphenylmethylazocarboxylates at 60° in benzene or cumene are reported. These and other results indicate that these tritylazocarboxylates decompose to trityl radicals, nitrogen, and the corresponding alkoxy-carbonyl radicals (ROC=O) which can escape from a solvent cage and couple with other radicals before decarboxylating or decarbonylating. These alkoxy-carbonyl radicals seem to be relatively unreactive radicals since no evidence for the addition into benzene or the abstraction of the  $\alpha$ -hydrogen atom of cumene by these radicals was obtained.

Several reports of a class of free radicals which we prefer to call alkoxy-carbonyl radicals (ROC=O) have been published.<sup>2–15</sup> The most detailed remarks on

alkoxy-carbonyl radicals came from decomposition studies of ethyl and benzyl *tert*-butyl monoperoxyoxalates as well as di-*tert*-butyl monoperoxyoxalate.<sup>5,6</sup> These studies demonstrated that alkoxy-carbonyl radicals were stable enough to escape from the solvent cage to be trapped by molecules of solvent such as benzene or cumene or by molecules of a scavenger such as galvinoxyl, and to abstract a hydrogen atom from some active hydrogen atom donating species such as cumene.

(1) (a) This research was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences and Grant 3219-A from the Petroleum Research Fund administered by the American Chemical Society. We thank these organizations for their support. (b) Based on work by D. E. Z. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University. (c) Alfred P. Sloan Research Fellow, 1970–1972.

(2) R. Stolle and W. Reichert, *J. Prakt. Chem.*, **123**, 82 (1929).

(3) W. H. Urry and E. S. Huyser, *J. Amer. Chem. Soc.*, **75**, 4876 (1953).

(4) A. D. Petrov, G. I. Nikishin, and V. D. Vorob'ev, *Fette, Seifen, Anstrichm.*, **59**, 1023 (1957); *Chem. Abstr.*, **53**, 1127i (1959).

(5) P. D. Bartlett and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1769 (1960).

(6) P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962).

(7) J. C. J. Thynne and P. Gray, *Trans. Faraday Soc.*, **59**, 1149 (1963), and references cited therein.

(8) P. B. Ayscough, B. R. Brooks, and H. E. Evans, *J. Phys. Chem.*, **68**, 3889 (1964).

(9) J. Hancock, *Tetrahedron Lett.*, 1585 (1964).

(10) Y. Shigemitsu, T. Tominaga, T. Shimodaira, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **39**, 2463 (1966).

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

(12) J. Warkentin and D. M. Singleton, *Can. J. Chem.*, **45**, 3035 (1967).

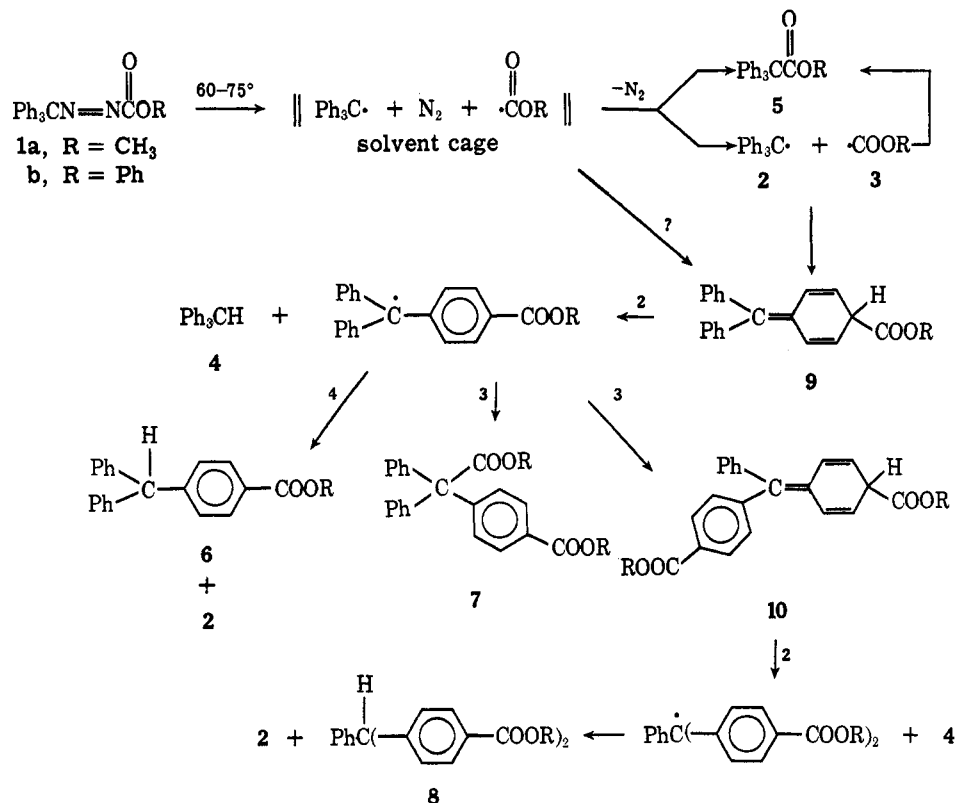
(13) M. J. Yee Quee and J. C. J. Thynne, *Ber. Bunsenges. Phys. Chem.*, **72**, 211 (1968).

(14) D. Griller and B. P. Roberts, *J. Chem. Soc. D*, 1035 (1971).

(15) T. Sakikibara and Y. Odaira, *J. Org. Chem.*, **36**, 3644 (1971).



SCHEME I



Just how much of the triphenylacetate (5) is a result of cage recombination of radicals and how much is formed by an intermolecular coupling reaction is not known. Formation of the other products, 4-benzhydrylbenzoates (6) and the diester compounds 7 and 8, can occur only if the alkoxy-carbonyl radicals survive long enough to choose their point of attack on the trityl or substituted trityl radical. Indeed, the diester products can arise only if alkoxy-carbonyl radicals escape from the solvent cage and are free in solution.

On the basis of the products isolated and identified, 63–68% of the trityl groups and 42–48% of the methoxy-carbonyl groups from the decomposition of 1a and 60% of the trityl groups and 42% of the phenoxy-carbonyl groups from the decomposition of 1b can be directly accounted for. In addition, a total of five other compounds (0.1–0.3 g each) from both decompositions containing trityl and/or alkoxy-carbonyl groups were isolated but could not be conclusively identified. The number and nature of the decomposition products were further complicated by the reaction of oxygen with the excess trityl radicals after decomposition of 1 was complete, so that at least 20 distinct bands for each decomposition could be seen on the tlc plates.

The formation of considerable amounts of triphenylmethane (4) in these decompositions implies that the trityl radical is abstracting a hydrogen atom from another substituted triarylmethane or from some other species which readily donates a hydrogen atom.

In Scheme I, we present the most likely routes to the products that were identified. This scheme suggests that other tri- and tetracarboalkoxy compounds and compounds which contain ortho carboalkoxy groups should also form and thus readily accounts for the complex mixture of unidentified compounds that we observed.

Bartlett and Pincock observed ethyl benzoate, formate, and phenyldimethylacetate in their study,<sup>5</sup> but we did not observe similar products in our study. It is possible that in our system the concentration of the very stable trityl radicals was high enough to rapidly trap the alkoxy-carbonyl radicals before they had a chance to undergo other reactions to a significant extent.

Alternatively, the ethyl benzoate that was obtained from the decomposition of ethyl *tert*-butyl monoperoxyoxalate in benzene could come from the coupling of an ethoxy-carbonyl radical with a phenyl radical. The decomposition of ethyl *tert*-butyl monoperoxyoxalate produces, in addition to the ethoxy-carbonyl radical, a *tert*-butoxy radical which can further cleave to give acetone and a methyl radical. The methyl radicals could attack benzene to give rise to phenyl radicals, whereas the very stable trityl radicals, produced from the decomposition of the tritylazocarboxylate, would not lead to phenyl radicals. Along the same lines, the ethyl formate produced from the decomposition of the monoperoxyoxalate in cumene could come from the ethoxy-carbonyl radical abstracting a hydrogen atom from some other source besides cumene. In cumene, the *tert*-butoxy radical readily abstracts the  $\alpha$  hydrogen atom of cumene to give a cumyl radical.<sup>21</sup> Possibly the ethoxy-carbonyl radical abstracts a hydrogen atom from the cumyl radical to give the formate as well as coupling with it to give ethyl phenyldimethylacetate.

Our failure to detect oxalates in the product mixture from either tritylazocarboxylate could indicate that the coupling of two alkoxy-carbonyl radicals is relatively slow due to an unfavorable polar effect or that the alk-

(21) C. Walling and B. E. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6108 (1960), and references cited therein.

oxycarbonyl radicals are rapidly taken up by the high concentration of trityl radicals. Some reactions which consume alkoxy carbonyl radicals but not trityl radicals must be occurring, since trityl radicals were detected at the end of the reaction by esr spectroscopy. These reactions, however, must lead to products which were not identified.

It has recently been suggested that the photolysis of carbomethoxymercury compounds produces methoxy-carbonyl radicals.<sup>15</sup> If this is true, then those methoxy-carbonyl radicals must be produced in an excited state, since the products of the photolysis require that the methoxycarbonyl radicals must rapidly decarbonylate, a finding which is inconsistent with the results in this paper and previous reports.<sup>5-7,14,19</sup>

In conclusion, then, the tritylazocarboxylates seem to be a convenient means of generating alkoxy carbonyl radicals, which are relatively unreactive radicals that do not readily decarboxylate, decarbonylate, add into benzene rings, or abstract hydrogen atoms from cumene.

### Experimental Section

**Methods and Materials.**—Most equipment and methods have been previously described.<sup>22</sup> ESR spectra were measured using a Varian Associates V-4500 spectrometer with a 100-kHz field modulation and a 9-in. magnet regulated by a Fieldial control. For glpc analysis, a 6 ft  $\times$  0.25 in. 15% SE-30 on 60/80 mesh Chromosorb P column at 125–265° was used. Glpc peak areas were measured with a planimeter.

**Methyl carbazate** was prepared by the method of Diels<sup>23</sup> and recrystallized from hexane-dichloromethane: yield 89.5%; mp 67–69° (lit.<sup>23</sup> mp 73°); ir (CHCl<sub>3</sub>) 3425 (m), 1720 (vs), 1628 (m), 1479 (s), 1355 (w), 1265 (s), and 1057 cm<sup>-1</sup> (m); nmr (CDCl<sub>3</sub>)  $\delta$  6.9 (very broad s, 1), 3.90 (broad s, 2), and 3.70 (s, 3).

**Methyl 3-Tritylcarbазate.**—Using a variation of the method of Carpino, Terry, and Crowley,<sup>24</sup> 11.43 g (41.1 mmol) of trityl chloride in 20 ml of benzene was added dropwise to 3.7 g (41.1 mmol) of methyl carbazate in 25 ml of pyridine. After standing for 1 hr at room temperature the pyridinium chloride formed was removed by extracting the reaction mixture with an equal volume of water. Dichloromethane was added to the organic layer to increase the solubility of methyl 3-tritylcarbазate. The organic layer was dried (MgSO<sub>4</sub>), filtered, and concentrated. The residue was recrystallized from hexane-dichloromethane twice to yield 10.8 g (79%) of white crystals: mp 175–177°; ir (CHCl<sub>3</sub>) 3335 (w), 2990 (b w), 1725 (bs), 1590 (w), 1487 (s), 1442 (s), 1355 (m), 1243 (m), 1157 (s), and 905 cm<sup>-1</sup> (m); nmr (CDCl<sub>3</sub>)  $\delta$  7.6–7.9 (m, 15), 5.56 (s, 1), 4.47 (broad s, 1), and 3.50 (s, 3).

*Anal.* Calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 75.91; H, 6.02; N, 8.43. Found: C, 76.11; H, 6.12; N, 8.39.

**Methyl tritylazocarboxylate (1a)** was prepared by the method of Carpino, Terry, and Crowley,<sup>24</sup> by oxidation of 8.37 g (25.2 mmol) of methyl 3-tritylcarbазate with 4.50 g (25.2 mmol) of freshly recrystallized *N*-bromosuccinimide (NBS). The yellow solid left after work-up was recrystallized from pentane-dichloromethane to yield 7.56 g (91%) of 1a, mp 98–100° with decomposition (yellow and orange crystals were obtained and the orange crystals were converted to the yellow crystals with explosive violence at ca 90°). Both kinds of crystals were examined by nmr and no solvent of crystallization was found: ir (CHCl<sub>3</sub>) 1765 (vs), 1595 (w), 1489 (w), 1440 (m), 1250 (b s), 1026 (w), 1003 (w), 949 (w), 898 (w), and 885 cm<sup>-1</sup> (w); nmr (CDCl<sub>3</sub>)  $\delta$  7.20 (m, 15) and 3.86 (s, 3).

**Phenyl carbazate** was prepared by the method of Diels.<sup>18</sup> The water formed during the reaction was drawn off, and the organic layer was dried (MgSO<sub>4</sub>), filtered, and concentrated to about half of the original volume. Anhydrous ether was added until all of the phenyl carbazate was precipitated. The phenol by-product remained soluble in the ether-dichloromethane.

The product was collected by filtration and recrystallized from hexane-dichloromethane: yield 58%; mp 103–104° (lit.<sup>25</sup> mp 105°); ir (CHCl<sub>3</sub>) 3430 (w), 1736 (vs), 1628 (m), 1593 (w), 1465 (vs), 1350 (w), 1250 (m), 1163 (m), 1067 (w), 1026 (m), 1005 (w), and 910 cm<sup>-1</sup> (w); nmr (CDCl<sub>3</sub>)  $\delta$  7.23 (m, 5), 6.65 (very broad s, 1), and 3.86 (broad s, 2).

**Phenyl 3-tritylcarbазate** was prepared by the method used to prepare methyl 3-tritylcarbазate and recrystallized from hexane-dichloromethane: yield 78%; mp 161–162°; ir (CHCl<sub>3</sub>) 3330 (m), 2970 (b w), 1750 (b vs), 1595 (m), 1487 (vs), 1444 (s), 1423 (s), 1352 (m), 1152 (s), 1130 (s), 1100 (m), 1025 (m), 1000 (m), 940 (m), and 905 cm<sup>-1</sup> (m); nmr (CDCl<sub>3</sub>)  $\delta$  7.30 (m, 20), 5.92 (s, 1), and 4.53 (broad s, 1).

*Anal.* Calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.32; H, 5.92; N, 6.95.

**Phenyl tritylazocarboxylate (1b)** was prepared by the method of Carpino, *et al.*,<sup>24</sup> by oxidation of 6.65 g (16.9 mmol) of phenyl 3-tritylcarbазate with 3.00 g (16.9 mmol) of freshly recrystallized NBS. After work-up the yellow solid residue was recrystallized from pentane-dichloromethane to produce 4.67 g (71%) of 1b: mp 105–106° with decomposition; ir (CHCl<sub>3</sub>) 1778 (vs), 1590 (m), 1490 (s), 1446 (m), 1170 (m), 1080 (m), 1067 (w), 1025 (w), and 1005 cm<sup>-1</sup> (w); nmr (CDCl<sub>3</sub>)  $\delta$  7.26 (m).

**Determination of the Rate of Decomposition of Methyl Tritylazocarboxylate (1a).**—Nitrogen was bubbled for 3 min through a solution of 0.0203 g (0.067 mmol) of 1a dissolved in 0.5 ml of benzene in an nmr tube. The solution was heated at 60° under nitrogen. The decomposition was followed by observing the disappearance of the methyl absorption at  $\delta$  3.86 in the nmr spectrum. The integrated areas of the signal were 114, 44, and 5 after 0, 30, and 300 min, respectively. The value at 300 min was used as the infinity point.

**Analysis of the Gases Evolved<sup>18</sup> during the Thermal Decomposition of Methyl Tritylazocarboxylate (1a) in Benzene.**—The total volume of the system (flask, condenser, and capillary tubing) in which the decomposition was carried out was 42 ml. The system was flushed with nitrogen for 45 min before 4.02 g (12.2 mmol) of 1a dissolved in enough benzene to make 24 ml of solution was added to the flask. After nitrogen was bubbled through the solution for 20 min, the solution was heated at 60° for 3 hr and the gas evolved was collected under a beaker submerged in a water tank. The collected gas was placed in a funnel submerged in a large water tank and approximately 100 ml of the gas was transferred to a 100-ml gas buret. The gas was then transferred to a Hemple pipette containing 30% aqueous potassium hydroxide to remove carbon dioxide; the remaining gas was transferred back to the gas buret; and the new volume was recorded. This transfer was repeated until no further decrease in volume was noted. Transfer of the gas to another Hemple pipette containing freshly prepared ammoniacal cuprous chloride removed carbon monoxide; the residual gas was returned to the gas buret; and the residual volume was recorded. This transfer was repeated until no further decrease in volume was noted. The residual gas was assumed to be nitrogen. The pertinent data are recorded in Table III.

**Examination of the Decomposition of Methyl Tritylazocarboxylate (1a) by ESR.**—An esr tube containing a deoxygenated solution of 20 mg (0.06 mmol) of 1a in 0.2 ml of benzene under a nitrogen atmosphere was heated at 60° for 2 hr. After three dilutions with deoxygenated benzene, the esr spectrum could be measured and was identical with that published<sup>26</sup> for the trityl radical.

**Separation and Identification of the Nonvolatile Decomposition Products from Methyl Tritylazocarboxylate (1a) in Benzene.**—The benzene was removed from the benzene solution of non-gaseous products obtained from the decomposition of the 4.02 g (12.2 mmol) of 1a used for the gas analysis experiment. The crude products were dissolved in ca. 25 ml of dichloromethane and applied with a syringe to seven 8  $\times$  20 cm glass plates coated with a 1-mm thickness of silica gel PF<sub>254+366</sub> (E. Merck, Darmstadt). The plates were developed with hexane, 50% hexane-50% benzene, and benzene, a total of 20 times per plate. Each plate was divided into four bands (at least 20 bands were visible); each band was vacuumed into a Soxhlet thimble and extracted with ca. 250 ml of ethyl acetate for 7 hr in a Soxhlet extractor. The ethyl acetate was removed under aspirator pressure.

(22) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

(23) O. Diels, *Chem. Ber.*, **47**, 2187 (1914).

(24) L. A. Carpino, P. H. Terry, and P. J. Crowley, *J. Org. Chem.*, **26**, 4336 (1961).

(25) E. Merck, Patent Kl. 120. Nr. 285800; *Chem. Zentrallbl.*, **86**, II, 508 (1915).

(26) H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, **22**, 1783 (1954).

TABLE III  
ANALYSIS OF GASES PRODUCED BY DECOMPOSITION OF METHYL TRITYLAZOCARBOXYLATE (1a) AND PHENYL TRITYLAZOCARBOXYLATE (1b)

Gas	Pressure, mm <sup>a</sup>	Volume, ml <sup>b,c</sup>
From Methyl Tritylazocarboxylate		
Carbon dioxide	714	0.00
Carbon monoxide	714	2.00 <sup>d,e</sup>
Nitrogen	714	90.00 <sup>e</sup>
From Phenyl Tritylazocarboxylate		
Carbon dioxide	713	0.10
Carbon monoxide	713	2.20 <sup>d,e</sup>
Nitrogen	713	96.50 <sup>e</sup>

<sup>a</sup> Barometer and water vapor corrections have been applied; temperature was 298° K. <sup>b</sup> Total volume collected was 295 ml from 1a and 280 ml from 1b. <sup>c</sup> Volume of the sample analyzed was 92.00 ml for 1a and 98.80 ml for 1b. <sup>d</sup> Maximum volume of carbon monoxide present. <sup>e</sup> Final volume after treatment with ammoniacal cuprous chloride was 101 ml for 1a and ca. 108 ml for 1b due to the presence of ammonia vapor which was not removed; correction for volume of ammonia was estimated to be 11 ml for 1a since addition of a small amount of hydrochloric acid to the water in the leveling bulb for 1b removed the ammonia and reduced the volume by 11 ml.

Band 1 yielded 0.62 g (2.54 mmol or 21 mol %) of triphenylmethane (4), mp 92–94°. Melting point, glpc retention time, and nmr and ir spectra were identical with those of authentic 4.

When band 2 (1.43 g) was treated with hot hexane, most of the solid did not dissolve. This material, when recrystallized from a mixture of hexane–dichloromethane, gave 0.87 g (2.88 mmol or 24 mol %) of a crystalline compound which had the same melting point (182–184°), glpc retention time, nmr spectrum, and ir spectrum as authentic methyl triphenylacetate (5a) prepared by a different route.<sup>27</sup>

When the hot hexane solution was allowed to cool, 0.41 g (1.36 mmol or 11 mol %) of methyl 4-benzhydrylbenzoate (6a) crystallized: mp 78–79° (lit.<sup>28</sup> mp 78–79°); ir (CHCl<sub>3</sub>) 1716 (vs), 1610 (m), 1600 (m), 1492 (m), 1450 (m), 1435 (m), 1413 (w), 1277 (vs), 1115 (s), 1105 (s), 1075 (w), 1017 (m), 967 (w), and 880 cm<sup>-1</sup> (w); nmr (CDCl<sub>3</sub>) δ 7.95 (d, 2, *J* = 8 Hz), 7.21 (m, 12), 5.57 (s, 1), and 3.85 (s, 3).

Band 4 (0.56 g) contained small amounts of many compounds and was not further examined. Band 3 (0.83 g) was again dissolved in dichloromethane, applied to three 8 × 20 cm plates coated with a 1-mm thickness of silica gel, developed in 50% hexane–50% benzene 15 times, and divided into 5 bands. Each of the new bands was extracted with ethyl acetate, and the ethyl acetate was removed under aspirator pressure.

From band 3' was recrystallized 0.24 g (0.80 mmol or 6.5 mol %) of methyl 4-carbomethoxytriphenylacetate (7a): mp 133–134°; ir (CHCl<sub>3</sub>) 1718 (vs), 1607 (w), 1492 (w), 1433 (m), 1315 (m), 1277 (vs), 1110 (s), and 1010 cm<sup>-1</sup> (m); nmr (CDCl<sub>3</sub>) δ 7.95 (d, 2, *J* = 8 Hz), 7.23 (m, 12), 3.87 (s, 3), and 3.77 (s, 3); mass spectrum parent ion at *m/e* 360.

Anal. Calcd for C<sub>23</sub>H<sub>20</sub>O<sub>4</sub>: C, 76.65; H, 5.59. Found: C, 76.39; H, 5.50.

Bands 1' (0.08 g), 4' (0.26 g), and 5' (0.07 g) did not yield crystalline materials and could not be identified. Band 2' (0.11 g) yielded a crystalline material for which no complete structural assignment could be made.

**Analysis of Thermal Decomposition Products from Methyl Tritylazocarboxylate (1a) by Glpc.**—Samples of 0.0200 g (0.0606 mmol) of 1a in 0.31 g (4.0 mmol) of benzene (run 1) and 0.0225 g (0.0681 mmol) of 1a in 0.41 g (3.4 mmol) of purified cumene<sup>29</sup> (run 2) were degassed three times each and sealed under vacuum (0.1 mm). After heating at 60° for 9 and 7.5 hr, respectively, the tubes were opened, and benzil was added as an internal stan-

dard. The glpc peak areas of the only detectable products are given in Table IV. No methyl formate, methyl benzoate, di-

TABLE IV  
PRODUCTS FROM THE THERMAL DECOMPOSITION OF METHYL TRITYLAZOCARBOXYLATE (1a)

Compd	Area of Glpc Peak	
	Run 1 <sup>a</sup>	Run 2 <sup>b</sup>
Triphenylmethane (4)	0.46	2.43
Benzil <sup>c</sup>	2.03	9.70
Methyl triphenylacetate (5a)	0.70	3.91
Methyl 4-benzhydrylbenzoate (6a)	0.49	1.91
Methyl 4-carbomethoxytriphenylacetate (7a)	0.10	0.55

<sup>a</sup> In benzene as solvent. <sup>b</sup> In cumene as solvent. <sup>c</sup> Internal standard; 0.0610 mmol added to both runs.

methyl oxalate, dimethyl carbonate, or methyl 2-phenylisobutyrate were observed.

**Analysis of the Gases Evolved<sup>18</sup> during the Thermal Decomposition of Phenyl Tritylazocarboxylate (1b) in Benzene.**—After deoxygenation of 4.54 g (11.6 mmol) of 1b the decomposition was brought about by heating the solution at 75° for 3 hr, the gas evolved being collected under a beaker submerged in a water tank. Conventional gas analysis as previously described for 1a was performed and the data are tabulated in Table III.

**Examination of the Decomposition of Phenyl Tritylazocarboxylate (1b) by Esr.**—A deoxygenated solution of 8 mg (0.02 mmol) of 1b in 0.2 ml of benzene was heated in an esr tube under a nitrogen atmosphere at 75° for 2 hr. The esr spectrum observed was identical with that of the trityl radical.<sup>26</sup>

**Separation and Identification of the Nonvolatile Decomposition Products from Phenyl Tritylazocarboxylate (1b) in Benzene.**—The nongaseous products obtained from the decomposition of 4.54 g (11.6 mmol) of 1b were separated and isolated, as previously described for the decomposition products of 1a.

From band 1, 0.52 g (2.13 mmol or 18 mol %) of triphenylmethane (4) was isolated, mp 92–94°. Authentic 4 had the same melting point, glpc retention time, and nmr and ir spectra as band 1.

The material from band 2 was recrystallized from hexane to yield 0.48 g (1.32 mmol or 11 mol %) of phenyl triphenylacetate (5b), mp 124–125°. The melting point, glpc retention time, and nmr and ir spectra were identical with those of 5b prepared by a different route.<sup>30</sup>

Band 3 by nmr analysis contained a mixture of 5b and phenyl 4-benzhydrylbenzoate (6b) (see discussion of band 4) amounting to 0.45 g (1.24 mmol or 11 mol %).

Upon recrystallization of band 4 from hexane, 0.69 g (1.90 mmol or 16 mol %) of 6b was obtained: mp 125–126°; ir (CHCl<sub>3</sub>) 1725 (vs), 1595 (m), 1493 (s), 1445 (w), 1408 (w), 1263 (vs), 1160 (s), 1073 (s), 1017 (m), 1000 (w), 913 (w), and 878 cm<sup>-1</sup> (w); nmr (CDCl<sub>3</sub>) δ 8.15 (d, 2, *J* = 8 Hz), 7.23 (m, 17), and 5.63 (s, 1); mass spectrum parent ion at *m/e* 364.

Anal. Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>2</sub>: C, 85.69; H, 5.53. Found: C, 85.35; H, 5.74.

Band 6 (0.35 g) was a mixture of many highly colored bands; no further separation was attempted. Band 5 (0.94 g) was redissolved in dichloromethane, applied to three 8 × 20 cm plates coated with a 1-mm thickness of silica gel, developed in 50% hexane–50% benzene 15 times, and divided into five bands. Each of these new bands was extracted with ethyl acetate, and the ethyl acetate was removed from each band by rotary evaporation.

From band 3' was isolated by recrystallization from hexane–dichloromethane 0.18 g (0.372 mmol or 3.2 mol %) of 4,4'-dicarbophenoxytriphenylmethane (8b): mp 151–153°; ir (CHCl<sub>3</sub>) 3010 (w), 1733 (vs), 1610 (m), 1595 (m), 1495 (s), 1415 (m), 1265 (vs), 1176 (vs), 1160 (s), 1074 (vs), 1017 (s), 1000 (w), 924 (m), 876 (w), and 847 cm<sup>-1</sup> (m); nmr (CDCl<sub>3</sub>) δ 8.16 (d, 4, *J* = 8 Hz), 7.25 (m, 19), and 5.70 (s, 1).

Band 1' (0.01 g) was too small to obtain any positive information. Bands 2' (0.24 g), 4' (0.28 g), and 5' (0.11 g) yielded crystalline products upon recrystallization from hexane–dichloro-

(27) J. F. Norris and A. Cresswell, *J. Amer. Chem. Soc.*, **56**, 423 (1934).

(28) C. S. Marvel and J. Harkema, *ibid.*, **63**, 2221 (1941).

(29) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960).

(30) J. Schmidlin and H. H. Hodgson, *Chem. Ber.*, **41**, 444 (1908).

methane, but complete structural assignments could not be made for these compounds.

**Registry No.**—1a, 34839-56-0; 1b, 34839-57-1; 4, 519-73-3; 5a, 5467-21-0; 5b, 34823-77-3; 6a, 34823-78-4; 6b, 34823-79-5; 7a, 34823-80-8; 8b, 34823-81-9;

methyl carbazate, 6294-89-9; methyl 3-tritylcarbazate, 34823-82-0; phenyl carbazate, 20605-43-0; phenyl 3-tritylcarbazate, 34823-83-1.

**Acknowledgment.**—We thank Professor Glen A. Russell for helpful discussions of this work.

## Strained Ring Systems. XII.<sup>1a</sup> The Synthesis of Several Dimethyl $\Delta^1$ -Cycloalkene-1,2-dicarboxylates and Certain 4-Substituted Bicyclo[2.1.0]pentane-1-carboxylic Acids

RICHARD N. McDONALD\* AND ROBERT R. REITZ<sup>1b</sup>

Department of Chemistry, Kansas State University, Manhattan, Kansas 66502

Received December 7, 1971

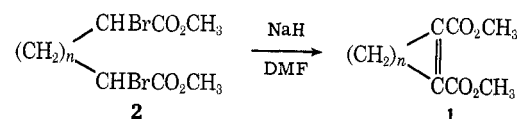
A one-step synthesis of dimethyl  $\Delta^1$ -cycloalkene-1,2-dicarboxylates (1) (cyclobutene to cycloheptene) from the corresponding dimethyl  $\alpha, \alpha'$ -dibromoalkanedicarboxylates is given. While dimethyl  $\Delta^1$ -cyclopropene-1,2-dicarboxylate (1a) is believed produced from the reaction of dimethyl  $\alpha, \alpha'$ -dibromoglutarate (2a) and potassium *tert*-butoxide, *cis* addition of an alcohol to 1a proceeds to yield the dimethyl 1-alkoxycyclopropane-*cis*-1,2-dicarboxylates 4 and 5. Reaction of dimethyl  $\Delta^1$ -cyclobutene-1,2-dicarboxylate (1b) with diazomethane followed by photolysis of the product pyrazoline yields dimethyl bicyclo[2.1.0]pentane-1,4-dicarboxylate (6). Through standard reaction sequences 6 is converted to bicyclo[2.1.0]pentane-1,4-dicarboxylic acid, 4-carbomethoxy-, 4-carbamyl-, and 4-cyanobicyclo[2.1.0]pentane-1-carboxylic acids. Bicyclo[2.1.0]pentane-1-carboxylic acid was prepared by hydrolysis of its methyl ester.

We recently reported the preparation of several 5-substituted bicyclo[3.1.0]hexane-1-carboxylic acids<sup>2</sup> using standard reaction sequences for modifying the carboxylic acid group<sup>3-6</sup> of 5-carbomethoxybicyclo[3.1.0]hexane-1-carboxylic acid. We wish to report in this paper the synthesis of certain 4-substituted bicyclo[2.1.0]pentane-1-carboxylic acids which were required to determine the effect of bridgehead substituent groups on the acidity of bicyclo[*n*.1.0]alkane-1-carboxylic acids.

The synthetic approach to dimethyl bicyclo[2.1.0]pentane-1,4-dicarboxylate (6) which appeared most promising was the addition of diazomethane to dimethyl  $\Delta^1$ -cyclobutene-1,2-dicarboxylate (1b) followed by photolytic decomposition of the resulting pyrazoline, similar to the reported method used for preparing methyl bicyclo[2.1.0]pentane-1-carboxylate.<sup>7,8</sup>

**Synthesis of Dimethyl  $\Delta^1$ -Cycloalkene-1,2-dicarboxylates.**—The reported procedures for the preparation of diester 1b or its diacid are quite lengthy<sup>9,10</sup> and involve cyclobutane-1,2-dicarboxylic acid as an intermediate. By analogy to the four-membered ring formation in the reaction of dimethyl  $\alpha, \alpha'$ -dibromoadipate (2b) with cyanide ion, which is part of the sequence leading to cyclobutane-1,2-dicarboxylic acid,<sup>11</sup> it appeared that reaction of 2b with 2 equiv of base should accomplish both cyclization and vicinal elimination of hydrogen bromide to yield 1b directly.

Our first attempt at such a reaction proved fruitful. When 2b was allowed to react with 2 equiv of sodium hydride in dimethylformamide, 1b was isolated in 68%



a, *n* = 1      d, *n* = 4  
b, *n* = 2      e, *n* = 5  
c, *n* = 3      f, *n* = 6

yield. Since this procedure offered a simple, reasonably direct synthesis of 1b, we decided to examine its possible generality for the synthesis of dimethyl  $\Delta^1$ -cycloalkene-1,2-dicarboxylates. A series of dimethyl  $\alpha, \alpha'$ -dibromoalkanedicarboxylates (2) derived from glutaric acid through sebacic acid<sup>12a</sup> were prepared and allowed to react with sodium hydride in dimethylformamide; the conditions and results are given in Table I.<sup>12b,13,14</sup>

The reactions of 2a-d proceeded smoothly at ice-bath or room temperature. However, the reactions with 2e and 2f were quite slow even at room temperature. While this procedure gives good yields of 1b-d and an acceptable yield of 1e, none of the desired products 1a or 1f were obtained from 2a and 2f, respectively.

(1) (a) For paper XI in this series, see R. N. McDonald, D. G. Frickey, and G. M. Muschik, *J. Org. Chem.*, **37**, 1304 (1972). (b) NDEA Fellow, 1968-1970; NSF Trainee, 1970-1971.

(2) R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **35**, 2666 (1970).

(3) F. W. Baker and L. M. Stock, *ibid.*, **32**, 3344 (1967).

(4) J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, **75**, 2167 (1953).

(5) C. F. Wilcox and C. Leung, *J. Org. Chem.*, **33**, 877 (1968).

(6) C. F. Wilcox and J. S. McIntyre, *ibid.*, **30**, 777 (1965).

(7) W. G. Dauben and J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 3545 (1967).

(8) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967).

(9) F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, **51**, 1537 (1929).

(10) W. H. Perkins, *ibid.*, **65**, 950 (1894).

(11) R. C. Fuson and T. Y. Kao, *J. Amer. Chem. Soc.*, **51**, 1537 (1929).

(12) (a) The procedure used in the synthesis of esters 2 followed that reported for the preparation of 1b: E. Buchman, A. Reims, T. Skei, and M. Schlatter, *ibid.*, **64**, 2697 (1942); P. C. Guha and D. K. Sankaran, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 623. (b) A similar procedure for the synthesis of 1c has been reported by D. C. Owsley and J. J. Bloomfield, *Org. Prep. Proceed. Int.*, **3**, 61 (1971).

(13) (a) Small amounts of the diacids of 1b, 1c, and 1d have been obtained from base hydrolyses of the corresponding esters of 2; see A. Hassell and C. K. Ingold, *J. Chem. Soc.*, 1465 (1926), and F. R. Goss and C. K. Ingold, *ibid.*, 1471 (1926). (b) 1b has been obtained in low yield from the dehalogenation of dimethyl *cis*-1,2-dihalo-cyclobutane-1,2-dicarboxylate (X = Cl, Br) with Ni(CO)<sub>4</sub>; see H.-D. Scharf and F. Korte, *Chem. Ber.*, **98**, 764 (1965).

(14) A reported attempt at formation of  $\Delta^1$ -cyclobutene-1,2-dicarboxylic acid by a Ramberg-Bachlund reaction was unsuccessful; see T. Bacchetti and A. Arnaboldi, *Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis., Mat. Natur.*, **15**, 75 (1953); *Chem. Abstr.*, **49**, 2301b (1955).