ORGANIC
LETTERS

2004
Vol. 6, No. 15
2539−2542

Double- and Triple-Consecutive O-Insertion into *tert*-Butyl and Triarylmethyl Structures

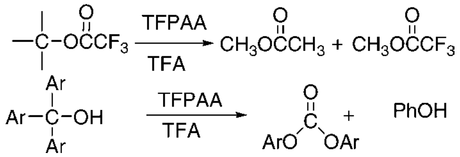
Pavel A. Krasutsky,*,[†] Igor V. Kolomitsyn,[†] Sergiy G. Krasutsky,[‡] and Paul Kiprof[‡]

Natural Resources Research Institute, 5013 Miller Trunk Highway,
Duluth, Minnesota 55811-1442, and Department of Chemistry,
University of Minnesota, 10 University Drive, Duluth, Minnesota 55812

pkrasuts@d.umn.edu

Received May 6, 2004

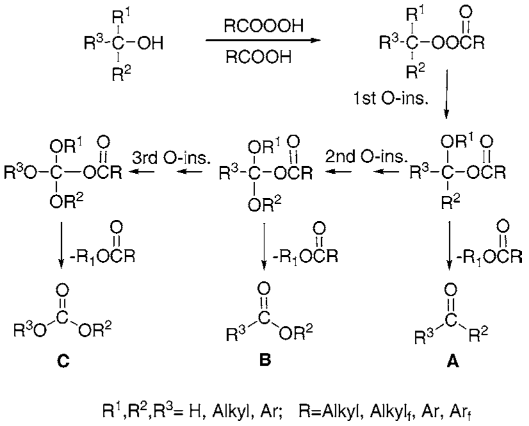
ABSTRACT



The concecutive Criegee rearrangement reactions were studied for *tert*-butyl trifluoroacetate, triarylcarbinols, and benzophenone ketales with trifluoroperacetic acid (TFPAA) in trifluoroacetic acid (TFA). The formation of methyl acetate and methyl trifluoroacetate indicates that the consecutive double-O-insertion process has taken place for *tert*-butyl trifluoroacetate. The intermediate dimethoxymethylcarbonium ion was detected below 5 °C. A consecutive triple-O-insertion process has been observed for triarylmethanols and benzophenone ketals. A new high yield method of corresponding diaryl carbonates synthesis was developed.

Criegee postulated[1] the formation of intermediate peroxyesters in Baeyer−Villiger reaction[2] based on the discovery of the ionic decomposition of 9-acylperoxydecalin.[3] The Criegee rearrangement,[1,3] in contrast to the Baeyer−Villiger reaction, can occur with consecutive O-insertions (Scheme 1).[4,5] Moreover, consecutive O-insertions have never been reported for aldehydes or ketones,[6−8] therefore, the Criegee and Baeyer−Villiger process are rather different from a synthetic point of view.

Scheme 1



The hypothetic triple-O-insertion pathway of the consecutive Criegee rearrangement is shown in Scheme 1. Stable

---

[†] Natural Resources Research Institute.

[‡] University of Minnesota.

(1) Criegee, R. *Justus Liebigs Ann.* **1948**, *560*, 127.

(2) Baeyer, A.; Villiger, V. *Ber.* **1889**, *32*, 3625. Baeyer, A.; Villiger, V. *Ber.* **1890**, *33*, 8585.

(3) Criegee, R. *Chem. Ber.* **1944**, *77*, 722.

(4) (a) Krasutsky, P. A.; Baula, O. P.; Yurchenko, A. G. *Russ. J. Org. Chem.* **1994**, *30*, 370. (b) Krasutsky, P. A.; Baula, O. P.; Botov, E. M. *Russ. J. Org. Chem.* **1996**, *32*, 1225. (c) Krasutsky, P. A.; Kolomitsyn, I. V.; Kiprof, P.; Carlson, R. M.; Fokin, A. A. *J. Org. Chem.* **2000**, *65*, 3926. (d) Krasutsky, P. A.; Kolomitsyn, I. V.; Kiprof, P.; Carlson, R. M.; Sydorenko, N. A.; Fokin, A. A. *J. Org. Chem.* **2001**, *66*, 1701.

(5) (a) Bailey, W. F.; Shih, M.-J. *J. Am. Chem. Soc.* **1982**, *104*, 1769. (b) Bailey, W. F.; Bischoff, J. J. *J. Org. Chem.* **1985**, *50*, 3009.

(6) Hassal, C. H. *Org. React.* **1957**, *9*, 73. Plesnicar, B. In *Organic Chemistry, Part C*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; p 254. Krow, G. R. *Tetrahedron* **1981**, *37*, 2697.

(7) Renz, M.; Meunier, B. *Eur. J. Org. Chem.* **1999**, 737.

(8) Krow, R. G. *Org. React.* **1993**, *43*, 251.

10.1021/ol049171p CCC: $27.50

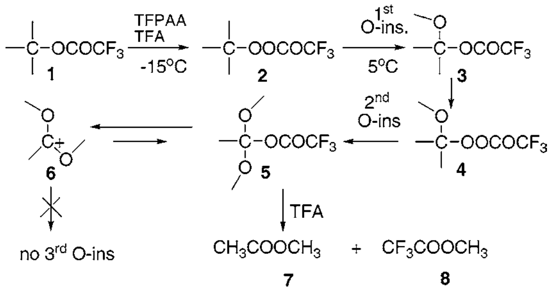
products of every O-insertion step (**A**−**C**) are easily recognized. The formation of **B** could be the mistaken as proceeding from **A** through the Baeyer−Villiger reaction. However, the possibility of distinguishing the Baeyer−Villiger reaction of ketone **A** to ester **B** from the consecutive Criegee rearrangement by kinetic consideration has been shown in our previous research.[4d]

A solution of TFPAA in TFA has been found to be a very favorable system for consecutive O-insertions into cage structures.[4]

Further generalization of this approach to acyclic and arylic structures is the main goal of this study. The specific desire to find structures susceptible to the triple O-insertion also motivated this work. The synthetic peculiarity of the solution of TFPAA in TFA allow the selective double-O-insertions in the consecutive Criegee rearrangements.[4] This became understandable when a stable dioxacarbonium ion was observed in the reactions of 2-methyladamantane-2-ol with the TFPAA in TFA.[4c] It was demonstrated earlier that relative stabilities decrease when a methyl group is replaced by a phenyl group in methyl- and phenyl-substituted delocalized carbocations.[9] Moreover, the dimethoxymethylcarbonium ion is stable,[10] and can be generated in TFA.[11] At the same time, the aryl group has better migratory aptitude than the methyl group in the Baeyer−Villiger reaction[7,12] and Criegee rearrangement.[13] These observations prompted our research on *tert*-butyl trifluoroacetate (**1**), triarylmethanols **11**−**14**, and benzophenone ketals **19** and **25**.

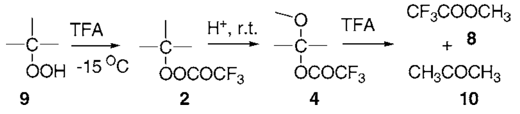
The consecutive Criegee rearrangement[14] of *tert*-butyl trifluoroacetate (**1**) with 10-fold excess of TFPAA in TFA at −15 °C was not observed, in contrast to consecutive Criegee rearrangement of cage compounds,[3c,d] within 10 h. The only formation of corresponding *tert*-butyl trifluoroperacetate (**2**)[15] was detected at −15 °C in situ by ^{1}H NMR and ^{13}C NMR (Scheme 2). This method can be considered as a new and simple method of synthesizing trifluoroperacetate **2**.[16]

Scheme 2



When the temperature was allowed to rise to 5 °C, and after 2 h of stirring, the formation of the intermediate 1,1-dimethoxyethyl cation (**6**) was detected (Scheme 2) by ^{1}H and ^{13}C NMR at −25 °C (total conversion of perester **2** was 35%). The spectrum of cation **6** is identical to a previously reported one.[11,17] Methyl acetate (**7**), methyl trifluoroacetate (**8**), and traces of acetone were also present in the reaction mixture. Formation of traces of acetone can be explained by the relatively low stability of ester **3** that decomposes to acetone and trifluoroacetate **8**. Further stirring at 5 °C results in the increase of acetate **7** and trifluoroacetate **8** and decrease of trifluoroperacetate **2**. Therefore, acetate **7** and trifluoroacetate **8** are evidently the product of the double-O-insertion and the subsequent decomposition of the intermediate ortho ester **5** in TFA. At room temperature, the final products **7** and **8** were formed in 4 h. Cation **6** does not perform a third O-insertion. When perester **2** was generated[15b] from *tert*-butyl hydroperoxide (**9**) and trifluoroacetic anhydride (TFAA), methyl trifluoroacetate (**8**) and acetone (**10**) were formed in equivalent amounts at rt in TFA as the only products of mono-O-insertion in the Criegee rearrangement process (Scheme 3).[18] The comparatively lower acidity of TFA, compared to superacids, does not stabilize the intermediate carboxonium ion,[19] but its acidity is enough to catalyze Criegee rearrangements.

Scheme 3



The reaction of triarylmethanols **11**−**14** with 10-fold excess of TFPAA in TFA, in contrast to *tert*-butyl trifluo-

---

(9) Larsen, J. W.; Bouis, P. A.; Riddle, C. A. *J. Org. Chem.* **1980**, *45*, 4969.

(10) (a) Taft, R. H.; Martin, R. H.; Lampe, F. W. *J. Am. Chem. Soc.* **1965**, *87*, 2490. (b) Martin, R. H.; Lampe, F. W.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 1353.

(11) Ramsey, B. G.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 3058.

(12) Strucul, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 1198.

(13) (a) Goodman, R. M.; Kishi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9392. (b) Sheldon, R. A.; van Doorn, J. A. *Tetrahedron Lett.* **1973**, *13*, 1021.

(14) **Reaction of *tert*-Butyl Trifluoroacetate with TFPAA.** A solution of *tert*-butyl trifluoroacetate (**1**) (0.1 g, 0.6 mmol) in TFA (1 mL) was added to a solution of TFPAA in TFA (1.73 g, 6 mmol of TFPAA) at −15 °C. (a) The temperature was allowed to rise to 5 °C. After the solution was stirred for 2 h at 5 °C the formation in situ of **1,1-dimethoxyethyl cation** (**6**) was detected by ^{1}H and ^{13}C NMR analysis at −25 °C. The observed level of *tert*-butyl trifluoroperacetate (**2**) conversion was 35%. (b) The temperature was allowed to rise room temperature, and after the solution was stirred for 4 h at room temperature the formation *in situ* of methyl acetate (**7**) and methyl trifluoroacetate (**8**) was detected by ^{1}H NMR analysis. Ratio of products was **7**/**8** = 1:1.

(15) ***tert*-Butyl Trifluoroperacetate** (**2**). (a) A solution of *tert*-butyl trifluoroacetate (**1**) (0.1 g, 0.6 mmol) in TFA (1 mL) was added to a solution of TFPAA in TFA (1.73 g, 6 mmol of TFPAA) at −15 °C. After 1 h, the formation of *tert*-butyl trifluoroperacetate (**2**) in situ was observed by NMR analysis at −15 °C. TMS in CD_3COCD_3 was used as external standard. ^{1}H NMR (CF_3COOH, 300 MHz): δ. 0.927. ^{13}C NMR (CF_3COOH, 75 MHz): δ 149.9 (q, $^{2}J_{CF}$ = 48.1 Hz), 113.5 (q, $^{1}J_{CF}$ = 283.2 Hz), 88.3, 26.4. (b) Modified literature procedure:[16] trifluoroacetic anhydride (0.47 g, 2.2 mmol) was added to *tert*-butyl hydroperoxide (0.1 g, 1.1 mmol) at −15 °C. The formation of *tert*-butyl trifluoroperacetate in situ was observed by NMR analysis after 30 min at −15 °C.

(16) Bartlett, P. D.; Hiatt, R. R. *J. Am. Chem. Soc.* **1958**, *80*, 1398.

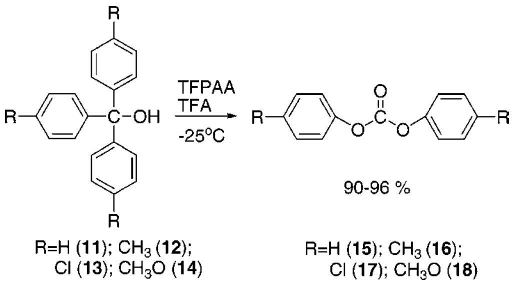
(17) Olah, G. A.; Hartz, N.; Rasul, G.; Burrichter, A.; Prakash, G. K. S. *J. Am. Chem. Soc.***1995**, *117*, 6421.

(18) **Criegee Rearrangement of *tert*-Butyl Trifluoroperacetate (2).** TFA (3 mL) was added to a solution of *tert*-butyl trifluoroperacetate (**2**) in TFAA (0.6 g, 1.16 mmol of peroxide **2**) at −15 °C. The formation in situ of acetone (**10**) and methyl trifluoroacetate (**8**) was detected by ^{1}H NMR analysis. Ratio of products was **10**/**8** = 1:1.

(19) Olah, G. A.; Parker, D. G.; Yoneda, N. *J. Org. Chem.* **1977**, *42*, 32.

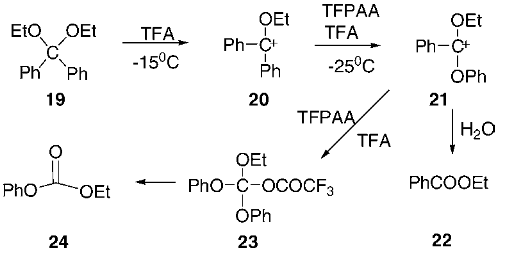
roacetate (**1**), occurs at −25 °C yielding triple-O-insertion products **15**−**18** (Scheme 4). Diphenyl carbonate (**15**),[20a] di(*p*-methylphenyl) carbonate (**16**),[21] di(*p*-chlorophenyl) carbonate (**17**),[22] and di(*p*-methoxyphenyl) carbonate (**18**)[23] were obtained with high yields (90−96%). Only traces (<1%) of double-O-insertion products and traces (<1%) of mono-O-insertion products were detected by GC/MS analysis of the reaction mixtures. All spectral data of the products **15**−**18** were identical to the corresponding literature values.[24] The NMR monitoring of reaction at −25 °C did not reveal any signs of intermediate carboxonium ions. However, benzophenone was converted quantitatively to phenyl benzoate at the described oxidation conditions. Moreover, phenyl benzoate was stable for 10 h in a solution of TFPAA in TFA at room temperature. This result supports the assumption that carbonates **15**−**18** are products of triple-O-insertions of alcohols **11**−**14** as well as clearly demonstrating that consecutive O-insertions are not possible for Baeyer−Villiger reaction under these conditions.

Scheme 4



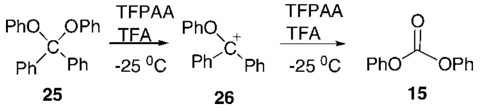
Benzophenone diethyl ketal (**19**)[25] undergoes the consecutive Criegee rearrangement with TFPAA in TFA at −25 °C with the formation of ethyl phenyl carbonate (**24**) in 96% yield (Scheme 5).[26] The formation of diphenylethoxycarbenium ion (**20**)[27] was detected at −15 °C by ^{1}H and ^{13}C NMR in situ when ketal **19** was dissolved in TFA. The ^{1}H NMR spectral data of cation **20** are identical to the data previously reported.[28] The quantitative formation of carbonate **24** occurred when 10-fold excess of TFPAA was added to the solution of carboxonium ions **20** in TFA.[26b] When the reaction mixture was quenched with water (after 1 h) the second O-insertion product[26a] ester **22** was obtained with 95% yield. Ester **22** was stable in a solution of TFPAA in TFA even at room temperature and no traces of carbonate **24** were found. Consequently, the formation of ester **22** is the result of the reaction of water with the intermediate cation **21** (double-O-insertion product[29]) and subsequent decomposition of the corresponding orthoester.[30] Cation **21** undergoes Criegee rearrangement with intermediate formation of ester **23**, which decomposes giving carbonate **24**—a triple-O-insertion product.

Scheme 5



When benzophenone diphenylketal (**25**)[31−33] was treated[20b] with 10-fold excess of TFPAA in TFA at −25 °C and carbonate **15** (Scheme 6) was observed as the only product of a consecutive Criegee rearrangement of ketal **25**. In contrast to ketal **19**, ketal **25** decomposed to benzophenone and phenol under the same reaction conditions (TFA, −15 °C) in which cation **20** was generated.[27] This results support

Scheme 6



---

(20) **Diphenyl Carbonate (15).** (a) A solution of triphenylmethanol (**11**) (0.1 g, 0.38 mmol) in dry CF_2ClCCl_2F (1 mL) was added to a solution of TFPAA in TFA (1.1 g, 3.8 mmol of TFPAA) at −25 °C and stirred for 1 h. The solution was then quenched with H_2O (20 mL) and extracted with three portions of CH_2Cl_2 (20 mL), and the organic part was washed with water and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (ether/hexanes = 2/3). Crystallization from ether yielded white crystals of carbonate **15** (0.078 g, 96%). (b) A solution of benzophenone diphenyl ketal (**25**) (0.1 g, 0.28 mmol) in dry $CFCl_3$ (0.6 mL) was added dropwise to a solution of TFPAA in TFA (0.91 g, 2.8 mmol of TFAA) at −25 °C and stirred for 1 h. The solution was then quenched with H_2O (20 mL) and extracted with three portions of CH_2Cl_2 (20 mL); the organic part was washed with water and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (ether/hexanes = 2/3). Crystallization from ether yielded white crystals of carbonate **15** (0.058 g, 96%).

(21) **Di(*p*-methylphenyl) Carbonate (16).**[24a] Using the same procedure as for diphenyl carbonate (**15**) from tri(*p*-methylphenyl)methanol (**12**) (0.1 g, 0.33 mmol), 0.073 g (91%) of di(*p*-methylphenyl) carbonate (**16**) was obtained.

(22) **Di(4-chlorophenyl) Carbonate (17).**[24b] Using the same procedure as for diphenyl carbonate (**15**) from tri(4-chlorophenyl)methanol (**13**) (0.1 g, 0.28 mmol), 0.07 g (90%) of di(4-chlorophenyl) carbonate (**17**) was obtained as colorless crystals.

(23) **Di(4-methoxyphenyl) Carbonate (18).**[24a] Using the same procedure as for diphenyl carbonate (**15**) from tri(4-methoxyphenyl)methanol (**14**) (0.1 g, 0.29 mmol), 0.073 g (92%) of di(4-methoxyphenyl) carbonate (**18**) was obtained as white crystals.

(24) (a) Lu, X.; Reid, D. L.; Warkentin, J. *Can. J. Chem.* **2001**, *79*, 319. (b) Lu, X.; Warkentin, J. *Can. J. Chem.* **2002**, *80*, 228.

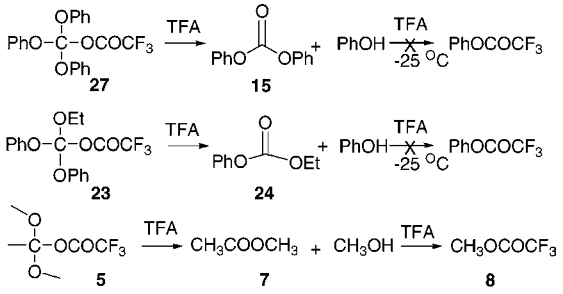
(25) Verevkin, S. P.; Peng, W.-H.; Beckhaus, H.-D.; Ruechardt, C. *Eur. J. Org. Chem.* **1998**, 2323.

(26) **Reaction of Benzophenone Diethyl Ketal (19) with TFPAA.** Ketal **19** (0.1 g, 0.4 mmol) was dissolved a solution of TFAA (0.1 mL) in TFA (1 mL) at −15 °C. The resulting solution was added to a solution of TFPAA in TFA (1.18 g, 4 mmol of TFPAA) at −25 °C. (a) After 1 h, the reaction mixture was quenched with H_2O (20 mL), extracted with three portions of CH_2Cl_2 (20 mL), and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (ether/hexanes = 2/3) to yield 0.056 g (95%) of **ethyl benzoate** (**22**). (b) After 2 h, the reaction mixture was quenched with H_2O (20 mL), extracted with three portions of CH_2Cl_2 (20 mL), and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (ether/hexanes = 2/3) to yield **ethyl phenyl carbonate** (**24**) (0.059 g, 96%).

the observation[9] that the relative stability of carboxonium ions decreases when methyl or ethyl is replaced by phenyl. Furthermore, the quantitative formation of carbonate **15** from ketal **25** allows for the assumption that cation **26** is generated from ketal **25** on the way to carbonate **15** at −25 °C.

Trifluoroacetates **23** and **27** may be considered as the most feasible intermediates on the way to carbonate **24** and **15** respectively (Scheme 7). The lack of the intermediate carboxonium ion at −25 °C in a case of alcohols **11**−**14** may be explained by their instability and the fast decomposition of corresponding esters to carbonates **15**−**18** in TFA media at −25 °C. This assumption was supported by the formation of phenol that was observed by GC/MS from alcohol **11** and ketal **19** when the ratio was **11**/TFPAA = 1/5 and **19**/TFPAA = 1/4, respectively. A similar reaction apparently occurs with intermediate esters **5**. The only difference is that methanol immediately esterifies in TFA at 5 °C.

Scheme 7



Triarylmethyl as well as diphenylalkoxy and diphenylphenoxy structures undergo the consecutive Criegee rearrangement with TFPAA in TFA with the formation of the triple-O-insertion products. In contrast to triarylmethyl structures, only a double-O-insertion reaction occurs with *tert*-butyl trifluoroacetate under similar conditions. The relative stability of the intermediate 1,1-dimethoxyethyl cation (**6**) in TFA and low migratory aptitude of the methyl group may be the reason for selective double-O-insertion into the *tert*-butyl group. The relative lower stability of aryloxycarbonium ions, as well as high migratory aptitude of aryl groups, results in a triple-O-insertion. The triple-O-insertion into triarylmethyl structures results in a high-yield formation of diaryl carbonates. This new one-step synthesis leads to easy access to diaryl carbonates and alkyl aryl carbonates.

Acknowledgment. This work was supported by the graduate student program of the University of Minnesota, Duluth, Department of Chemistry. We are grateful to Natural Resources Research Institute (UMD) for providing help with spectral equipment.

Supporting Information Available: H NMR and ^{13}C NMR spectra of all new structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OL049171P

---

(27) **Diphenylethoxycarbenium Ion (20).** Benzophenone diethyl ketal (**19**) (0.1 g, 0.4 mmol) was dissolved in a solution of trifluoroacetyl anhydride (0.1 mL) in TFA (1 mL) at −15 °C, and the formation of cation **20** was detected in situ by NMR analysis at −15 °C. TMS in CD_3COCD_3 was used as external standard. ^{1}H NMR (CF_3COOH, 300 MHz): δ 7.46 (m, 4H), 7.17 (m, 6H), 4.66 (q, $J = 6.9$ Hz, 2H), 1.16 (t, $J = 6.9$, 3H). ^{13}C NMR (CF_3COOH, 75 MHz) APT: δ 204.9(+), 135.5 (+), 134.4 (−), 130.8 (−), 128.3 (−), 65.7 (+), 15.1 (−).

(28) Olah, G. A.; DeMember, J. R.; Mo, Y. K.; Svoboda, J. J.; Schilling, P.; Olah, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 884.

(29) Assuming that cation **20** is the mono-O-insertion product.

(30) Deslongchamps, P.; Dory, Y. L.; Li, S. *Tetrahedron* **2000**, *56*, 3533.

(31) **Benzophenone Diphenyl Ketal (25).**[32] Ketal **25** was synthesized by a modified literature procedure:[33] dichlorodiphenylmethane (3 g, 12.7 mmol) was added to a solution of sodium phenolate (3.67 g, 31.6 mmol) in chlorobenzene (300 mL) and refluxed overnight. Water (300 mL) was added to the reaction mixture, which was extracted with three portions of CH_2Cl_2 (100 mL). The solvent was evaporated under vacuum, and the residue was purified by flash chromatography on silica gel (ether/hexanes = 2/3). Crystallization from ether yielded ketal **25** (4 g, 90%) as white crystals. IR (film, cm^{-1}): 3026, 1599, 1588, 1491. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66 (m, 4H), 7.24−7.06 (m, 14H), 6.86 (tt, $^1J = 6.3$ Hz, $^2J = 2.1$ Hz, 2H). ^{13}C NMR APT ($CDCl_3$, 75 MHz): δ 154.2 (+), 142.2 (+), 128.9 (−), 128.1 (−), 127.7 (−), 126.7 (−), 122.2 (−), 120.0 (−), 105.2 (+). MS *m*/*z* (rel intensity): 259 (100), 216 (10), 165 (25), 105 (26), 77 (48).

(32) Borkovec, A. B. *J. Org. Chem.* **1961**, *26*, 4866.

(33) Korshak, V. V.; Bulgakova, I. A.; Salazkin, S. N.; Vinogradova, S. V. Study of the reaction of diphenyldichloromethane with phenol. *Inst. Elementoorg. Soedin., Moscow, USSR* **1973**.